1992

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Order Number 9311530

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Iowa State University, 1992

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Ligand and metal effects on the heats of protonation of organometallic compounds

by

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

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1992

DEDICATION

To my parents and grandparents

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GENERAL INTRODUCTION

Preface

This dissertation contains three papers describing the research I performed at Iowa State University. Preceding these papers is a general introduction, which is a literature review of quantitative organic acid-base strengths as determined by calorimetry. In the introduction as well as the papers, the literature citations, tables, figures and schemes pertain only to the papers in which they appear. After the final paper is a general summary and the references cited in the general introduction.

Introduction

Quantitative values for acid-base strengths of organic compounds have been essential to the development of synthetic organic chemistry.[1] For example, by knowing the relative strengths of acid-base pairs one can control chemical processes to give the desired product(s).[2] Some of the first pK_a values measured were of amines, carboxylic acids and phenols in aqueous solutions.[3] However, the leveling effect and the solvation of the compounds in water can mask the overall strengths and trends of the acids and bases. Measurement of the acid-base strengths in the gas phase eliminates solvation and leveling effects; however, few organic reactions are run in the gas phase. Dimethylsulfoxide (DMSO) has, therefore, been chosen as the solvent in which to measure the pK_a values of a large number of organic compounds due to the fact that the trends in DMSO are usually very similar to those found in the gas phase.

Beginning in the 1960's Arnett and coworkers used calorimetry as a method to quantify the strengths of weak organic bases by measuring the heats of protonation (ΔH_i) of the bases (B) with neat fluorosulfonic acid (FSO_3H) at 25.0 °C (eq 1).[4] The heats of protonation (ΔH_i, which can also be classified as the heats of ionization) reported below have been corrected for the heat of dissolution of the base in CCl_4, since it is not possible to measure the heat of dissolution of a base in FSO_3H. Both extremely weak and strong bases can be completely and quantitatively protonated in neat FSO_3H; thus, the basicities (ΔH_i) of a large number of bases could be measured and compared in the same solvent and on the same scale using this method.

$$:B + FSO_3H \xrightarrow[FSO_3H]{25.0\ ^\circ C} HB^+FSO_3^-;\ \Delta H_i \qquad (1)$$

Calorimetry has also been used to determine the heats of deprotonation (ΔH_D) of organic acids (HA) with 0.1 M $K^+CH_3S(O)CH_2^-$(K^+DMSYL$^-$) in DMSO at 25.0 °C (eq 2).[5] Since K^+DMSYL$^-$ is a strong base in DMSO, it quickly

$$HA + K^+DMSYL^- \xrightarrow[DMSO]{25.0\ ^\circ C} K^+A^- + DMSO;\ \Delta H_D \qquad (2)$$

and quantitatively deprotonates even weak acids. In order to convert these heats of deprotonation (ΔH_D) to heats of ionization (ΔH_i) in DMSO, the heat of deprotonation (ΔH_D = -48.0 kcal/mol) of FSO_3H in DMSO by 0.1 M K^+DMSYL$^-$ (eq 3a) is required. Since FSO_3H is completely dissociated in DSMO (eq 3b), this yields the heat of autoprotolysis (ΔH_{aut}). By subtracting eq 3b from eq 2,

the heats of deprotonation (ΔH_D) of acids (HA) by K^+DMSYL^- (eq 2) can be converted to the heats of ionization (ΔH_i) in DMSO (eq 4) using eq 5.

$$FSO_3H + K^+DMSYL^- \xrightarrow[DMSO]{25.0\ ^\circ C} K^+FSO_3^- + DMSO \qquad (3a)$$

$$FSO_3^-(DMSO)H^+ + K^+(DMSYL^-) \xrightarrow[DMSO]{25.0\ ^\circ C} 2\ DMSO + K^+FSO_3^- \qquad (3b)$$

$$HA + DMSO \xrightarrow[DMSO]{25.0\ ^\circ C} A^- + (DMSO)H^+;\ \Delta H_i \qquad (4)$$

$$\Delta H_i = \Delta H_D + 48.0\ kcal/mol \qquad (5)$$

In this review the quantitative acid-base strenths of organic compounds as measured by calorimetry will be presented.

HEATS OF DEPROTONATION

Compiled in Tables I - XI are the heats of deprotonation (ΔH_i) of approximately 100 organic acids by FSO_3^- (eq 4), which were calculated by Arnett et al., from the ΔH_D of the acids using eq 5. These acids listed in Tables I - XI are listed from top to bottom in order of decreasing acidity. The errors, which are not listed in Tables I - XI, for the heats of deprotonation (ΔH_i) are generally 0.9 - 1.1 kcal/mol. In many cases there is a linear correlation between the heats of deprotonation and the aqueous pK_a values; thus, all pK_a values listed in this introduction are estimated from these ΔH_i values. However, in some families of compounds (i. e., HX, RSH, ROR',and RCO_2H) the correlation between the heats of deprotonation (ΔH_i) and the aqueous pK_a values is extremely poor and the pK_a values are not estimated.

Hydrogen Halides

The heats of deprotonation (ΔH_i) of the hydrogen halides (HX) in Table I show that the acidity increases in the order: HF << HCl ≈ HBr < HI. Since HF is known to hydrogen bond, its low acidity is explained by F⁻·····H-F interactions. A similar trend is observed for the hydrogen halides in the gas phase.

Table I. Heats of deprotonation (ΔH_i)[a] of hydrogen halides in DMSO at 25.0 °C

HYDROGEN HALIDES	ΔH_i, kcal/mol
hydrogen iodide	7.0
hydrogen bromide	14.0
hydrogen chloride	13.0
hydrogen fluoride	38.8

[a]Reference 5a.

Carboxylic Acids

The acidities (ΔH_i) of the substituted benzoic acids (RCO_2H) in Table II appear to increase a total of 1.0 kcal/mol; however, these heats of deprotonation are the same within experimental error.

Table II. Heats of deprotonation (ΔH_i)[a] of substituted benzoic acids in DMSO at 25.0 °C

SUBSTITUTED BENZOIC ACIDS	ΔH_i, kcal/mol
4-chlorobenzoic acid	13.4
benzoic acid	13.9
4-methoxybenzoic acid	14.4

[a]References 5b.

Phenols

The acidities (ΔH_i) of phenol (PhOH) and its derivatives listed in Table III range from 25.4 kcal/mol ($pK_a \approx 19.4$) for 4-cresol to 15.1 kcal/mol ($pK_a \approx 12.1$) for 4-nitrophenol. Comparing the substituents in the *para* position the acidities of the alcohols increase in the order: 4-cresol ($pK_a \approx 19.4$) ≈ 4-*t*-butylphenol < phenol < 4-chlorophenol ≈ 4-fluorophenol < 4-cyanophenol < 4-nitrophenol ($pK_a \approx 12.1$). Thus, as the electron withdrawing ability of the substituent in the *para* position increases, the acidity of the alcohol increases.

Amines

Nitro ($-NO_2$) groups are strong electron withdrawing groups; the acidities (ΔH_i) of the diphenylamines (Ph_2NH) in Table IV increase by 10.7 kcal/mol (7.2 pK_a units) in the order: diphenylamine ($pK_a \approx 24.2$) < (2-nitrophenyl)phenylamine < (4-nitrophenyl)phenylamine ($pK_a \approx 16.6$).

Table III. Heats of deprotonation (ΔH_i)[a,b] of substituted phenols in DMSO at 25.0 °C

SUBSTITUTED PHENOLS	ΔH_i, kcal/mol
4-nitrophenol	15.1
4-cyanophenol	18.1
2-chlorophenol	19.2
3-chlorophenol	20.9
4-fluorophenol	21.0
3-fluorophenol	21.3
2,6-di-*t*-butylphenol	21.8
4-chlorophenol	22.2
2-cresol	23.1
phenol	23.7
3-cresol	23.8
4-*t*-butylphenol	24.9
4-cresol	25.4

[a]Reference 5b. [b]$pK_a = 0.71\Delta H_i + 1.36$.

Table IV. Heats of deprotonation (ΔH_i)[a,b] of substituted diphenylamines in DMSO at 25.0 °C

SUBSTITUTED DIPHENYLAMINES	ΔH_i, kcal/mol
(4-nitrophenyl)phenylamine	21.4
(2-nitrophenyl)phenylamine	23.5
diphenylamine	32.1

[a]Reference 5b. [b]$pK_a = 0.71\Delta H_i + 1.36$

By replacing one of the phenyl groups in diphenylamine (Ph_2NH) with a hydrogen to give aniline ($PhNH_2$), the acidity (ΔH_i) is decreased by 8.8 kcal/mol (7.6 kcal/mol). Thus, a phenyl group is more electron withdrawing than a hydrogen, which agrees with the Taft σ^* parameters.[1a] The acidity of

Table V. Heats of deprotonation (ΔH_i)[a,b] of substituted anilines and imidazole in DMSO at 25.0 °C

SUBSTITUTED ANILINES	ΔH_i, kcal/mol
imidazole	24.9
4-chloro-2-nitroaniline	25.8
2,3,5,6-tetrachloroaniline	28.7
3-chloroaniline	37.0
aniline	40.9

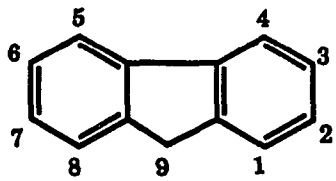
[a]Reference 5b. [b]$pK_a = 0.71\Delta H_i + 1.36$.

the aniline complexes increases in the order: aniline ($pK_a \approx 30.4$) < 3-chloroaniline < 2,3,5,6-tetrachloroaniline < 4-chloro-2-nitroaniline < imidazole ($pK_a \approx 19.0$).

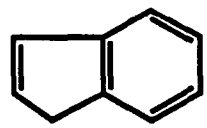
Hydrocarbons

The acidities (ΔH_i) of hydrocarbons range from 23.6 kcal/mol ($pK_a \approx 7.9$) for 9-cyanofluorene to 42.0 kcal/mol ($pK_a \approx 29.9$) for phenylacetylene. As the electon withdrawing ability of the groups on fluorene (Scheme 1) increase, the acidities (ΔH_i) of the complexes increase in the order: fluorene ($pK_a \approx 21.4$) < 9-phenylfluorene < 9-cyanofluorene ($pK_a \approx 7.9$). That triphenylmethane is 2.8 kcal/mol (2.5 pK_a units) more acidic than diphenylmethane is supported by the greater electon withdrawing ability of the phenyl vs. the hydrogen. The acidities (ΔH_i) of the hydrogen on the methylene carbon of the five membered ring (Scheme 1) increase in the order: 2,3-benzofluorene ($pK_a \approx 23.3$) < fluorene ≈ 4,5-methylenephenanthrene < indene < cyclopentadiene ($pK_a \approx 17$).

Scheme I

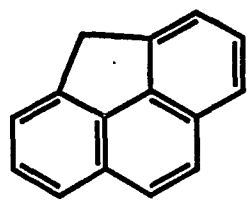


fluorene



indene

cyclopentadiene



4,5-methylenephenanthrene

Table VI. Heats of deprotonation (ΔH_i)[a,b] of hydrocarbons in DMSO at 25.0 °C

HYDROCARBONS	ΔH_i, kcal/mol
9-cyanofluorene	10.5
cyclopentadiene	23.6
9-phenylfluorene	23.9
indene	25.2
4,5-methylenephenanthrene	29.7
fluorene	29.8
1,1,3-triphenylpropene	30.6
2,3-benzofluorene	33.4
t-butylacetylene	33.4
biphenylyldiphenylmethane	37.7
triphenylmethane	38.6
xanthene	39.6
1,4-pentadiene	40.0
diphenylmethane	41.4
phenylacetylene	42.0

[a]Reference 5b. [b]$pK_a = 0.70\Delta H_i + 0.53$.

Nitriles

The acidities (ΔH_i) of the nitrile compounds in Table VII increase in the order: acetonitrile (CH_3CN) ($pK_a \approx 29.0$) < phenylacetonitrile ($PhCH_2CN$) < (3-chlorophenyl)phenylacetonitrile < diphenylacetonitrile (Ph_2CHCN) < malonitrile ($CH_2(CN)_2$) < 9-cyanofluorene ($pK_a \approx 7.9$). Thus, as the number and/or strength of electron withdrawing groups increase the acidities (ΔH_i) of compounds increase.

Table VII. Heats of deprotonation (ΔH_i)[a,b] of nitrile compounds in DMSO at 25.0 °C

NITRILES	ΔH_i, kcal/mol
9-cyanofluorene	10.5
malonitrile	15.5
diphenylacetonitrile	22.9
(3-chlorophenyl)phenylacetonitrile	26.5
phenylacetonitrile	28.9
acetonitrile	40.6

[a]Reference 5b. [b]$pK_a = 0.70\Delta H_i + 0.53$.

Nitro Complexes

Nitro ($-NO_2$) groups are more electron withdrawing than nitrile (-CN) groups as supported by nitromethane (CH_3NO_2, $pK_a \approx 18.9$) being 19.5 kcal/mol (10.1 pK_a units) more acidic than acetonitrile (CH_3CN, $pK_a \approx 29.0$). The acidity (ΔH_i) of the nitro compounds in Table VIII range from the least acidic compound nitromethane (21.1 kcal/mol, $pK_a \approx 18.9$) to the most acidic compound 2-nitropropane (13.3 kcal/mol, $pK_a \approx 13.1$). However, there appears to be no correlation between the length of the alkyl chain and the strength of the acid.

Table VIII. Heats of deprotonation (ΔH_i)[a,b] of nitro compounds in DMSO at 25.0 °C

NITRO COMPOUNDS	ΔH_i, kcal/mol
2-nitropropane	13.3
nitroethane	18.3
1-nitrobutane	18.8
1-nitropropane	19.1
nitrocyclobutane	19.6
nitromethane	21.1

[a]Reference 5b. [b]$pK_a = 0.74\Delta H_i + 3.26$.

Ketones

The acidities (ΔH_i) of the ketones ($R_2C=O$) in Table IX increase as the electron withdrawing abilities of the R groups increase; thus, the acidities (ΔH_i) increase in the order: acetone ($pK_a \approx 27.6$) < acetophenone < phenylacetone < 2-phenylacetophenone < acetylacetone < benzoylacetone < dibenzoylmethane < dimedone ($pK_a \approx 13.1$). There appears to be no correlation between the acidities (ΔH_i) of the cyclic ketones and the length of the methylene chain.

Alcohols

Deprotonation of the alcohols in Table X has yielded acidities (ΔH_i) that range from 14.2 kcal/mol for perfluoro-*t*-butyl alcohol to 40.6 kcal/mol for 2,2,5,5-tetramethylpentan-3-ol. That the perfluoro-*t*-butyl alcohol is much more acidic (ΔH_i = 24.6 kcal/mol) than *t*-butyl alcohol is expected, since fluoro groups are strong electron withdrawing groups. In the gas phase, acidities of alcohols increase in the order: methyl alcohol < ethyl alcohol < *i*-propyl

Table IX. Heats of deprotonation (ΔH_i)[a,b] of ketones in DMSO at 25.0 °C

KETONES	ΔH_i, kcal/mol
dimedone	14.1
dibenzoylmethane	14.8
benzoylacetone	15.1
acetylacetone	16.3
2-phenylacetophenone	21.4
phenylacetone	24.6
acetophenone	30.7
acetone	32.9
camphor	38.1
CYCLIC KETONES	
cyclopentanone	32.4
cyclohexanone	32.5
cyclooctanone	33.3
cycloheptanone	34.2
cyclododecanone	34.3

[a]Reference 5b. [b]$pK_a = 0.74\Delta H_i + 3.26$.

alcohol < *t*-butyl alcohol.[6] However, in solution (i.e., H_2O, DMSO, etc.), it has been determined that the acidities increase in the order: *t*-butyl alcohol < *i*-propyl alcohol < ethyl alcohol < methyl alcohol.[5a] This difference between the gas phase and the solution acidities illustrates the importance of solvation and ion pairing, which can ultimately affect the ordering of acidities in solution. Since an attempted correlation between ΔH_i values and pK_a values is so poor, it is not possible to estimate the pK_a of an alcohol from the heat of protonation (ΔH_i) with any degree of certainty.

Table X. Heats of deprotonation (ΔH_i)[a] of alcohols in DMSO at 25.0 °C

ALCOHOLS	ΔH_i, kcal/mol
perfluoro-*t*-butyl alcohol	14.2[b]
hexafluoroisopropyl alcohol	21.2[b]
ethylene glycol	26.2
triphenylsilanol	26.6
2-propyne-1-ol	27.4
2,2,2-trifluoroethanol	30.3
methanol	32.1
triphenylmethanol	32.6
2-methoxyethanol	34.3
1-heptanol	34.8
allyl alcohol	34.9
benzyl alcohol	35.1
water	35.8
1-propanol	36.4
2-pentanol	36.6
ethanol	36.9
1-butanol	36.9
neopentyl alcohol	37.4
1-adamantanol	38.4
2-propanol	38.5
t-butyl alcohol	38.8
2,2,5,5-tetramethylpentan-3-ol	40.6

[a]Reference 5a unless otherwise noted. [b]Reference 5b.

Thiols

Thiols (RSH) (Table XI) are more acidic than alcohols (ROH) as illustrated by MeSH being 12.4 kcal/mol more acidic than MeOH, while thiophenol (PhSH) is 11.8 kcal/mol more acidic than phenol (PhOH, ΔH_i = 23.7

kcal/mol). Unlike alchols (ROH), which increase in acidity as the length of the alkyl chain decreases (i. e., *t*-butyl alcohol < *i*-propyl alcohol < ethyl alcohol < methyl alcohol), there is no apparent correlation between the length of the alkyl chain and the acidities (ΔH_i) of the thiols (Table XI). As with the alcohols, it is not possible to estimate the pK_a values for thiols from the ΔH_i values with any degree of certainty.

Table XI. Heats of deprotonation (ΔH_i)[a] of thiols in DMSO at 25.0 °C

THIOLS	ΔH_i, kcal/mol
thiophenol	11.9[b]
triphenylmethanethiol	15.2
hydrogen sulfide	15.6
ethanethiol	18.0
2-propanethiol	19.5
1-butanethiol	19.6[b]
2,2-dimethylpropanethiol	19.6[b]
methanethiol	19.7

[a]Reference 5b unless otherwise noted. [b] Reference 5a.

HEATS OF PROTONATION OF ORGANIC BASES

In this section the quantitative basicities (ΔH_i) of over 150 organic complexes (Tables XII - XXIV) as measured by calorimetry in which a base (B) is added to neat FSO_3H (eq 2). However, the basicities of the alkyl lithium compounds in Table XXV were determined by adding a known amount of isopropyl alcohol to an excess of base in 90:10 hexanes-ether solvent. Heats of protonation (ΔH_i) of the bases listed in Tables XII - XXV have been corrected for the heat of dissolution and are listed from top to bottom in increasing order of basicity (ΔH_i). Although the errors are not listed in the tables, they are generally $\leq$ 0.4 kcal/mol. Since there is an excellent correlation between the heats of protonation (ΔH_i) of the organic bases in Tables XII - XXIV in FSO_3H and the pK_{BH+} values, the ΔH_i values can be converted to pK_{BH+} (pK_{BH+} = pKa of the base's conjucate acid) values using eq 6. The pK_{BH+} values listed in the text are estimated using eq 6.

$$pK_{BH+} = -0.56\Delta H_i - 15.8 \qquad (6)$$

Amines

Protonation of amines (Table XII) with FSO_3H was the first system studied by Arnett and coworkers using calorimetry. The basicities (ΔH_i) were found to increase, where R = Me or Et, in the order: $NH_3 < RNH_2 < R_2NH < R_3N$. Thus, as the number of methyl or ethyl groups on the nitrogen atom increase the greater the basicity of the nitrogen atom. However, when R = *n*-butyl, the basicities increases in the order: tri-*n*-butylamine < *n*-butylamine ≈

di-*n*-butylamine, which suggests that solvation or conformational requirements result in an order different than that found for R = Me or Et. The basicities of trialkylamine (NR_3) complexes increase in the order: NPh_3 ($pK_{BH+} \approx -5.1$) < NH_3 < $N(n\text{-}Bu)_3$ < NMe_3 < NEt_3 ($pK_{BH+} \approx +11.8$). Except for the basicity of $N(n\text{-}Bu)_3$, the NR_3 complexes increase in basicity as the electron donating ability of the alkyl (R) groups increase.

Table XII. Heats of protonation (ΔH_i)[a,b] of amines with FSO_3H at 25.0 °C

AMINES	ΔH_i, kcal/mol
triphenylamine	-19.1[c]
pyridine	-38.6[d]
2,6-lutidine	-41.3[c]
ammonia	-43.3
tri-*n*-butylamine	-45.2[c]
quinuclidine	-45.8[d]
n-propylamine	-46.2
n-butylamine	-46.2
methylamine	-46.3
di-*n*-butylamine	-46.4[c]
ethylamine	-46.8
dimethylamine	-47.5
diethylamine	-47.7
trimethylamine	-47.9
di-*n*-propylamine	-48.6
t-butylamine	-48.8
triethylamine	-49.2[c]
i-propylamine	-49.3

[a]Reference 4c unless otherwise noted. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$. [c]Reference 4b. [d]Reference 4a.

Solvents

The basicities (ΔH_i) of some common solvents (Table XIII) were found to increase in the order: H_2O ($pK_{BH+} \approx -6.6$) < EtOH < $(CH_3)_2CO$ < Et_2O< tetrahydrofuran < Me_2SO < pyridine ($pK_{BH+} \approx 5.8$).

Table XIII. Heats of protonation (ΔH_i)[a,b] of some common solvents with FSO_3H at 25.0 °C

SOLVENTS	ΔH_i, kcal/mol
water	-16.5
ethanol	-18.7
acetone	-19.1
diethyl ether	-19.5
tetrahydrofuran	-19.6
dimethyl sulfoxide	-28.6
pyridine	-38.6[c]

[a]Reference 4b unless otherwise noted. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$. [c]Reference 4a.

Anilines

The basicities (ΔH_i) of aniline complexes (Table XIV) increase from 17.4 kcal/mol ($pK_{BH+} \approx -6.1$) for 2-bromo-4,6-dinitroaniline to 37.7 kcal/mol ($pK_{BH+} \approx 5.3$) for *N,N*-dimethylaniline. By replacing the hydrogen in the *para* position of aniline ($PhNH_2$) by other substituents, the basicities (ΔH_i) of the compounds increase in the order: NO_2 ($pK_{BH+} \approx 1.6$) < aniline < I < Br < Cl ≈ Me < F ($pK_{BH+} \approx 5.0$); however, no correlation between these basicities (ΔH_i) and the Hammett σ values[1a] is observed. Finally, by substituting both hydrogens on the nitrogen in aniline (ΔH_i = -34.0 kcal/mol) with two electron donating methyl groups to give *N,N*-dimethylaniline (ΔH_i = -37.7 kcal/mol), the basicity of the nitrogen atom increases by 3.7 kcal/mol (2.1 pK_a units).

Table XIV. Heats of protonation (ΔH_i)[a,b] of the nitrogen in substituted anilines with FSO_3H at 25.0 °C

SUBSTITUTED ANILINES	ΔH_i, kcal/mol
2-bromo-4,6-dinitroaniline	-17.4
2,6-dinitroaniline	-17.9
2,4-dinitroaniline	-21.5
2,6-dichloro-4-nitroaniline	-21.8
2,5-dichloro-4-nitroaniline	-24.1
4-chloro-2-nitroaniline	-25.3
2,4,6-tribromoaniline	-25.3
2-nitroaniline	-26.8
2,4-dichloroaniline	-30.3
4-nitroaniline	-31.1
2-iodoaniline	-32.4
2-chloroaniline	-32.5
2-fluoroaniline	-33.9
aniline	-34.0
3-nitroaniline	-24.0
3-chloroaniline	-34.2
4-iodoaniline	-34.5
4-bromoaniline	-35.2
2-methylaniline	-35.6
4-chloroaniline	-36.9
4-methylaniline	-36.9
4-fluoroaniline	-37.2
N,N-dimethylaniline	-37.7

[a]Reference 4b. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Pyridines

The basicities (ΔH_i) of the substituted pyridine compounds in Table XV range from -30.2 kcal/mol ($pK_{BH+} \approx 1.1$) for 2-bromopyridine to -42.7 kcal/mol ($pK_{BH+} \approx 8.1$) for 2,4,6-trimethylpyridine. When electron withdrawing groups (i. e., Cl, Br) are present in the pyridine ring, the basicity is less than that of pyridine (ΔH_i = -38.6 kcal/mol). However, when electron donating methyl groups are present, the basicity is greater than that of pyridine.

Table XV. Heats of protonation (ΔH_i)[a,b] of substituted pyridines with FSO_3H at 25.0 °C

SUBSTITUTED PYRIDINES	ΔH_i, kcal/mol
2-bromopyridine	-30.2
3,5-dichloropyridine	-30.7
2-chloropyridine	-31.7
3-bromopyridine	-34.6
quinoline	-37.0
pyridine	-38.6
4-methylpyridine	-39.0
2,6-dimethylpyridine	-40.7
2,4,6-trimethylpyridine	-42.7

[a]Reference 4a. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Ketones

The heats of protonation (ΔH_i) of the oxygen in various ketones are listed in Table XVI. The basicities (ΔH_i) of cyclic aliphatic ketones increase in the order: cyclobutanone ($pK_{BH+} \approx -7.7$) < cyclododecanone < cyclodecanone < cyclopentanone < cyclohexanone ≈ cycloheptanone ($pK_{BH+} \approx -5.6$),thus, as the ring strain decreases the basicity (ΔH_i) increases. Cyclododecanone and cyclodecanone are out of order due to conformational requirements.[4d]

In Table XVI the acetophenone derivatives increase in basicity a total of 2.6 kcal/mol (1.4 pK_{BH+} units) in the order: 3-chloroacetophenone (pK_{BH+} ≈ -6.6) < 4-chloroacetophenone ≈ 2,4,6-trimethylacetophenone < 3-nitroacetophenone < 4-nitroacetophenone ≈ acetophenone ≈ 3-methylacetophenone (pK_{BH+} ≈ -5.2). Although no correlation between Hammett σ_{para}[1a] and ΔH_i is apparent, the correlation between the ΔH_i values and pK_a values measured in DMSO is excellent.

Derivatives of benzophenone increase in basicity (ΔH_i) by 5.3 kcal/mol (3.0 pK_{BH+} units) in the order: 4,4'-dichlorobenzophenone (pK_{BH+} ≈ -7.5) < 4-bromobenzophenone < 4-chlorobenzophenone < 4-methylbenzophenone < 4,4'-dimethylbenzophenone < 4-methoxybenzophenone (pK_{BH+} ≈ -4.5). There is an excellent correlation between the heats of protonation and the pK_a values of these compounds as measured in DMSO.[4d]

Table XVI. Heats of protonation (ΔH_i)[a,b] of the carbonyl of the ketones in FSO_3H at 25.0 °C

KETONES	ΔH_i, kcal/mol
fluorenone	-14.2
cyclobutanone	-14.4
cyclododecanone	-16.0
dibenzosuberone	-16.5
cyclodecanone	-16.9
2-norbornanone	-17.1
cyclopentanone	-17.6
adamantanone	-17.6
1-acetylnaphthalene	-18.0
2-acetylnaphthalene	-18.1
cyclohexanone	-18.2

Table XVI. continued

cycloheptanone	-18.2
dibenzosuberenone	-18.8
2-pentanone	-18.8
acetone	-19.1
anthrone	-19.2
coumarin	-19.6
xanthone	-20.6
4-methyl-3-penten-2-one	-20.8
4-dichloromethyl-4-methylcyclo-hexadienone	-21.3
diphenylcyclopropenone	-23.9
ACETOPHENONES	
3-chloroacetophenone	-16.4
4-chloroacetophenone	-17.1
2,4,6-trimethylacetophenone	-17.2
3-nitroacetophenone	-17.9
4-nitroacetophenone	-18.7
acetophenone	-18.9
3-methylacetophenone	-19.0
BENZOPHENONES	
4,4'-dichlorobenzophenone	-14.9
4-bromobenzophenone	-15.1
4-chlorobenzophenone	-15.6
4-methylbenzophenone	-17.8
4,4'-dimethylbenzophenone	-18.1
4-methoxybenzophenone	-20.2

[a]From reference 4d. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Aldehydes

Fluorosulfonic acid quantitatively protonates the oxygen atom of the aldehydes listed in Table XVII. That the ketones are more basic (ΔH_i) than the analogous aldehyde complexes is illustrated by 4-nitroacetophenone being 5.0 kcal/mol (2.8 pK_{BH+} units) more basic than 4-nitrobenzaldehyde. The basicities (ΔH_i) of the aldehydes in Table XVII increase in the order: 4-nitrobenzaldehyde ($pK_{BH+} \approx -10.8$) < 3-nitrobenzaldehyde < benzaldehyde < 4-*i*-propylbenzaldehyde < 4-methylbenzaldehyde < crotonaldehyde ($CH_3C(H)=CHCHO$, $pK_{BH+} \approx -4.9$). Thus, relative to benzaldehyde the electron withdrawing $-NO_2$ group decreases the basicity (ΔH_i) of the oxygen atom, and electron donating alkyl groups increase the basicity of the oxygen atom. Benzoyl chloride (PhC(O)Cl) is 10.1 kcal/mol less basic (ΔH_i) than benzaldehyde (PhC(O)H); thus, Cl is more electron withdrawing than H.

Table XVII. Heats of protonation (ΔH_i)[a,b] of the carbonyl oxygen of aldehydes and benzoyl chloride with FSO_3H at 25.0 °C

ALDEHYDES	ΔH_i, kcal/mol
benzoyl chloride	-6.0[c]
4-nitrobenzaldehyde	-13.7
3-nitrobenzaldehyde	-14.3
benzaldehyde	-16.1
4-*i*-propylbenzaldehyde	-16.5
4-methylbenzaldehyde	-17.1
crotonaldehyde	-19.5

[a]Reference 4d unless otherwise noted. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$. [c]Reference 4a.

Esters

Basicities (ΔH_i) of the carbonyl group in the ester derivatives (RCO_2R') listed in Table XVIII increase by 3.5 kcal/mol (1.9 pK_{BH+} units) in the order: ethyl benzoate ($pK_{BH+} \approx -7.7$) < diethyl carbonate < ethyl acetate < propylene carbonate ($pK_{BH+} \approx -5.8$). The carbonyl oxygen in ethyl acetate ($MeCO_2Et$) is 3.0 kcal/mol (1.8 pK_{BH+} units) more basic than that in ethyl benzoate ($PhCO_2Et$); therefore, the methyl group is more electron donating than the phenyl group.

Table XVIII. Heats of protonation (ΔH_i)[a,b] of the carbonyl oxygen in esters with FSO_3H at 25.0 °C

ESTERS	ΔH_i, kcal/mol
ethyl benzoate	-14.5
diethyl carbonate	-16.4[c]
ethyl acetate	-17.5
propylene carbonate	-17.8[c]

[a]Reference 4d unless otherwise noted. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$. [c]Reference 4a.

Sulfur Compounds

The basicities (ΔH_i) of sulfur atoms in the following compounds increase by 14.4 kcal/mol (8.0 pK_{BH+} units) in the order: H_2S ($pK_{BH+} \approx -12.8$) < Ph_2S < $ClCH_2SMe$ < PhSMe < $Me_2S \approx (n\text{-}Bu)_2S$ < $Et_2S \approx$ MeSH < tetrahydrothiophene ($pK_{BH+} \approx -4.8$).

Table XIX. Heats of protonation (ΔH_i)[a,b] of the sulfur atom in thioethers with FSO_3H at 25.0 °C

SULFUR COMPOUNDS	ΔH_i, kcal/mol
hydrogen sulfide	-5.3
diphenyl sulfide	-7.6
chloromethyl methyl sulfide	-11.9
phenyl methyl sulfide	-13.2
dimethyl sulfide	-18.1
di-*n*-butyl sulfide	-18.5
diethyl sulfide	-19.0
methanethiol	-19.2
tetrahydrothiophene	-19.7

[a]Reference 4a. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Sulfur Oxides

Protonation of sulfur oxide complexes (Table XX) with fluorosulfonic acid presumably occurs at the monovalent oxygen (S=O).[4a] The basicity (ΔH_i) of this oxygen increases in the order: $(MeO)_2SO_2$ ($pK_{BH+} \approx -12.8$) < tetramethylene sulfone < $(MeO)_2SO$ < PhS(O)Me < $Me_2S(O)$ < $(n\text{-}Bu)_2S(O)$ ($pK_{BH+} \approx 0.7$).

Table XX. Heats of protonation (ΔH_i)[a,b] of the monovalent oxygen of sulfur oxides with FSO_3H at 25.0 °C

SULFUR OXIDES	ΔH_i, kcal/mol
dimethylsulfate	-5.3
tetramethylene sulfone	-11.8
dimethyl sulfite	-16.0
phenyl methyl sulfoxide	-25.2
dimethyl sulfoxide	-28.6
di-*n*-butyl sulfoxide	-29.5

[a]Reference 4a. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Phosphines

Addition of the phosphines in Table XXI to FSO_3H results in quantitative protonation of the phosphorus atom; thus, the basicities (ΔH_i) of the phosphine compounds increase in the order: PH_3 ($pK_{BH+} \approx -8.0$) < PPh_3 < $CyPH_2$ < Cy_2PH < PMe_3 ($pK_{BH+} \approx 9.2$).

Table XXI. Heats of protonation (ΔH_i)[a,b] of the phosphorus atom of phosphines with FSO_3H at 25.0 °C

PHOSPHINES	ΔH_i, kcal/mol
phosphine	-14.0
triphenylphosphine	-28.7[c]
cyclohexyl phosphine	-30.3
dicyclohexyl phosphine	-32.5
trimethyl phosphine	-44.6

[a]Reference 4c unless otherwise noted. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$. [c]Reference 4b.

Phosphine Oxides

The oxide compounds in Table XXII are protonated at the monovalent oxygen upon addition to neat FSO_3H. The basicities (ΔH_i) of these complexes increase in the order: $Cl_3P{=}O$ ($pK_{BH+} \approx -13.1$) < $Cl_2PhP{=}O$ < $(EtO)_2ClP{=}O$ < $Cl_2PhP{=}O$ < $Ph_3P{=}O$ < $Me_3P{=}O$ < pyridine oxide ($pK_{BH+} \approx 2.9$). As in the phosphine compounds (PR_3), increasing the electron donating ability of the groups on the phosphorus results in an increase in the basicity of the compound (i. e., the oxygen atom in $Me_3P{=}O$ is 9.2 kcal/mol (7.0 pK_{BH+} units) more basic than $Ph_3P{=}O$).

Table XXII. Heats of protonation (ΔH_i)[a,b] of phosphine oxides with FSO_3H at 25.0 °C

PHOSPHINE OXIDES	ΔH_i, kcal/mol
phosphoroxychloride	-4.9
dichlorophenylphosphine oxide	-10.7
diethyl chlorophosphate	-15.5
triphenylphosphine oxide	-23.0
trimethylphosphine oxide	-32.2
pyridine *N*-oxide	-33.4

[a]Reference 4a. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Amides

It is conceivable that amides ($RC(O)NR_2$) can protonate at either the oxygen or the nitrogen atom; however, spectroscopic evidence shows that protonation occurs at the oxygen.[4a] The heats of protonation (ΔH_i) of the amides listed in Table XXIII increase from -27.4 kcal/mol ($pK_{BH+} \approx -0.5$) for *N,N*-dimethylchloroacetamide to -29.6 kcal/mol ($pK_{BH+} \approx 0.8$) for *N*-methylformamide. Thus, the substituents on the amide influence the basicity (ΔH_i) only slightly.

Table XXIII. Heats of protonation (ΔH_i)[a,b] of the carbonyl oxygen in amides and 1,1,3,3-tetramethylurea with FSO_3H at 25.0 °C

AMIDES	ΔH_i, kcal/mol
N,N-dimethylchloroacetamide	-27.4
N,N-dimethylbenzamide	-29.1
N,N-dimethylformamide	-29.5
N-methylformamide	-29.6
1,1,3,3-tetramethylurea	-37.6

[a]Reference 4a. [b]$pK_{BH+} = -0.56\Delta H_i - 15.8$.

Alcohols and Ethers

The basicities (ΔH_i) of the alcohol and ether compounds listed in Table XXIV increase in the order: H_2O ($pK_{BH+} \approx -6.6$) < MeOH < Me_2O < EtOH < Et_2O < 1,4-dioxane < 1,2-dimethoxyethane ($pK_{BH+} \approx -0.1$). Thus, as stronger electron donating groups are placed on the oxygen atom the basicity (ΔH_i) increases.

Table XXIV. Heats of protonation (ΔH_i)[a,b] of alcohols and ethers by FSO_3H at 25.0 °C

ALCOHOLS AND ETHERS	ΔH_i, kcal/mol
water	-16.5
methanol	-17.1
dimethyl ether	-18.2
ethanol	-18.7
diethyl ether	-19.5
1,4-dioxane	-21.5
1,2-dimethoxyethane	-28.0

[a]Reference 4e unless otherwise noted. [b]$pK_a = -0.56\Delta H_{BH+} - 15.8$. [c]Reference 4a.

Alkyl Lithium Complexes

The heats of protonation (ΔH_i) of the alkyl lithium complexes listed in Table XXV are measured with *i*-propanol as the acid in 90:10 hexanes-ether at 25 °C. The basicities increase down the column; however, these basicities cannot be converted to the aqueous pK_a scale nor can they be directly compared with the heats of protonation (ΔH_i) measured for the compounds listed in Tables XII - XXIV. Quantitative comparisons can, however, be made within Table XXV.

Table XXV. Heats of protonation (ΔH_i)[a] of alkyl lithium compounds by isopropyl alcohol in 90:10 hexanes-ether at 25.0 °C

ALKYL LITHIUM COMPLEXES	ΔH_i, kcal/mol
lithium *t*-butoxide	-2.1[b]
lithium pinacolonate	-3.4[c]
lithium bis(trimethylsilyl)amide (LiHMDS)	-12.1
lithium *n*-octylamide	-18.9
lithium *t*-butylamide	-21.2
lithium isopropylamide	-21.0[d]
lithium cyclohexylamide	-21.5[d]
lithium diethylamide	-23.4
lithium diisopropylamide	-28.6
lithium isopropylcyclohexylamide	-29.6
lithium 2,2,6,6-tetramethylpiperidide	-30.4
lithium dicyclohexylamide	-31.8
((trimethylsilyl)methyl)lithium	-40.0
methyllithium	-41.6[e]
phenyllithium	-42.3
n-butyllithium	-50.0
s-butyllithium	-52.8
t-butyllithium	-56.2

[a]Basicities were measured by adding a known amount of isopropyl alcohol to an excess of base, Reference 4f.

[b]Value is calculated by the difference in the ΔH_i for LiHMDS + *i*-PrOH (-12.0) and LiHMDS + pinacolone (-8.7).

[c]Value is calculated by the difference in the ΔH_i for LiHMDS + *i*-PrOH (-12.0) and LiHMDS + *t*-BuOH (-10.0).

[d]1 equiv lithium *t*-butoxide was added to the organolithium bases prior to measuring ΔH_i with isopropyl alcohol.

[e]Solvent was 100% Et_2O to maintain solubility.

There is an excellent correlation between the heats of deprotonation (ΔH_i) of organic compounds and the aqueous pK_a values; however, different equations are required for different families of compounds. Using eq 7 the heats of deprotonation (ΔH_i) of phenols, diphenylamines, and anilines can

$$pK_a = 0.71\Delta H_i + 1.36 \quad (7)$$

be converted to pK_a values; heats of deprotonation (ΔH_i) of hydrocarbons and nitriles can be converted to pK_a values with eq 8, and the pK_a values of nitro

$$pK_a = 0.70\Delta H_i + 0.53 \quad (8)$$

compounds and ketones can be estimated using eq 9. In contrast to the organic acids, which require different equations to estimate the aqueous pK_a

$$pK_a = 0.74\Delta H_i + 3.26 \quad (9)$$

values, there is an excellent correlation between the heats of protonation (ΔH_i) of the organic bases and the aqueous pK_a values (eq 10).

$$pK_a = -0.56\Delta H_i - 15.8 \quad (10)$$

PAPER I. LIGAND AND METAL EFFECTS ON THE ENTHALPIES OF PROTONATION OF $Cp'M(PR_3)(PR'_3)X$ COMPLEXES (M = Ru or Os)

ABSTRACT

Titration calorimetry has been used to determine the enthalpies of protonation (ΔH_{HM}) of twenty two $Cp'M(PR_3)(PR'_3)X$ complexes (Cp' = η^5-C_5H_5(Cp) or η^5-C_5Me_5(Cp*); M = Ru, Os; PR_3 = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $P(OEt)_3$, dppm, dppe, dppp; X = H, Cl, Br, I) with CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C to give $Cp'M(PR_3)(PR'_3)(X)(H)^+CF_3SO_3^-$. Systematically changing the ligands and/or the metal in these complexes has yielded ΔH_{HM} values for protonation at the metal that range from -14.1 kcal/mol for $CpOs(PPh_3)_2I$ to -39.2 kcal/mol for $CpOs(PPh_2Me)_2H$. Metal basicities (ΔH_{HM}) of the $CpOs(PPh_3)_2X$ complexes correlate linearly with the gas phase proton affinities of the X^- ligands, both of which increase in the order: $I^- < Br^- < Cl^- << H^-$. Substitution of a halide ligand with a hydride causes the metal basicity to increase by as much as 23.2 kcal/mol. The basicicities of $CpOs(PPh_3)(PR_3)Br$ complexes increase in the order: $P(OEt)_3 < PPh_3 < PMe_3$. There is a linear correlation between the basicities (ΔH_{HM}) of the $CpOs(PR_3)_2Br$ complexes and the basicities (ΔH_{HP}) of their PR_3 ligands. In a series of complexes, the Cp* ligand increases the basicity of the metal by 5.5-9.0 kcal/mol over that of the corresponding Cp derivative, and Os complexes are 6.0-8.5 kcal/mol more basic than analogous Ru complexes. Basicities of the $CpOs(PR_3)_2Br$ and $CpRu(PR_3)_2H$ complexes are reduced when the protonated product is forced to have the *cis*, rather than *trans*, structure by a small-ring chelating diphosphine ligand (dppm). These studies

demonstrate that the metal, ligands and geometries of the protonated product all substantially affect the heats of protonation (ΔH_{HM}) of $Cp'M(PR_3)(PR'_3)X$ complexes.

INTRODUCTION

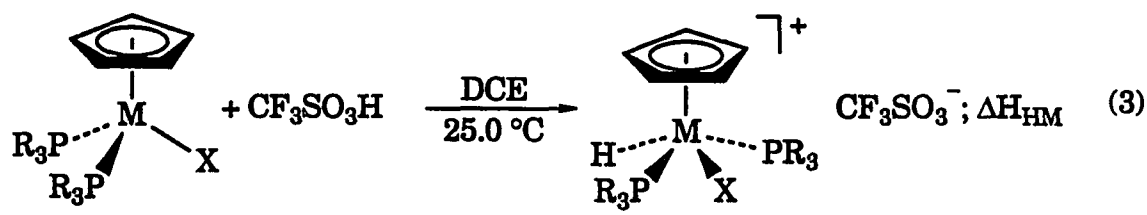
There is currently much interest in quantitative relationships between properties of ligands and their transition metal complexes. Several studies[1] of ligand effects on spectroscopic, electrochemical, and kinetic properties of complexes have been reported. Especially relevant for this present paper are investigations of the acidity of transition metal hydrides.[2] For example, Norton and coworkers have determined pK_a values of organometallic complexes such as $HMn(CO)_4(PR_3)$,[3] $HCo(CO)_3(PR_3)$,[4] and $CpM(CO)_3H$ ($Cp=\eta^5$-C_5H_5, M=Cr, Mo, W).[5] Oxidation potentials of transition-metal hydrides have been used to calculate acidities of the corresponding 17e$^-$ hydride radical cations such as $Cp'M(CO)_2(L)H^{\bullet+}$ ($Cp'=C_5H_5(Cp)$, $C_5Me_5(Cp^*)$; M=Cr, Mo, W; L=PMe_3, PPh_3, $P(OMe)_3$, PEt_3, CO),[6] while Morris et al.[7] have determined pK_a values of $Cp'Ru(\overset{\frown}{P\ \ P})H_2^+$ ($Cp'=Cp, Cp^*$) complexes.

In these laboratories, we have determined the effects of ligand basicities on the basicities of their metal complexes, as measured by the enthalpies of protonation (ΔH_{HM}) with CF_3SO_3H in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1).[8] The basicities of phosphine ligands (PR_3) were measured by

$$ML_n + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HML_n^+CF_3SO_3^-;\ \Delta H_{HM} \qquad (1)$$

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HPR_3^+CF_3SO_3^-;\ \Delta H_{HP} \qquad (2)$$

their heats of protonation (ΔH_{HP}, eq 2). Excellent linear correlations are realized between ΔH_{HM} and ΔH_{HP} values for the series of phosphine complexes, $CpIr(CO)(PR_3)$,[9] $Fe(CO)_3(PR_3)_2$[9] and $W(CO)_3(PR_3)_3$.[10] Similarly, increasing the number of methyl groups in the η^5-cyclopentadienyl ligand of $(\eta^5\text{-}C_5Me_xH_{5-x})Ir(COD)$,[11] where COD is 1,5-cyclooctadiene, increases the basicity (ΔH_{HM}) of the metal. In a recent communication[12] we noted that the basicities (ΔH_{HM}) of $CpOs(PR_3)_2X$ ($PR_3 = PPh_3$, PPh_2Me; X = Cl, Br, I, H) increase with changes in the X ligand in the order: I < Br < Cl << H. The most remarkable finding was that the hydride complexes are up to 23.2 kcal/mol more basic than the corresponding halide complexes. In this paper we expand upon that study to include twenty two $Cp'M(PR_3)_2X$ complexes (eq 3), where the metal and the X, PR_3 and Cp'(Cp'=Cp or Cp*) ligands are systematically varied.



1-22 **$1H^+$-$22H^+$**

EXPERIMENTAL SECTION

General Procedures

All preparative reactions were carried out under an argon atmosphere using standard Schlenk techniques. The 1.0 M PMe_3 in toluene and neat PMe_3 were purchased and used as received from Aldrich. Hexanes and CH_2Cl_2 were refluxed over CaH_2, then distilled under N_2. Diethyl ether was purified by distillation from Na/benzophenone under N_2; the 1,2-dichloroethane solvent (99.8%, HPLC Grade) was purchased from Aldrich and was distilled from P_4O_{10} under argon immediately prior to use. The CF_3SO_3H was purchased from 3M Co. and purified as previously described.[8] Ethanol and methanol were dried over the magnesium alkoxide according to Perrin et al.,[13] while decahydronaphthalene (decalin) was degassed with N_2(g) and then stored over molecular sieves for 12 h before use. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were stored over molecular sieves in air. Brockman, activity I, neutral Al_2O_3 was deoxygenated for 18 h at room temperature under high vacuum, deactivated with 5% (w/w) Ar-saturated water and stored under argon.

The ^1H NMR spectra were recorded in $CDCl_3$ unless otherwise noted using a Nicolet-NT 300 MHz or Varian VXR-300 MHz spectrometer with TMS (δ=0.00 ppm) as the internal standard. T_1 values were determined using the standard inversion recovery sequence 180-τ-90.[14] The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer in CD_2Cl_2 using 85% phosphoric acid (δ=0.00 ppm) as the external standard. Elemental analyses

were performed by either Galbraith Laboratories, Inc., Knoxville, TN or Desert Analytics, Tuscon, AZ.

Syntheses of $CpOs(PPh_3)_2X$ (X = Cl (**1**),[15] Br (**2**),[16] I (**3**),[15] H (**4**)[17]), $CpRu(PMe_3)_2X$ (X = Cl (**14**), Br (**15**), I (**16**))[18], $CpRu(PPh_3)_2H$ (**17**)[17], $Cp^*Ru(PMe_3)_2Cl$ (**18**)[19], $Cp^*Ru(PPh_3)_2H$ (**19**)[7a], $CpRu(\overset{\frown}{P\ \ P})H$ ($\overset{\frown}{P\ \ P}$ = dppm (**20**), dppe (**21**), dppp (**22**))[17], and CpOs(dppm)Br (**12**)[20] were carried out according to the cited literature procedures. Ligand abbreviations are dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, dppp = $Ph_2PCH_2CH_2CH_2PPh_2$.

Synthesis of $CpOs(PMe_3)_2Br$ (8)

A suspension of $CpOs(PPh_3)_2Br$ (460 mg, 0.54 mmol) and neat PMe_3 (1.0 mL, 9.7 mmol) in 20 mL of decalin was heated to reflux for 12 h. The solution was cooled to room temperature, then placed on an alumina column (1.5 x 30 cm) packed in hexanes. The decalin and excess phosphines were eluted with 150 mL of hexanes. The desired yellow product was eluted with CH_2Cl_2; the solvent was then removed under vacuum. The residue was recrystallized by dissolving it in a minimum of CH_2Cl_2; this solution was layered with a 10-fold excess of hexanes, and the mixture was cooled to -20 °C for 24 h to yield orange crystals of $CpOs(PMe_3)_2Br$ (**8**) (150 mg, 66%). ^1H NMR ($CDCl_3$) δ 4.58 (s, 5H, Cp), 1.66 (d, $^2J_{PH}$ = 8.7 Hz, 18H, Me).

Characterization of 4, 7, 9, 10, 13

The following compounds were prepared in a manner similar to that used for **8**. Superscripts refer to literature preparations of the complexes by similar routes.

$CpOs(PPh_2Me)_2Br$ (**5**):[21b,c] 300 mg (0.35 mmol) of $CpOs(PPh_3)_2Br$ and 0.40 mL (2.1 mmol) of PPh_2Me in 20 mL of decalin; reaction time 12 h; yield 84%. ^1H NMR ($CDCl_3$) δ 7.1-7.3 (m, Ph), 4.51 (s, 5H, Cp), 1.72 (d, $^2J_{PH}$ = 8.1 Hz, 6H, CH_3). Anal. Calcd for $C_{31}H_{31}BrOsP_2$: C, 50.61; H, 4.25. Found: C, 50.23; H, 4.47.

$CpOs(PPhMe_2)_2Br$ (**7**):[21b,c] 200 mg (0.23 mmol) of $CpOs(PPh_3)_2Br$ and 0.20 mL (1.4 mmol) of $PPhMe_2$ in 20 mL of decalin; reaction time 12 h; yield, 66%. ^1H NMR ($CDCl_3$) δ 7.3-7.1 (m, Ph), 4.50 (s, 5H, Cp), 1.72 (d, $^2J_{PH}$ = 8.1 Hz, 12H, CH_3).

$CpOs(PPh_3)(PMe_3)Br$ (**9**):[21b,c] 200 mg (0.23 mmol) of $CpOs(PPh_3)_2Br$ and 1.0 mL (1.0 mmol) of PMe_3 (1.0 M solution in toluene) in 20 mL of toluene; reaction time 12 h; yield, 54%. ^1H NMR ($CDCl_3$) δ 7.3-7.1 (m, Ph), 4.47 (s, 5H, Cp), 1.39 (d, $^2J_{PH}$ = 9 Hz, 9H, CH_3). Anal. Calcd for $C_{26}H_{29}BrOsP_2$: C, 46.37; H, 4.34. Found: C, 46.61; H, 4.36.

$CpOs(PMe_3)_2I$ (**10**): 236 mg (0.23 mmol) of $CpOs(PPh_3)_2I$ and 5 mL (5.0 mmol) of PMe_3 (1.0 M solution in toluene) in 40 mL of decalin; reaction time 6 h; yield, 72%. ^1H NMR ($CDCl_3$) δ 4.59 (s, 5H, Cp), 1.72 (virtual t, $^2J_{PH}$ = 8.7 Hz, 18H, CH_3). Anal. Calcd for $C_{11}H_{23}IOsP_2$: C, 24.92; H, 4.33. Found: C, 25.12; H, 4.57.

$CpOs(dppp)Br$ (**13**) was prepared from $CpOs(PPh_3)_2Br$ (100 mg, 0.12 mmol) and dppp (50 mg, 0.12 mmol) in a manner exactly like $CpOs(dppm)Br$;[20] yield, 50-80%. ^1H NMR ($CDCl_3$) δ 7.5-7.1 (m, Ph), 4.58 (s, 5H, Cp), 3.08 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 2.45 (m, 1H, CH_2), 1.72 (m, 1H, CH_2). Anal. Calcd for $C_{32}H_{31}BrOsP_2$: C, 51.41; H, 4.18. Found: C, 50.94; H, 4.26.

Synthesis of $CpOs(PPh_3)(P(OEt)_3)H$ (11)

First, $CpOs(PPh_3)(P(OEt)_3)Br$ was prepared from $CpOs(PPh_3)_2Br$ (200 mg, 0.23 mmol) and $P(OEt)_3$ (164 μL, 0.96 mmol) exactly like $CpOs(PPh_3)(P(OMe)_3)Br$;[20] reaction time, 3 h; yields a yellow oil. ^1H NMR ($CDCl_3$) δ 7.5-7.3 (m, Ph), 4.60 (s, 5H, Cp), 3.81 (q, $^2J_{HH}$ = 6.9 Hz, 6H, CH_2), 1.06 (t, $^2J_{HH}$ = 6.9 Hz, 9H, CH_3). To the $CpOs(PPh_3)(P(OEt)_3)Br$ oil was added a NaOMe solution, which was prepared by allowing 70 mg (3.0 mmol) of Na to react completely with 20 mL of MeOH. After refluxing the solution for 9 h, the volume was reduced to 3 mL in vacuo. The pale yellow precipitate that formed was filtered, washed (2 x 1 mL of MeOH) and dried in vacuo (50% overall yield). ^1H NMR ($CDCl_3$) δ 7.4-7.2 (m, Ph), 4.54 (s, 5H, Cp), 3.5 (m, ^2J = 50 Hz, 6H, CH_2), 0.87 (t, $^2J_{HH}$ = 8.7 Hz, 9H, CH_3), -15.64 (dd, $^2J_{PH}$ = 31.5 and 27.6 Hz, 1H, Os-H). Anal. Calcd for $C_{29}H_{36}O_3OsP_2$: C, 50.86; H, 5.30. Found: C, 50.68; H, 5.54.

Synthesis of $CpOs(PPh_2Me)_2H$ (6)

Complex **6** was prepared in a manner similar to that used for **11**; 200 mg (0.23 mmol) of $CpOs(PPh_2Me)_2Br$ added to a NaOMe solution prepared by reacting 70 mg (3.0 mmol) with 40 mL of MeOH; reaction time, 3 h; yield, 87%. ^1H NMR ($CDCl_3$) δ 7.0-7.6 (m, 20H, Ph), 4.42 (s, 5H, Cp), 1.83 (d, $^2J_{PH}$ = 8.1 Hz, 6H, CH_3), -14.62 (t, $^2J_{PH}$ = 29.0 Hz, 1H, Os-H).

Preparation of $[CpOs(PPh_3)_2(H)_2]CF_3SO_3(4H^+CF_3SO_3^-)$

The complex $CpOs(PPh_3)_2H$ (4) was prepared by reaction of 125 mg (0.15 mmol) of $CpOs(PPh_3)_2Br$ with a NaOMe solution, which was prepared by

reacting 100 mg (4.3 mmol) of Na with 10 mL of MeOH. After refluxing 1.5 h, the off-white precipitate was filtered from the cooled solution and washed with MeOH. This white solid (87 mg) was dissolved in Et_2O and protonated with 1.1 equiv (10.8 μL, 0.12 mmol) CF_3SO_3H. After stirring 5 min, the off-white precipitate was filtered and rinsed with Et_2O and dried in vacuo (50% overall yield). X-ray quality crystals were formed by dissolving **4H⁺CF₃SO₃⁻** in a minimal amount of CH_2Cl_2 and layering the solution with a 5-fold volume of hexanes; the resulting mixture was cooled to -20 °C for 4 d. Anal. Calcd for $C_{42}H_{37}F_3O_3OsP_2S$: C, 54.18; H, 4.01. Found: C, 53.98, H, 3.97.

Protonation Reactions

Compounds **1-22** were protonated for NMR characterization by dissolving ~5 mg of the complex in 0.5 mL of $CDCl_3$ (or CD_2Cl_2) in an NMR tube under Ar. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum. Spectroscopic data at room temperature for compounds **1H⁺-22H⁺** are listed below.

$[CpOs(PPh_3)_2(Cl)(H)]CF_3SO_3$ (**1H⁺CF₃SO₃⁻**): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.43 (s, 5H, Cp), -11.66 (t, $^2J_{PH}$ = 32.4 Hz, 1H, Os-H).

$[CpOs(PPh_3)_2(Br)(H)]CF_3SO_3$ (**2H⁺CF₃SO₃⁻**): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.43 (s, 5H, Cp), -12.13 (t, $^2J_{PH}$ = 34.0 Hz, 1H, Os-H).

$[CpOs(PPh_3)_2(I)(H)]CF_3SO_3$ (**3H⁺CF₃SO₃⁻**): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.35 (s, 5H, Cp), -12.74 (t, $^2J_{PH}$ = 34.7 Hz, 1H, Os-H).

$[CpOs(PPh_3)_2(H)_2]CF_3SO_3$ (**4H⁺CF₃SO₃⁻**): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.06 (s, 5H, Cp), -11.46 (t, $^2J_{PH}$ = 29.0 Hz, 2H, Os-H).

$[CpOs(PPh_2Me)_2(Br)(H)]CF_3SO_3$ (**5H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.66 (s, 5H, Cp), 1.77 (d, $^2J_{PH}$ = 8.7 Hz, 6H, CH_3), -12.70 (t, $^2J_{PH}$ = 33.4 Hz, 1H, Os-H).

$[CpOs(PPh_2Me)_2(H)_2]CF_3SO_3$ (**6H$^+$ CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 5.14 (s, 5H, Cp), 2.06 (d, $^2J_{PH}$ = 8.7 Hz, 6H, CH_3), -12.57 (t, $^2J_{PH}$ = 30.6 Hz, 2H, Os-H).

$[CpOs(PPhMe_2)_2(Br)(H)]CF_3SO_3$ (**7H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.46 (s, 5H, Cp), 2.14 (d, $^2J_{PH}$ = 9 Hz, 6H, CH_3), 1.76 (d, $^2J_{PH}$ = 9 Hz, 6H, CH_3), -13.78 (t, $^2J_{PH}$ = 36.5 Hz, 1H, Os-H).

$[CpOs(PMe_3)_2(Br)(H)]CF_3SO_3$ (**8H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 5.74 (s, 5H, Cp), 1.95 (d, $^2J_{PH}$ = 10.5 Hz, 18H, CH_3), -14.34 (t, $^2J_{PH}$ = 36.2 Hz, 1H, Os-H).

$[CpOs(PPh_3)(PMe_3)(Br)(H)]CF_3SO_3$ (**9H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.5 (m, Ph), 5.64 (s, 5H, Cp), 1.55 (d, $^2J_{PH}$ = 11.7 Hz, 9H, CH_3), -13.98 (dd, $^2J_{PH}$ = 32.4 and 36.9 Hz, 1H, Os-H).

$[CpOs(PMe_3)_2(I)(H)]CF_3SO_3$ (**10H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 5.64 (s, 5H, Cp), 2.02 (virtual t, $^2J_{PH}$ = 8.4 Hz, 18H, CH_3), -15.33 (t, $^2J_{PH}$ = 37.3 Hz, 1H, Os-H).

$[CpOs(PPh_3)(P(OEt)_3)(H)_2]CF_3SO_3$ (**11H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.34 (s, 5H, Cp), 3.71 (pentet, ^2J = 7.0 Hz, 6H, CH_2), 1.06 (t, $^2J_{HH}$ = 7.0 Hz, 9H, CH_3), -12.26 (t, $^2J_{PH}$ = 30.2 Hz, 2H, Os-H).

$[CpOs(dppm)(Br)(H)]CF_3SO_3$ (**12H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.6 (m, Ph), 5.45 (s, 5H, Cp), 6.26 (dt, 1H, CH_2), 5.70 (dt, 1H, CH_2), -10.81 (s, 1H, Os-H).

$[CpOs(dppp)(Br)(H)]CF_3SO_3$ (**13H$^+$ CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.3 (m, Ph), 5.70 (s, 5H, Cp), 3.30 (dt, J = 6.3, 12.9 Hz, 2H, CH_2), 2.96 (m, 2H, CH_2), 2.22 (br m, 2H, CH_2), -12.49 (t, $^2J_{PH}$ = 32.7 Hz, 1H, Os-H).

$[CpRu(PMe_3)_2(Cl)(H)]CF_3SO_3$ (**14H$^+$ $CF_3SO_3^-$**): ^1H NMR ($CDCl_3$) δ 5.52 (s, 5H, Cp), 1.77 (d, $^2J_{PH}$ = 9.9 Hz, 18H, CH_3), -9.52 (t, $^2J_{PH}$ = 30.0 Hz, 1H, Ru-H).

$[CpRu(PMe_3)_2(Br)(H)]CF_3SO_3$ (**15H$^+$ $CF_3SO_3^-$**): ^1H NMR ($CDCl_3$) δ 5.53 (s, 5H, Cp), 1.88 (d, $^2J_{PH}$ = 10.2 Hz, 18H, CH_3), -9.48 (t, $^2J_{PH}$ = 29.4 Hz, 1H, Ru-H).

$[CpRu(PMe_3)_2(I)(H)]CF_3SO_3$ (**16H$^+$ $CF_3SO_3^-$**): ^1H NMR ($CDCl_3$) δ 5.75 (s, 5H, Cp), 2.00 (d, $^2J_{PH}$ = 10.5 Hz, 18H, CH_3), -9.60 (t, $^2J_{PH}$ = 29.4 Hz, 1H, Ru-H).

$[CpRu(PPh_3)_2(H)_2]CF_3SO_3$ (**17H$^+$ $CF_3SO_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 4.91 (s, 5H, Cp), -7.30 (t, $^2J_{PH}$ = 23.9 Hz, 2H, Ru-H).

$[Cp^*Ru(PMe_3)_2(Cl)(H)]CF_3SO_3$ (**18H$^+$ $CF_3SO_3^-$**): ^1H NMR ($CDCl_3$) δ 1.83 (s, 15H, Cp*), 1.63 (d, $^2J_{PH}$ = 9.3 Hz, 18H, CH_3), -9.91 (t, $^2J_{PH}$ = 34.2 Hz, 1H, Ru-H).

$[Cp^*Ru(PPh_3)_2(H)_2]CF_3SO_3$ (**19H$^+$ $CF_3SO_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.3 (m, Ph), 1.35 (s, 15H, Cp*), -7.29 (t, $^2J_{PH}$ = 26.5 Hz, 2H, Ru-H).

$[CpRu(dppm)(H_2)]CF_3SO_3$ (**20H$^+$ $CF_3SO_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.18 (s, 5H, Cp), 5.35 (m, 1H, CH_2), 4.31 (m, 1H, CH_2), -6.98 (br s, 2H, Ru-(H_2)).

$[CpRu(dppe)(H)_2]CF_3SO_3$ (**21H$^+$ $CF_3SO_3^-$**): ^1H NMR ($CDCl_3$) δ 7.4 (m, Ph), 5.18 (s, 5H, Cp of *trans* complex), 4.82 (s, 5H, Cp of *cis* complex), 2.50 (br s, 2H, CH_2 of *trans* complex), 2.45 (s, 2H, CH_2 of *cis* complex), -9.09 (br s, 2H, *cis*-Ru-(H_2)), -8.49 (t, $^2J_{PH}$ = 28.0 Hz, 2H, *trans*-Ru-H).

$[CpRu(dppp)(H)_2]CF_3SO_3$ (**22H$^+$ $CF_3SO_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.4 (m, Ph), 5.01 (s, 5H, Cp), 2.89 (m, 2H, CH_2), 2.24 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), -8.70 (t, $^2J_{PH}$ = 25.7 Hz, 2H, Ru-H).

Calorimetric Titrations

Calorimetric titrations were performed under an argon atmosphere using a Tronac model 458 isoperibol calorimeter as originally described[8] and then modified.[9] In general a two minute titration period was used for all complexes except for **3**, which was run using a 3-minute titration. The titration period was preceded and followed by heat capacity calibrations. 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 to 50 mL of a 1.7 mM solution of the metal complex (5-10% excess) in DCE.

The heat of dilution (ΔH_{dil}) of the acid in DCE (-0.2 kcal/mol)[9] was used to correct the reaction enthalpies. The ΔH_{HM} values were obtained using two different standardized acid solutions and are reported as the average of at least four titrations and as many as eight. Errors are reported as the average deviation from the mean.

The combination of CF_3SO_3H and DCE used in these and previous ΔH_{HM} studies was chosen for the following reasons. Trifluoromethanesulfonic acid is one of the strongest acids known, H_o = -14.1;[22] therefore, it protonates a large number of even weakly basic metal complexes. The $CF_3SO_3^-$ anion is weakly coordinating so it has a low tendency to displace other ligands from the protonated product. 1,2-Dichloroethane (DCE) has been chosen as the solvent for these and previous ΔH_{HM} studies, because it is easily purified,[8] has low volatility (b.p. = 83 °C), is weakly coordinating and is weakly basic so that it is not protonated by CF_3SO_3H. It also dissolves a broad range of neutral and protonated complexes. The low

dielectric constant ($\varepsilon = 10.46$)[23] for DCE means that the protonated ionic products occur as ion pairs. It has been estimated that dissociation of these ion pairs, autoprotolysis and dimerization of CF_3SO_3H contribute little to the measured ΔH_{HM} values.[8] Solvation effects, which can be substantial in hydrogen bonding solvents,[24] are assumed to be very similar for protonation reactions of related complexes in this acid-solvent system. Evidence that solvation and ion-pairing effects are not major contributors come from ΔH_{HP} values for PMe_3 (-31.6 kcal/mol)[8] and P(cyclohexyl)$_3$ (-33.2 kcal/mol).[8] As alkyl phosphines, both would be expected to have similar ΔH_{HP} values. If the protonated phosphine HPR_3^+ were stabilized by ion-pairing or solvation, one would expect this stabilization to be greater for the smaller $HPMe_3^+$ than HP(cyclohexyl)$_3^+$, which would make PMe_3 more basic than P(cyclohexyl)$_3$. That P(cyclohexyl)$_3$ is, in fact, more basic than PMe_3 indicates that solvation and ion-pairing energies for these phosphines are similar in this system. Thus, trends in ΔH_{HM} values for these complexes are likely to be determined by the energetics of protonation rather than ion-pairing or solvation effects. In fact, Abboud, et al.,[25] report that "gas-phase like behavior" can prevail in solution chemistry for acid-base reactions if hydrogen bonding is minimized by using saturated hydrocarbons or CH_2Cl_2 as solvents.

Equilibrium Study and ΔH_{HM} Determination of 6

Due to small amounts of decomposition in the calorimeter that made the results unreliable, the ΔH_{HM} for complex **6** was determined from equilibrium constant (K_{eq}) measurements (eq 4) at different temperatures. An

$$\underset{\mathbf{4H^+}}{[CpOs(PPh_3)_2(H)_2]^+} + \underset{\mathbf{6}}{CpOs(PPh_2Me)_2H} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{4}}{CpOs(PPh_3)_2H} + \underset{\mathbf{6H^+}}{[CpOs(PPh_2Me)_2(H)_2]^+} \qquad (4)$$

air-tight 5 mm NMR tube containing 13.1 mg (0.020 mmol) of **6**, 18.6 mg (0.020 mmol) of $\mathbf{4H^+CF_3SO_3^-}$ and 0.5 mL of CD_2Cl_2 was allowed to equilibrate for 8 h. After 8 h, no changes in the spectrum occurred with time indicating that equilibrium had been achieved. Relative concentrations of the species in solution were determined by integration of the Cp resonances of the reactants and products. Calculation of the K_{eq} was done using equation 5. The K_{eq} values measured at various temperatures were 15.0 °C, 15.4; 20.0 °C, 15.3; 22.5 °C, 15.1; 25.0 °C, 14.6; 27.5 °C, 14.2; 30.0 °C, 13.2; and 35.0 °C, 12.7.

$$K_{eq} = \frac{[CpOs(PPh_3)_2H(4)][CpOs(PPh_2Me)_2(H)_2^+(\mathbf{6H^+})]}{[CpOs(PPh_2Me)_2H(\mathbf{6})][CpOs(PPh_3)(H)_2^+(\mathbf{4H^+})]} \qquad (5)$$

X-ray Diffraction Study of [*trans*-$CpOs(PPh_3)_2(H)_2^+$][$CF_3SO_3^-$]•CH_2Cl_2 ($\mathbf{4H^+}$ $\mathbf{CF_3SO_3^-}$)

A colorless crystal of $\mathbf{4H^+CF_3SO_3^-}$ was mounted on a glass fiber for data collection at -50± 1 °C on an Enraf-Nonius CAD4 diffractometer. The cell constants for the data collection were determined from a list of reflections found by an automated search routine. Data collection and reduction information are given in Table I. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections of 3.0% was applied to the data. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was

1.6% based on F. The triclinic space group $P\bar{1}$ was determined by intensity statistics, and the structure was solved by direct methods.[26] Most non-hydrogen atoms were placed directly from the E-map. All remaining non-hydrogen atoms were found in one successive difference-Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were of the riding-model type and the isotropic temperature factors were fixed at the accompanying carbon atom values. One molecule of dichloromethane was found per formula unit. The hydride atoms were located at 1.19 and 1.45Å from the Os using a difference-Fourier map. Selected bond distances and angles for $4H^+$ are given in Table II. The ORTEP drawing of the cation $4H^+$ has the hydride atoms placed at 1.68Å (discussed in Results Section) in Figure 1.

Table I. Crystal and Data Collection Parameters for [*trans*-$CpOs(PPh_3)_2(H)_2]CF_3SO_3$ ($4H^+$)

Formula	$[OsP_2C_{41}H_{32}]^+[SO_3CF_3]^- CH_2Cl_2$
Space Group	$P\bar{1}$
a, Å	11.346(2)
b, Å	13.061(2)
c, Å	14.108(2)
α, deg	80.24(2)
β, deg	85.88(2)
γ, deg	75.11(2)
V, Å^3	1990.3(7)
Z	2
d_{calc}, g/cm^3	1.69
Crystal size, mm	0.45 x 0.15 x 0.15
$\mu(MoK_\alpha)$, cm^{-1}	37.2
Data collection instrument	Enraf-Nonius, CAD4

Table I. continued

Radiation (monochromated in incident beam)	$MoK_\alpha(\lambda=0.71073Å)$
Orientation reflections, number, range (2θ)	25, $17.4 < \theta < 32.0$
Temperature, °C.	-50(1)
Scan method	θ-2θ
Data col. range, 2θ, deg	4.0-50.0
No. data collected:	7340
No. unique data, total:	6672
with $F_o^2 > 3.0\sigma(F_o^2)$:	5811
Number of parameters refined	504
Trans. factors, max., min. (ψ-scans)	0.994, 0.875
R^a	0.028
R_w^b	0.036
Quality-of-fit indicator[c]	1.12
Largest shift/esd, final cycle	0.01
Largest peak, e/Å^3	0.93(9)

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$

[c] Quality-of-fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$

Table II. Selected Bond Distances (Å)[a] and Angles (deg)[a] for [*trans*-$CpOs(PPh_3)_2(H)_2]^+$ ($4H^+$)

Distances (Å)					
Os-P(1)	2.310(1)	Os-C(3)	2.230(5)	C(3)-C(4)	1.425(8)
Os-P(2)	2.310(1)	Os-C(4)	2.210(5)	C(4)-C(5)	1.418(7)
Os-Cp(cent)[b]	1.89	Os-C(5)	2.226(5)	C(5)-C(1)	1.398(7)
Os-C(1)	2.260(5)	C(1)-C(2)	1.408(7)		
Os-C(2)	2.267(5)	C(2)-C(3)	1.411(7)		

Bond Angles (deg)			
P(1)-Os-P(2)	105.71(4)	P(2)-Os-H_b	77(2)
P(1)-Os-H_a	66(2)	H_a-Os-H_b	121(3)
P(1)-Os-H_b	71(2)	P(1)-Os-Cp(cent)[b]	127
P(2)-Os-H_a	78(2)	P(2)-Os-Cp(cent)[b]	127

[a]Numbers in parentheses are estimated standard deviations in the least significant digits. [b]cent = centroid of Cp ring.

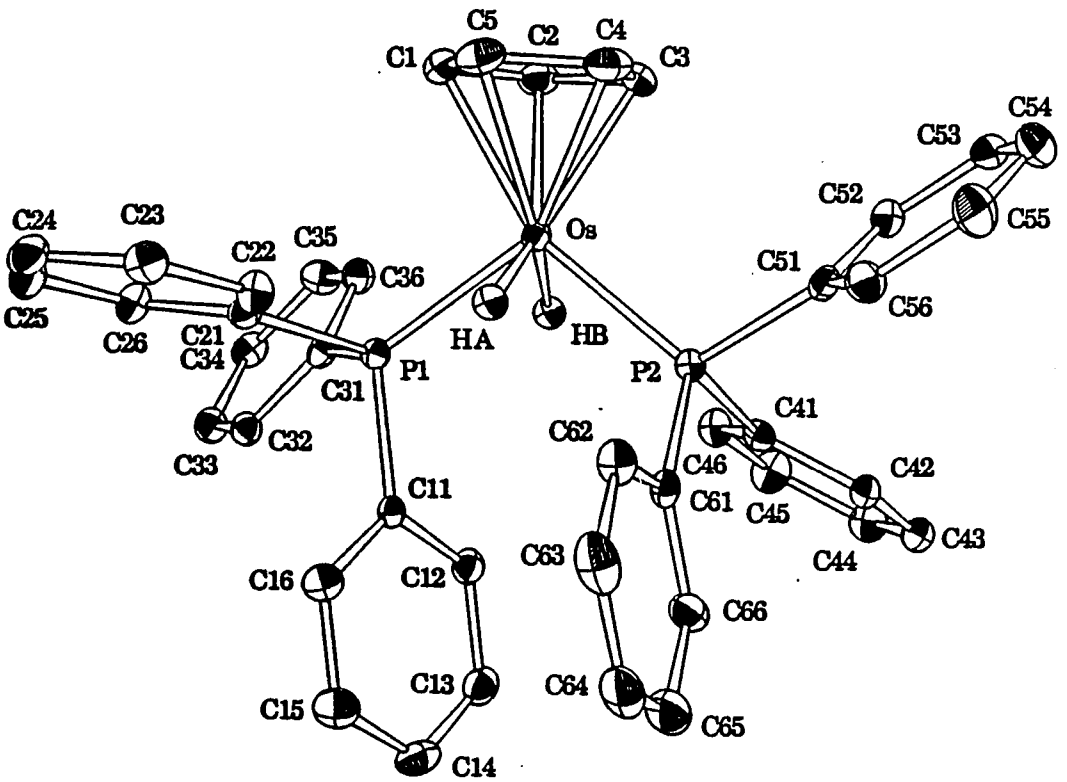


Figure 1. Molecular structure of *trans*-$CpOs(PPh_3)_2(H)_2^+$ ($4H^+$).

RESULTS

Characterization of Complexes and Their Protonated Products

Complexes **1-22** have the three-legged piano stool geometry (eq 3); X-ray structural studies of **1**[27] and **14**[28] show that there are approximately 90° angles between the PR_3 and X ligands. The complexes are slightly air-sensitive in the solid state, except for the osmium halides which are air-stable.

Quantitative formation of the four-legged piano-stool complexes **1H$^+$-22H$^+$** occurs upon addition of 1 equiv of CF_3SO_3H to the neutral complexes **1-22** (eq 3) as evidenced by ^1H NMR spectroscopy. These protonated complexes are air-sensitive in solution; complex **4H$^+$CF$_3$SO$_3^-$** was isolated as an off-white, air-stable solid. The ^1H NMR spectra of these complexes are the same as those of **2H$^+$PF$_6^-$**,[21a] **4H$^+$BPh$_4^-$**,[15] **8H$^+$PF$_6^-$**,[21a] **14H$^+$PF$_6^-$**,[28] **17H$^+$BPh$_4^-$**,[29] **18H$^+$PF$_6^-$**,[19] **19H$^+$BF$_4^-$**,[7b] **20H$^+$-22H$^+$PF$_6^-$** [30], which have previously been isolated and characterized.

The *trans*-configuration has previously been assigned to the protonated halide compounds **2H$^+$**,[21a] **8H$^+$**,[21a] and **14H$^+$**[28] based on the triplet ($^2J_{PH}$ = 30.0-36.2 Hz) for the hydride ligand in their ^1H NMR spectra. The *trans* structure is also assigned to the halide complexes **1H$^+$**, **3H$^+$**, **5H$^+$**, **7H$^+$**, **9H$^+$**, **10H$^+$**, **13H$^+$-16H$^+$** and **18H$^+$**, since the hydride resonances occur as triplets between -7.29 (**17H$^+$**) and -15.33 (**10H$^+$**) ppm with $^2J_{PH}$ coupling constants between 23.9 and 37.3 Hz. Although a doublet of doublets is expected for $CpOs(PPh_3)[P(OEt)_3](H)_2^+$ (**11H$^+$**), a triplet with a $^2J_{PH}$ coupling constant of 30.2 Hz is observed, which is similar to $^2J_{PH}$ values of the above complexes; apparently the $^2J_{PH}$ coupling constants for the phosphine and the phosphite

ligands are similar. The complex $CpOs(PPh_3)(PMe_3)(Br)(H)^+$ (**9H$^+$**) does exhibit a doublet of doublets for the hydride resonance (-13.98 ppm, $^2J_{PH}$ = 32.4 and 26.9 Hz).

The dihydride complexes $Cp'Ru(PPh_3)_2(H)_2^+$ (Cp'=Cp, **17H$^+$** and Cp*, **19H$^+$**) were assigned the *trans* structure by Chinn and Heinekey[31] based on the two distinct ^{1}H NMR hydride ($^2J_{PH}$ = 29.4 and 30.7 Hz) signals observed for $CpRu[(R)\text{-}(+)\text{-}Ph_2PCH_2CH(CH_3)PPh_2](H)_2^+$, which rules out the *cis* isomer. The structures of **4H$^+$** and **6H$^+$** are also assigned the *trans* geometry since their $^2J_{PH}$ values (29.0 and 30.6 Hz) are very similar to those in the Ru complexes. The structure of **4H$^+$** (Figure 1) was found to be a regular 4-legged piano stool molecule of *trans* geometry with a P_1-Os-P_2 bond angle of 105.71° (4). The Os-P bond lengths are both 2.310(1) Å, which is within the normal Os-P bond length range.[32] The structure solution yielded Os-H bond distances (1.19 and 1.45Å) that are much shorter than the average Os-H bond length (1.66(2)Å) in $H_4Os(PPhMe_2)_3$, which was determined by neutron diffraction.[32] The short Os-H distances are almost certainly not real since most of the electron density located by X-ray diffraction is between the Os and hydride atoms, rather than around the hydrogen nucleus. The H_a-Os-H_b bond angle is 121°, which is somewhat smaller than the 138° H_a-Re-H_b bond angle for the isostructural $CpRe(PPh_3)_2H_2$ complex.[33]

Due to the small bite angle of the dppm ligand, $CpRu(dppm)(H_2)^+$ (**20H$^+$**) is forced to have *cis* phosphorus atoms and an η^2-(H_2) ligand. This geometry has been previously established[30] by J_{HD} coupling constants for **20H$^+$**; **21H$^+$** exists as a 1:2 mixture of *cis*-(η^2-$(H)_2$) and *trans*-$(H)_2$ isomers,

while complex **22H⁺** has exclusively the *trans*-$(H)_2$ geometry as evidenced by ^1H NMR studies.[30]

In contrast to **20H⁺**, the structure of CpOs(dppm)(Br)(H)⁺ (**12H⁺**) cannot be definitively assigned based on the ^1H and ^{31}P NMR spectra in CD_2Cl_2. At room temperature this complex exhibits a broad singlet for the hydride resonance at -11.43 ppm in the ^1H NMR spectrum. If the sample is cooled to -20 °C, the fluxionality of the system is slowed and the hydride resonance appears as a triplet ($^2J_{PH}$ = 22.5 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **12H⁺** shows sharp doublets at -38.3 and -58.5 ppm ($^2J_{PP}$ = 101 Hz for both doublets) in the temperature range from -78 to 15 °C, which indicates that the P atoms are inequivalent. However, selective irradiation of the methylene protons (5.8 ppm in the ^1H NMR spectrum) while running the ^1H coupled ^{31}P NMR spectrum at -30 °C results in a doublet of doublets ($^2J_{PH}$ = 22.1 Hz, $^2J_{PP}$ = 101 Hz) for both phosphorus atoms. Comparing this coupling constant (22.1 Hz) with the $^2J_{PH}$ coupling constant (22.5 Hz) of the hydride peak from the ^1H NMR spectrum indicates that the inequivalent phosphorus nuclei are equally coupled to the hydride ligand, which would be consistent with the *cis* four-legged piano stool geometry for **12H⁺** if the coupling constant $^2J_{PH}$ for the *cis* and *trans* P were coincidentally the same. Based on these results, we cannot confidently assign a structure to **12H⁺** although the other dppm complexes have *cis* structures; attempts to grow crystals for X-ray diffraction were unsuccessful.

Calorimetry Studies

Table III contains the heats of protonation (ΔH_{HM}) as determined by calorimetric titration of complexes **1-5** and **7-22** with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C according to eq 3. Plots of temperature vs. amount of acid added were linear indicating that the protonations occur rapidly and stoichiometrically. There was no decomposition of either the neutral or protonated species during the titration as evidenced by the normal pre- and post-titration curves. The protonated halide complexes in DCE solution were easily deprotonated with 1.0 equiv of diphenylguanidine; the resulting complexes were recovered by passing the mixtures down a short (~5 cm) alumina column using CH_2Cl_2 as the eluent. Crystallization of the complexes from CH_2Cl_2 layered with hexanes resulted in the pure unprotonated complexes. Recovery of the original hydride complexes was unsuccessful due to the air sensitivity of the protonated compounds in solution.

Equilibrium Study of Reaction (4)

A plot of $\ln K_{eq}$ vs 1/T, where the slope = $-\Delta\Delta H_{HM}/R$, was used to determine that $\Delta\Delta H_{HM}$ = -1.9 (±0.3) kcal/mol[34] for reaction (4). The ΔH_{HM} for $CpOs(PPh_2Me)_2H$ (**6**) was calculated (eq 6) to be -39.2 kcal/mol using

$$\Delta\Delta H_{HM}=\Delta H_{HM}\text{ (of }\mathbf{6}\text{)} - \Delta H_{HM}\text{ (of }\mathbf{4}\text{)} \qquad (6)$$

$$\Delta\Delta G^\circ=\Delta\Delta H_{HM}-T\Delta\Delta S^\circ \qquad (7)$$

the ΔH_{HM} for **4** and $\Delta\Delta H_{HM}$ (-1.9 kcal/mol) for reaction (4). The $\Delta\Delta S^\circ$ at 298 K for reaction (4) was calculated to be -1.0 (±1.0) eu using eq 7, where $\Delta\Delta G^\circ = -RT\ln K_{eq}$ at 298 K.

TABLE III. Heats of Protonation (ΔH_{HM}) of $Cp'M(PR_3)(PR'_3)X$ Complexes

metal complex	ΔH_{HM},[a,b] kcal/mol
$CpOs(PPh_3)_2Cl$, **1**	-19.7 (± 0.2)
$CpOs(PPh_3)_2Br$, **2**	-16.3 (± 0.1)
$CpOs(PPh_3)_2I$, **3**	-14.1 (± 0.1)
$CpOs(PPh_3)_2H$, **4**	-37.3 (± 0.1)
$CpOs(PPh_2Me)_2Br$, **5**	-20.0 (± 0.2)
$CpOs(PPh_2Me)_2H$, **6**	-39.2 (± 0.3)
$CpOs(PPhMe_2)_2Br$, **7**	-26.2 (± 0.1)
$CpOs(PMe_3)_2Br$, **8**	-29.4 (± 0.4)
$CpOs(PPh_3)(PMe_3)Br$, **9**	-25.6 (± 0.4)
$CpOs(PMe_3)_2I$, **10**	-26.6 (± 0.4)
$CpOs(PPh_3)[(P(OEt)_3]H$, **11**	-33.6 (± 0.3)
CpOs(dppm)Br,[c] **12**	-17.5 (± 0.4)
CpOs(dppp)Br,[c] **13**	-20.1 (± 0.4)
$CpRu(PMe_3)_2Cl$, **14**	-21.2 (± 0.4)
$CpRu(PMe_3)_2Br$, **15**	-20.9 (± 0.3)
$CpRu(PMe_3)_2I$, **16**	-20.6 (± 0.2)
$CpRu(PPh_3)_2H$, **17**	-29.7 (± 0.2)
$Cp^*Ru(PMe_3)_2Cl$, **18**	-30.2 (± 0.2)
$Cp^*Ru(PPh_3)_2H$, **19**	-35.2 (± 0.2)
CpRu(dppm)H,[c] **20**	-28.9 (± 0.2)
CpRu(dppe)H,[c,d] **21**	-29.0 (± 0.1)
CpRu(dppp)H,[c] **22**	-29.6 (± 0.1)

[a]For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b]Numbers in parentheses are average deviations from the mean of at least four titrations. [c]dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2P(CH_2)_2PPh_2$ and dppp = $Ph_2P(CH_2)_3PPh_2$. [d]*Cis* and *trans* isomers of the product contribute to the ΔH_{HM} of this complex. See text for details.

DISCUSSION

Halide and Hydride Ligand Effects on Metal Basicity (ΔH_{HM})

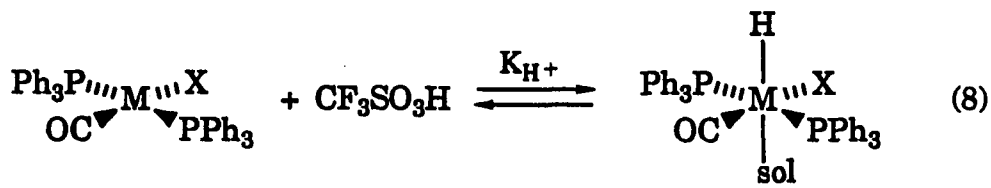
The heats of protonation (ΔH_{HM}) (Table III) for the halide complexes $CpOs(PPh_3)_2X$ (1-3) increase in the order: I^- (-14.1 kcal/mol) < Br^- (-16.3 kcal/mol) < Cl^- (-19.7 kcal/mol). One might have expected the reverse order for ΔH_{HM} since the higher electronegativity and lower polarizability of Cl^- should decrease the electron density on the metal. Previously, we showed that the basicity (ΔH_{HM}) of the metal in $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ increased with the basicity of the PR_3 ligand, as measured by its enthalpy of protonation (ΔH_{HP}) or pK_a. The simplest measure of the basicity of the halide ligand is the gas-phase proton affinity (P.A.) of $X^-(g)$,[35] which shows the basicities increase in the order: I^- (314.3 kcal/mol) < Br^- (323.6 kcal/mol) < Cl^- (333.3 kcal/mol). This trend in proton affinities is the same trend followed by the basicities of the $CpOs(PPh_3)_2X$ complexes; thus, increasing the basicity of X^- increases the basicity of its complex. The increasing donor ability of the halide ligands from I^- to Cl^- is supported by equilibrium constants[1i] for halide displacement reactions (eq 7) in CH_2Cl_2 solvent, which increase with Y^- as follows: I^- (3.5×10^{-4}) < Br^- (1.3×10^{-2}) < Cl^- (0.34).

$$Rh(PPh_3)_2(CO)(F) + PPN^+Y^- \rightleftharpoons Rh(PPh_3)_2(CO)Y + PPN^+F^- \qquad (7)$$

While the basicity (ΔH_{HM}) of the metal in $CpOs(PPh_3)_2X$ complexes is quite sensitive to the particular halide ion, changes in ΔH_{HM} for the ruthenium complexes $CpRu(PMe_3)_2X$ are much smaller: I^- (-20.6 kcal/mol) <

Br^- (-20.9 kcal/mol) < Cl^- (-21.2 kcal/mol). Although the same trend is observed, the ΔH_{HM} values are nearly the same within experimental error.

In earlier studies,[36] equilibrium constants (K_{H+}) for the reaction of CF_3SO_3H or RC(O)OH with $Ir(CO)(PR_3)_2(X)$ (PR_3 = PPh_3, $PPhMe_2$; X = Cl, Br, I) to give $M(CO)(PR_3)_2(X)(H)(sol)$ (eq 8) were determined. Equilibrium constants for the PPh_3 complexes increase in the order: Cl^- (1.14×10^2 M^{-1}) < Br^- (4.16×10^2 M^{-1}) < I^- (7.04×10^2); for the $PPhMe_2$ complexes they increase in the same order: Cl^- (0.60 M^{-1}) < Br^- (4.0 M^{-1}) < I^- (6.2 M^{-1}). It is not suprising that these reactions follow a different trend than we observe for simple protonation since the K_{H+} values include not only protonation of the metal,



(8)

but also coordination of a 6th ligand (sol = either a solvent molecule or the anion of the acid). The energetics of protonation and of ligand coordination probably follow trends that are opposite, as the halide (X) is changed. In these reactions (eq 8), it is not possible to determine whether it is the protonation or coordination of the sixth ligand that determines the overall trend.

Hydride compounds $CpOs(PPh_3)_2H$ (4) and $CpOs(PPh_2Me)_2H$ (6) (ΔH_{HM} = -37.3 and -39.2 kcal/mol, respectively) are dramatically more basic than the analogous halide compounds. For example, they are 21.0 kcal/mol and 19.2 kcal/mol more basic than the bromo complexes 2 and 5 (ΔH_{HM} = -16.3 and -20.0 kcal/mol, respectively). The magnitude of these differences is illustrated by the estimated equilibrium constants (K) for the bromide-hydride pairs of

complexes. They can be estimated if $\Delta S°$ is assumed to be the same for the protonation of both $CpOs(PR_3)_2H$ and $CpOs(PR_3)_2Br$. This assumption is supported by the $\Delta\Delta S°$ value (-1.0 (±1.0) e.u) for reaction 4, which means that $T\Delta\Delta S°$ (-0.30 kcal/mol) is small compared to $\Delta\Delta H_{HM}$ (-1.9 ± 0.3 kcal/mol); thus, $\Delta\Delta G° \approx \Delta\Delta H_{HM}$ and $\Delta\Delta H_{HM} \approx -RTlnK_{eq}$. Assuming that $\Delta\Delta S°$ is also small for the equilibrium constant comparisons of **2** vs. **4** and **5** vs. **6**, $CpOs(PPh_3)_2H$ is 2.5×10^{15} times (i.e., $\Delta\Delta H_{HM}$ = 21.0 kcal/mol) more basic than $CpOs(PPh_3)_2Br$, and $CpOs(PPh_2Me)_2H$ is 1.2×10^{14} times (i.e., 19.2 kcal/mol) more basic than $CpOs(PPh_2Me)_2Br$. While these comparisons are approximate, they do demonstrate that the hydride complexes are remarkably more basic than the bromide and other halide analogs of $CpOs(PR_3)_2X$ (Table III). The largest difference in basicity (23.2 kcal/mol) is between $CpOs(PPh_3)_2H$ and $CpOs(PPh_3)_2I$; this difference means that the hydride complex is approximately 1.1×10^{17} times more basic than the iodide complex.

Tilset et al.,[6b] determined that a $1e^-$ oxidation of $CpM(CO)_3H$ (M=Cr, Mo, W) produces the 17-electron radical cation $CpM(CO)_3H^+$, which is up to 22.8 pK_a units more acidic than the corresponding neutral $CpM(CO)_3H$ complex. For example, $CpW(CO)_3H^+$ (pK_a = -3.0) is 19.1 pK_a units more acidic than $CpW(CO)_3H$ (pK_a = 16.1); at 25.0 °C the 19.1 pK_a units translate into 26.0 kcal/mol using the equation $\Delta\Delta G° = -RTlnK_{eq}$. The increase of 19.1 pK_a units ($\Delta\Delta G°$ = 26.0 kcal/mol) caused by a one-electron oxidation is only slightly larger than the 23.2 kcal/mol increase in basicity ($\Delta\Delta H_{HM}$) that results from substitution of an I^- ligand by a hydride ligand. Thus, the replacement of I^- by H^- has nearly the same effect as reducing the metal by one unit (+3 to +2 for the $CpW(CO)_3H$ system). Thus, if Os has a +2 oxidation state in

$CpOs(PPh_3)_2I$, $CpOs(PPh_3)_2H$ behaves in its protonation reaction as if its oxidation state is approximately +1, i.e., the hydride ligand behaves as an H atom. Support for this view is found in molecular orbital calculations of Low and Goddard,[37] who concluded that the addition of H_2 to $Pt(PH_3)_2$ is not oxidative, since covalent bonds are formed. They suggested that formal oxidation numbers denote the maximum covalency of the metal not its oxidation state.

The trend in ΔH_{HM} values ($I^- < Br^- < Cl^- << H^-$) for the $CpOs(PPh_3)_2X$ complexes can be understood in terms of the basicity of the X^- ligand, as measured by the proton affinity (P.A.) of $X^-(g)$. These P.A. values increase in the same order, I^- (314.3 kcal/mol) < Br^- (323.6 kcal/mol) < Cl^- (333.3 kcal/mol) < H^- (400.4 kcal/mol),[35] as the ΔH_{HM} values of their $CpOs(PPh_3)_2X$ complexes. As the strongest X donor to the Os in the $CpOs(PR_3)_2X$ complexes, the hydride ligand should make **4** and **6** the most basic complexes in the series, as is observed (Table III). In fact, there is an excellent correlation ($r = 0.9995$ for eq 9) between the donor ability of the halide or hydride ligand as measured by the P.A. of $X^-(g)$ and ΔH_{HM} for complexes **1-4** (Fig 2). Since P.A. values of a

$$-\Delta H_{HM} = 0.2698(\text{P.A.}) - 70.64; \text{ in kcal/mol} \qquad (9)$$

variety of anions (A^-) (e.g., F^-, CN^-, $CH_3CO_2^-$, $C{\equiv}CH^-$ and CH_3^-) are known,[35] eq 9 allows one to estimate basicities for a range of $CpOs(PPh_3)_2(A)$ complexes.

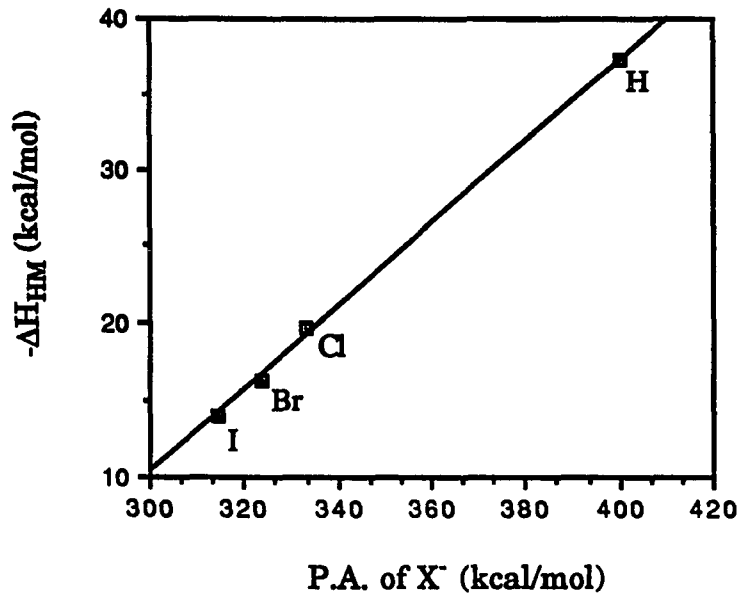


Figure 2. Correlation of metal basicities (ΔH_{HM}) of $CpOs(PPh_3)_2X$ with proton affinities (P.A.) of $X^-(g)$.

Phosphine Effect on Metal Basicity (ΔH_{HM}) in $CpOs(PR_3)_2Br$

The basicities (ΔH_{HM}) of the $CpOs(PR_3)_2Br$ complexes increase in the order: PPh_3 (-16.3 kcal/mol) < PPh_2Me (-20.0 kcal/mol) < $PPhMe_2$ (-26.2 kcal/mol) < PMe_3 (-29.4 kcal/mol). The basicities (ΔH_{HM}) of the free phosphines,[8] [PPh_3 (-21.0 kcal/mol) < PPh_2Me (-24.7 kcal/mol) < $PPhMe_2$ (-28.4 kcal/mol) < PMe_3 (-31.6 kcal/mol)] increase in the same order. A plot of $-\Delta H_{HM}$ vs $-\Delta H_{HP}$ (Fig 3) is fit by eq 10a with a correlation coefficient of 0.995. Equation 10a indicates that for the osmium series a 1.0 kcal/mol increase

$$-\Delta H_{HM} = -1.31\,\Delta H_{HP} - 11.6 \qquad (10a)$$

$$-\Delta H_{HM} = 2.30\,pK_a + 10.1 \qquad (10b)$$

in the basicity of the phosphine ligands increases the basicity of the complex by 1.31 kcal/mol. Since there are two phosphine ligands, each contributes 0.655 kcal/mol toward the basicity of the compound.

It is of particular interest to note that the basicity (ΔH_{HM}) of the mixed phosphine ligand complex $CpOs(PPh_3)(PMe_3)Br$ (**9**) (-25.6 kcal/mol) is not intermediate between that of $CpOs(PPh_3)_2Br$ (**2**) (-16.3 kcal/mol) and $CpOs(PMe_3)_2Br$ (-29.4 kcal/mol). Complex **9** is only 3.8 kcal/mol less basic than $CpOs(PMe_3)_2Br$ (**8**), but 9.3 kcal/mol more basic than $CpOs(PPh_3)_2Br$ (**2**). Steric or electronic factors could be responsible for **9** having a basicity closer to **8** than to **2**. The 9.3 kcal/mol increase in the ΔH_{HM} caused by substituting one PPh_3 in **2** ligand with PMe_3 is similar to the 10.4 kcal/mol increase in basicity of the free phosphine [PPh_3(ΔH_{HP} = -21.2 kcal/mol) and PMe_3(ΔH_{HP} = -31.6 kcal/mol)].[8] Since such a large change in ΔH_{HM} upon PPh_3 replacement by PMe_3 has not been observed in any other metal complex system (*vide infra*), it seems unlikely that it can be caused by an electronic effect only. On the other hand, steric repulsion among the ligands around Os increases when the metal is protonated. Thus, protonation will be sterically disfavored by bulky ligands such as PPh_3. For this reason, the basicity of $CpOs(PPh_3)_2Br$ may be unusually low. Replacement of one PPh_3 group in **2** by PMe_3 to form $CpOs(PPh_3)(PMe_3)$ (**9**) would reduce ligand repulsion and make **9** more basic than would be expected from the electronic effect of PMe_3 alone. Replacement of the second PPh_3 would result in less steric reduction and less change in basicity, as is observed.

Substitution of one PPh_3 ligand in $CpOs(PPh_3)_2H$ (4) (ΔH_{HM} = -37.3 kcal/mol) with $P(OEt)_3$ results in a decrease of 3.7 kcal/mol in the basicity of $CpOs(PPh_3)[P(OEt)_3]H$ (11) (ΔH_{HM} = -33.6 kcal/mol). Since $CpOs(PPh_3)[P(OEt)_3]Br$ is not protonated by CF_3SO_3H, it was not possible to measure its ΔH_{HM}. However, in order to compare the effect of $P(OEt)_3$ on the basicity of $CpOs(PPh_3)(L)Br$ complexes, one can estimate that $CpOs(PPh_3)[P(OEt)_3]Br$ would be ~ 21 kcal/mol less basic than $CpOs(PPh_3)[P(OEt)_3]H$, which is based on $CpOs(PPh_3)_2Br$ being 21.0 kcal/mol less basic than $CpOs(PPh_3)_2H$. With this assumption, ΔH_{HM} for $CpOs(PPh_3)[P(OEt)_3]Br$ would be 12.6 kcal/mol. Therefore, the basicities (ΔH_{HM}) of the $CpOs(PPh_3)(L)Br$ complexes increase in the order: L = $P(OEt)_3$ (-12.6 kcal/mol, estimated) < PPh_3 (-16.3 kcal/mol) < PMe_3 (-25.6 kcal/mol). Thus, $P(OEt)_3$ is the weakest donor ligand in this series.

The influence of phosphine ligand basicity (ΔH_{HP}) on metal complex basicity (ΔH_{HM}) has previously been observed in the $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ series of complexes (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$ and PMe_3),[9] which were also studied by titration calorimetry under the same conditions as in this present study. Plotting $-\Delta H_{HM}$ of these complexes vs $-\Delta H_{HP}$ of the free phosphine results in linear correlations for Ir (eq 11) and Fe (eq 12) (Fig 3). In

$$-\Delta H_{HM} = -0.298\ (\Delta H_{HP}) + 23.9;\ \text{in kcal/mol;}\ \text{for } CpIr(CO)(PR_3), \quad (11)$$

$$-\Delta H_{HM} = -0.916\ (\Delta H_{HP}) - 5.36;\ \text{in kcal/mol;}\ \text{for } Fe(CO)_3(PR_3)_2, \quad (12)$$

the Ir series, the phosphine causes a 0.298 kcal/mol change in the Ir basicity per 1.00 kcal/mol change in PR_3 basicity (ΔH_{HP}); in the Fe series each phosphine causes a 0.458 kcal/mol (0.916/2) change in Fe basicity (ΔH_{HM}) as

the basicity of the phosphine (ΔH_{HP}) changes by 1.00 kcal/mol. Thus, the change in ΔH_{HM} per PR_3 ligand per 1.00 kcal/mol change in ΔH_{HP} increases

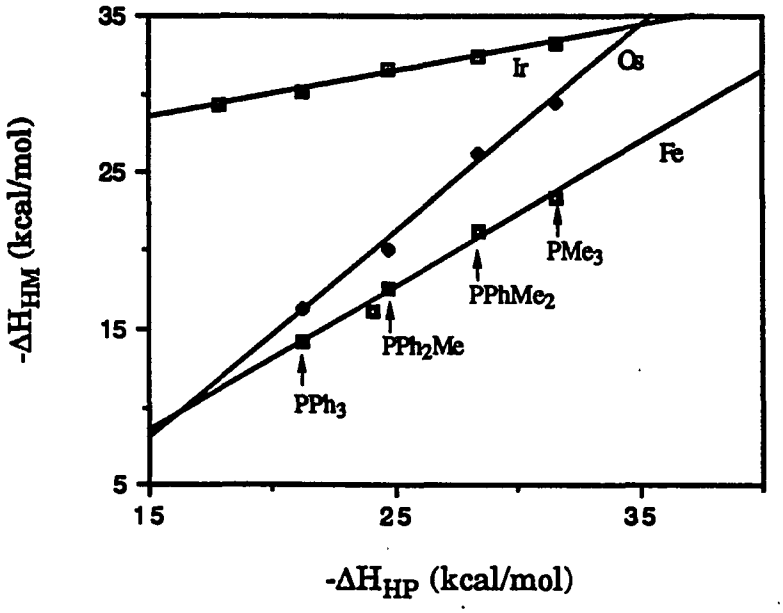


Figure 3. Correlations of metal basicity (ΔH_{HM}) with phosphine basicity (ΔH_{HP}) for the $CpIr(CO)(PR_3)$ (top line), $CpOs(PR_3)_2Br$ (middle line), and $Fe(CO)_3(PR_3)_2$ (lower line) series.

in the order: $CpIr(CO)(PR_3)$, 0.298 < $Fe(CO)_3(PR_3)_2$, 0.458 < $CpOs(PR_3)_2Br$, 0.655. A possible reason why the basicity of the Os compounds is most sensitive to the phosphine is that the higher coordination number (6) of the Os complexes causes more crowding in complexes which contain bulky PR_3 ligands, e.g., PPh_3 as noted above. These steric effects should be less important in the less crowded $CpIr(CO)(PR_3)$ and $Fe(CO)_3(PR_3)_2$ complexes. Another reason for the greater sensitivity of the Os complexes is the absence of CO ligands which could absorb some of the electron density donated to the

metal by basic PR_3 ligands. The π-accepting CO ligands in the Fe and Ir complexes would make the metals in these systems less sensitive to the donor ability of the PR_3 ligands.

With three π-accepting CO ligands in $Fe(CO)_3(PR_3)_2$, as compared with only one in $CpIr(CO)(PR_3)$, the Fe complexes are expected to be less sensitive to PR_3 basicity than the Ir complexes; however, as noted above, the reverse is true. The lower sensitivity of the Ir series could be due to the Cp ligand acting as a substantial π-accepting ligand. This is supported by MO calculations and ESCA studies of $CpRh(CO)_2$ that show the Cp π* and filled metal orbitals have similar energies which allows substantial π-bonding from the metal to the Cp ligand.[38]

Effect of Chelating Phosphines on Metal Basicity (ΔH_{HM})

The ΔH_{HM} of $CpOs(PPh_2Me)_2Br$ (**5**) is -20.0 kcal/mol, while the ΔH_{HM} of the chelated complex CpOs(dppp)Br (**13**) is the same within experimental error at -20.1 kcal/mol; both complexes give *trans* protonated products (eq 3). Since the free phosphines [PPh_2Me (ΔH_{HP} = -24.7 kcal/mol)[8] and dppp (ΔH_{HP1} = -23.4 kcal/mol)[40]] have nearly the same basicity, it is not surprising that **5** and **13** have the same basicity. The basicity (-17.5 kcal/mol) of CpOs(dppm)Br (**12**) is less than those of **5** and **13**, which is explained in part by the poorer σ-donor ability of the dppm ligand (ΔH_{HP1} = -22.0 kcal/mol).[39] In addition, the dppm ligand forces the product $CpOs(dppm)(Br)(H)^+$ (**12H⁺**) to adopt a *cis* structure; since the monodentate phosphine complex **5H⁺** could adopt either the *cis* or *trans* structure and it is observed to form only the *trans* isomer, the *cis* isomer must be of higher energy. The *cis* structure of $CpOs(dppm)(H)^+$

(**12H$^+$**) is therefore of relatively high energy which makes the protonation of **12** less favorable than that of **5** or **13**. Thus, the basicity of the metal is decreased as a result of dppm forcing the complex to assume the less stable *cis* structure.

A decrease in basicity of the metal complex also occurs when dppp is replaced by the shorter chelates dppe and dppm that give the *cis* isomers in the CpRu($\overset{\frown}{P\ P}$)H series [$\overset{\frown}{P\ P}$ = dppp (**22**, ΔH_{HM} = -29.6 kcal/mol), dppe (**21**, ΔH_{HM} = -29.0), dppm (**20**, ΔH_{HM} = -28.9)], although the effects are less dramatic. The dppp product **22H$^+$** is completely *trans*; the dppe derivative **21H$^+$** is a mixture of *cis* and *trans* isomers; and the dppm isomer is completely *cis* with the η^2-H_2 structure CpRu(dppm)(η^2-H_2)$^+$.[30] In this series, it was not possible to study the monodentate analog CpRu(PPh_2Me)$_2$H due to its partial decomposition in the calorimeter. However, comparison of **20-22** with CpRu(PPh_3)$_2$H (**17**, ΔH_{HM} = -29.7 kcal/mol) indicates that the basicities of the CpRu(P)$_2$X complexes depend little on the monodentate or bidentate nature of the phosphine ligands. Morris and Jia[7] determined pK_a values in CH_2Cl_2 solvent for the same complexes **20H$^+$-22H$^+$** and observed the same trend of decreasing basicity as the product adopts the *cis* structure: *trans*-CpRu(dppp)(H)$_2^+$ (pK_a = 8.4) > *trans*-CpRu(PPh_3)$_2$(H)$_2^+$ (8.3) > *trans*-CpRu(dppe)(H)$_2^+$ (7.3) > *cis*-CpRu(dppm)(H_2)$^+$ (7.1) > *cis*-CpRu(dppe)(H_2)$^+$ (7.0). For CpRu(dppe)H_2^+, where they were able to determine pK_a values for both the *cis* and *trans* isomers, the *cis* isomer was less basic than the *trans*.

Those complexes that are forced by the chelate to form the less stable *cis*-CpRu($\overset{\frown}{P\ P}$)(H_2)$^+$ products are the least basic. This effect was also observed in W(CO)$_3$(tridentate phosphine)[10] complexes in which the less

flexible $MeC(CH_2PPh_2)_3$ ligand forces the tungsten in the protonated product into a higher energy structure thereby decreasing the basicity of the metal by 6.2 kcal/mol compared to the basicity of the complex with the flexible $PhP(CH_2CH_2PPh_2)_2$ ligand. The opposite effect is observed when a small dppm chelate in $Fe(CO)_3$(dppm) distorts the geometry from the favored diaxial structure of $Fe(CO)_3(PPh_2Me)_2$ to a higher energy structure.[40] This distortion causes the Fe in $Fe(CO)_3$(dppm) to be 6.4 kcal/mol more basic than in $Fe(CO)_3(PPh_2Me)_2$. Similarly small-ring chelating ligands increase the basicities of the metal in the $M(CO)_2(\overset{\frown}{P\ P})_2$ (M = Cr, Mo, W) complexes.[41]

Effect of Cp and Cp* on Metal Basicity (ΔH_{HM})

The data in Table III show that the basicity of $Cp^*Ru(PMe_3)_2Cl$ is 9.0 kcal/mol greater than that of $CpRu(PMe_3)_2Cl$; $Cp^*Ru(PPh_3)_2H$ is 5.5 kcal/mol more basic than $CpRu(PPh_3)_2H$; and Cp*Ir(COD) is 5.7 kcal/mol more basic than CpIr(COD).[11] Converting the K_{eq} values reported by Norton and coworkers[3] for the protonation of various anions in acetonitrile to $\Delta G°$ values, $Cp^*Mo(CO)_3^-$ is 4.5 kcal/mol (3.2 pK_a units) more basic than $CpMo(CO)_3^-$, while $Cp^*Fe(CO)_2^-$ is 9.4 kcal/mol (6.9 pK_a units) more basic than $CpFe(CO)_2^-$. Thus, the basicity enhancement (4.5-9.4 kcal/mol) caused by the replacement of Cp by Cp* depends on the metal and the ligands in the complex.

Effect of the Metal (Ru vs. Os) on Metal Basicity (ΔH_{HM})

It has previously been reported by this group[41] that the third row metal complex Cp^*_2Os (ΔH_{HM} = -26.6 kcal/mol) is 6.0 kcal/mol more basic than the second row metal analog Cp^*_2Ru(ΔH_{HM} = -19.0 kcal/mol). We expand this

comparison (Chart I) by showing that $CpOs(PPh_3)_2H$ (4) is 7.6 kcal/mol more basic than $CpRu(PPh_3)_2H$ (18), $CpOs(PMe_3)_2Br$ (8) is 8.5 kcal/mol more basic than $CpRu(PMe_3)_2Br$ (15) and $CpOs(PMe_3)_2I$ (10) is more basic than $CpRu(PMe_3)_2I$ (16) by 6.0 kcal/mol; Norton and coworkers determined that $HOs(CO)_4^-$ is 2.9 kcal/mol (2.1 pK_a units) more basic (in CH_3CN) than $HRu(CO)_4^-$.[44] These comparisons illustrate that the magnitude of the increase in basicity when Ru is substituted by Os depends on the ligands in the complex.

Chart I

$CpRu(PPh_3)_2H$ (17) -29.7 kcal mol^{-1}
$CpOs(PPh_3)_2H$ (4) -37.3 kcal mol^{-1} } 7.6

$CpRu(PMe_3)_2Br$ (15) -20.9 kcal mol^{-1}
$CpOs(PMe_3)_2Br$ (8) -29.4 kcal mol^{-1} } 8.5

Cp_2^*Ru -19.0 kcal mol^{-1}
Cp_2^*Os -26.6 kcal mol^{-1} } 7.6

$HRu(CO)_4^-$
$HOs(CO)_4^-$ } 2.9

$CpRu(PMe_3)_2I$ (16) -20.6 kcal mol^{-1}
$CpOs(PMe_3)_2I$ (10) -26.6 kcal mol^{-1} } 6.0

CONCLUSIONS

Systematically changing the ligands and/or the metal in $Cp'M(PR_3)(PR'_3)X$ complexes yields metal basicities (ΔH_{HM}) that range from -14.1 to -39.2 kcal/mol. We have demonstrated that the basicities of the $CpOs(PPh_3)_2X$ complexes increase with the halide or hydride ligand in the order: $I^- < Br^- < Cl^- << H^-$; in fact, the substitution of a halide (X^-) ligand by a hydride (H^-) causes the basicity of the metal to increase by as much as 23.2 kcal/mol. A linear correlation between the ΔH_{HM} of these complexes and the gas-phase proton affinities of the anions X^- is observed. Studies of the $CpOs(PR_3)_2Br$ complexes shows that there is a linear correlation between the basicity (ΔH_{HM}) of the metal center and the basicity of the phosphine (pK_a or ΔH_{HP}), which increases in the order $PPh_3 < PPh_2Me < PPhMe_2 < PMe_3$ (Fig. 3). However, since the basicity (ΔH_{HM}) of the mixed phosphine complex $CpOs(PPh_3)(PMe_3)Br$ does not lie midway between those of $CpOs(PPh_3)_2Br$ and $CpOs(PMe_3)_2Br$ as one might expect, the basicities of the $CpOs(PR_3)_2Br$ complexes are probably not only determined by the basicities of the phosphines but also their steric properties. In the $CpM(\overset{\frown}{P\ P})X$ compounds with chelated phosphines, there was little difference in the basicity (ΔH_{HM}) of the metal when compared to the monodentate phosphine complexes; however the basicities (ΔH_{HM}) of the *cis*-complexes are less than those of the *trans*-complexes. These titration studies show that complexes with the Cp* ligand are 5.5-9.0 kcal/mol more basic than those with the Cp ligand, and Os complexes are 6.0-8.5 kcal/mol more basic than the analogous Ru complexes.

Acknowledgment

We thank the National Science Foundation (Grant CHE-9103948) for support of this work, Dr. Victor Young for solving the crystal structure of $4H^+CF_3SO_3^-$, Johnson-Mathey, Inc. for the generous loan of $RuCl_3 \cdot nH_2O$ and OsO_4, and Dr. Herbert Lehmkuhl for sending a copy of Eckhard Joussen's Dissertation.

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PAPER II. LIGAND EFFECTS ON HEATS OF PROTONATION OF MULTIHYDRIDO-TRANSITION METAL COMPLEXES OF OSMIUM AND IRIDIUM

ABSTRACT

Titration calorimetry has been used to determine heats of protonation (ΔH_{HM}) of the metal in $(H)_2Os(PR_3)_4$ (PR_3=$PPhMe_2$, PPh_2Me, $PPh(OEt)_2$, $P(OEt)_3$), $(H)_4Os(PR_3)_3$ (PR_3=$PPhMe_2$, PPh_2Me), $HIr(CO)(PPh_3)_3$, and $CpIr(ER_3)(H)_2$ (ER_3=PPh_3, $AsPh_3$, $P(OPh)_3$) complexes with CF_3SO_3H in 1,2-dichloroethane solvent at 25.0 °C. For the $(H)_2Os(PR_3)_4$ complexes, the basicity ($-\Delta H_{HM}$) increases from 34.2 to 43.3 kcal/mol in the order: $P(OEt)_3 < PPh(OEt)_2 < PPh_2Me < PPhMe_2$. The basicity ($-\Delta H_{HM}$) of the metal in $(H)_4Os(PR_3)_3$ (PR_3 = $PPhMe_2$, PPh_2Me) increases by ~15 kcal/mol when two hydride ligands are replaced by a PR_3 ligand to give $(H)_2Os(PR_3)_4$. Replacement of the two hydride ligands in $CpIr(PPh_3)(H)_2$ by a CO ligand to give $CpIr(PPh_3)(CO)$ results in a 10.4 kcal/mol increase in the basicity ($-\Delta H_{HM}$) of the metal. The basicities of the $CpIr(ER_3)(H)_2$ complexes increase in the order: $P(OPh)_3 << AsPh_3 \approx PPh_3$. Comparisons of the basicities of $CpIr(PPh_3)(CO)$ and $(PPh_3)_2(H)Ir(PPh_3)(CO)$ complexes show that replacement of Cp by the isoelectronic $(PR_3)_2(H)$ ligand set increases the basicity of the metal. In other complexes, this is also generally true, but the effect varies greatly.

INTRODUCTION

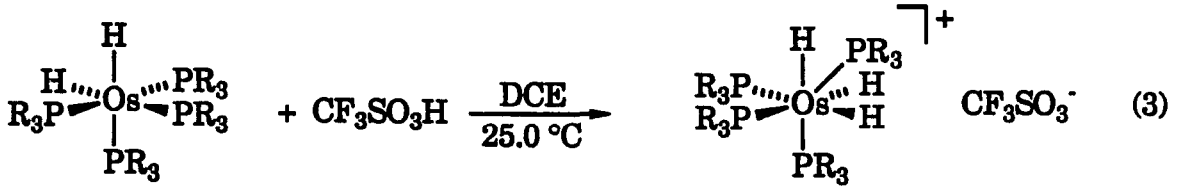
Many quantitative correlations of ligand parameters with spectroscopic, electrochemical, and kinetic properties of transition metal complexes have been reported.[1,2] In this research group, correlations have been observed between the basicities of phosphine (PR_3) ligands as measured by their heats of protonation (ΔH_{HP}) with CF_3SO_3H in 1,2-dichloroethane (DCE) solution (eq 1)[3] and the heats of protonation (ΔH_{HM}) of their transition metal complexes

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

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

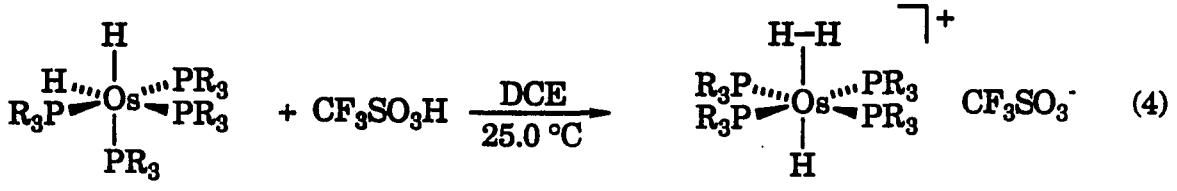
(eq 2). Such correlations were demonstrated in studies of $Fe(CO)_3(PR_3)_2$,[4] $CpIr(PR_3)(CO)$,[4] $W(CO)_3(PR_3)_3$,[5] $Fe(CO)_3(\widehat{P\ P})$[6] and $M(CO)_2(\widehat{P\ P})_2$ (M = Cr, Mo, W),[7] where $\widehat{P\ P}$ is a bidentate phosphine. Also, the effects of methyl-substituted cyclopentadienyl ligands on the basicity of the metal in (η^5-$C_5Me_xH_{5-x}$)Ir(1,5-cyclooctadiene)[8] have been determined previously. In this report, we extend our studies of the effects of phosphorus-donor ligands on metal basicity (ΔH_{HM}) to the $(H)_2Os(PR_3)_4$ series of complexes, where PR_3 = $P(OEt)_3$, $PPh(OEt)_2$, PPh_2Me, $PPhMe_2$ (eqs 3 and 4).

Also, we compare the donor ability of two hydride ligands with the donor ability of CO and PR_3 (Chart I). There are many examples of isoelectronic pairs of complexes that are related by the replacement of $(H)_2$



1 (PR_3 = $PPhMe_2$)
2 (PR_3 = PPh_2Me)

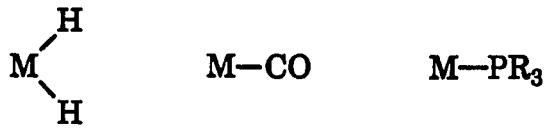
1H$^+$, 2H$^+$



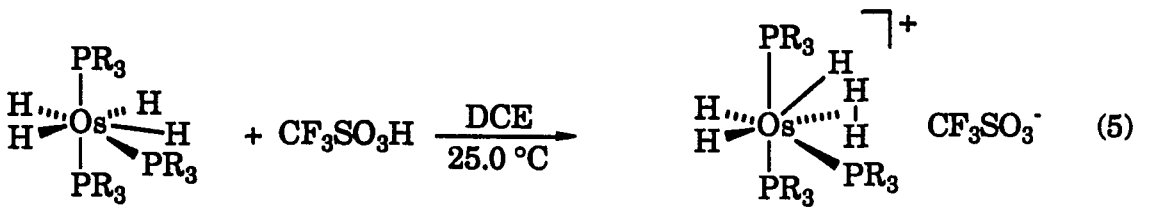
3 (PR_3 = $PPh(OEt)_2$)
4 (PR_3 = $P(OEt)_3$)

3H$^+$, 4H$^+$

Chart I



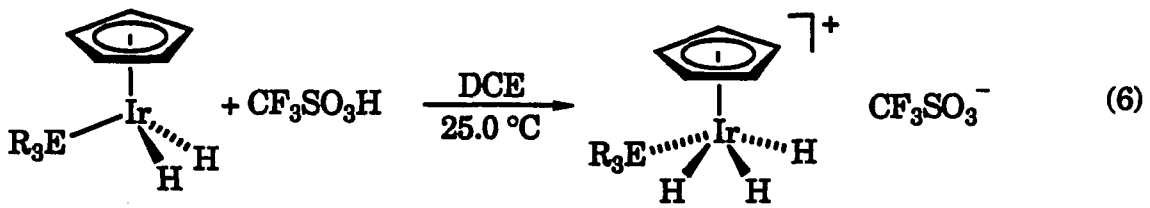
ligands by a CO or PR_3 ligand. In the present study, we compare basicities (ΔH_{HM}, eq 5) of $(H)_4Os(PR_3)_3$, where PR_3 = $PPhMe_2$, PPh_2Me, with those (eq 3)



5 (R = $PPhMe_2$)
6 (R = PPh_2Me)

5H$^+$, 6H$^+$

of $(H)_2Os(PR_3)_4$, which contain one more PR_3 but two fewer hydride ligands. Also, we examine the effects of $(H)_2$ and CO on the basicities of the metal in $CpIr(PPh_3)(H)_2$ (eq 6) and the isoelectronic $CpIr(PPh_3)(CO)$ complex. In considering whether $(H)_2$ would make the metal more or less basic than



(6)

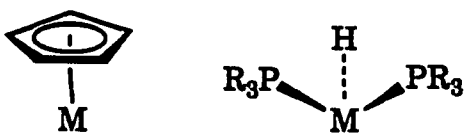
7 ($ER_3 = PPh_3$)
8 ($ER_3 = AsPh_3$)
9 ($ER_3 = P(OPh)_3$)

7H⁺-9H⁺

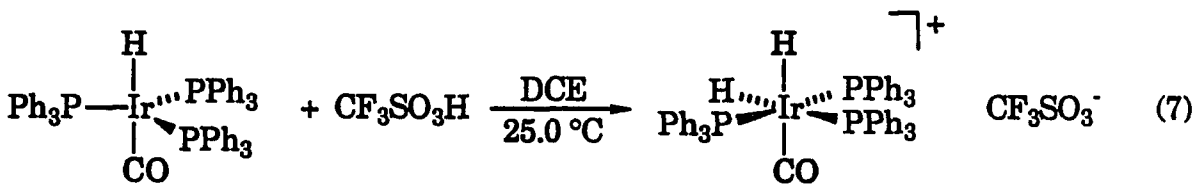
the analogous CO or PR_3 complex, we note that the hydride ligand in $CpOs(PPh_3)_2H$ makes the Os 23.2 kcal/mol more basic than the corresponding iodide complex $CpOs(PPh_3)_2I$.[9] So, as compared with a halide ligand, the hydride is a very strong donor. This suggests that dihydride complexes may be very basic as compared with the analogous CO and PR_3 complexes. On the other hand, the formal oxidation state of the metal in the dihydride is +2 units higher than in the CO or PR_3 complexes which should make the dihydride complex less basic. Further complicating this comparison are differences in the geometries of the $(H)_2$ and CO or PR_3 complexes because there is one more ligand (two H's) in the $(H)_2$ complexes. The ΔH_{HM} measurements of reactions (3), (5) and (6) clarify the effects of $(H)_2$, CO, and PR_3 ligands on the basicities of the metals in these complexes.

We also sought to compare the effects of the η^5-cyclopentadienyl (Cp) ligand and isoelectronic $(PR_3)_2(H)$ ligand set (Chart II) on the basicity of a metal. Again, there are many analogous CpM and $(PR_3)_2(H)$ complexes;

Chart II



we have chosen to compare ΔH_{HM} for $CpIr(PPh_3)(CO)$ with $(PPh_3)_2(H)Ir(PPh_3)(CO)$ (eq 7). In this comparison, the oxidation state of the metal is the same (+1) but the nature of the ligands is quite different.



(7)

10 **10H$^+$**

EXPERIMENTAL SECTION

General Procedures

All preparative reactions and solvent purifications were carried out under an Ar atmosphere using standard Schlenk techniques. The complexes $(H)_2Os(PPhMe_2)_4$ (**1**),[10] $(H)_2Os(PPh_2Me)_4$ (**2**),[10] $(H)_2Os[PPh(OEt)_2]_4$ (**3**),[11] $(H)_2Os[P(OEt)_3]_4$ (**4**),[11] $(H)_4Os(PPhMe_2)_3$ (**5**),[12] $(H)_4Os(PPh_2Me)_3$ (**6**),[12] $CpIr(PPh_3)(H)_2$ (**7**),[13] $CpIr(AsPh_3)(H)_2$ (**8**),[13] and $CpIr[P(OPh)_3](H)_2$ (**9**)[13] were prepared as previously described. The complex $HIr(CO)(PPh_3)_3$ (**10**) was used as received from Strem Chemicals, Inc. Deuterated solvents (CD_2Cl_2 or $CDCl_3$) were stored over molecular sieves in air. The 1,2-dichloroethane (99.8%, HPLC grade) was purchased from Aldrich and distilled from P_4O_{10} immediately before use. The CF_3SO_3H was purchased from 3M Co. and purified as previously described.[3] The ^1H NMR spectra were recorded in either CD_2Cl_2 or $CDCl_3$ using a Nicolet-NT 300 MHz or a Varian VXR-300 MHz spectrometer with TMS (δ=0.00 ppm) as the internal standard. T_1 values were measured from 25 °C to -85 °C using the standard inversion recovery sequence 180-τ-90.[14] The T_1(min) value is the minimum value of T_1 determined from a T_1 vs temperature plot. The $^{31}P\{^1H\}$ NMR spectra were recorded in CD_2Cl_2 on a Varian VXR-300 MHz spectrometer using 85% phosphoric acid (δ=0.00 ppm) as the external standard.

Calorimetric titrations were performed under an Ar atmosphere using a Tronac model 458 isoperibol calorimeter as originally described[3] and then modified.[4] A two minute titration period was used for all complexes and was preceded and followed by heat capacity calibrations. 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 to 50 mL of a 1.7 mM solution of the metal complex (5-10% excess) in DCE at 25.0 °C.

The ΔH_{HM} values 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)[4] was used to correct the reaction enthalpies.

Protonation Reactions

Compounds **1-10** were protonated for NMR characterization by dissolving ~5 mg of the complex in 0.5 mL of CD_2Cl_2 (or $CDCl_3$) in an NMR tube under an Ar atmosphere at room temperature. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum. Solutions of the protonated complexes are stable as long as they are kept under argon. Complexes **3H$^+$BF$_4^-$**,[11] **4H$^+$BPh$_4^-$**,[11] **5H$^+$BPh$_4^-$**,[11] **7H$^+$BF$_4^-$**,[13] **8H$^+$BF$_4^-$**,[13] **9H$^+$BF$_4^-$**,[13] and **10H$^+$SiF$_5^-$**[16] have been previously isolated and characterized; their ^1H NMR spectra are very similar to those of the same complexes that we prepared by protonation with CF_3SO_3H. The ^1H NMR spectra of all the protonated complexes are given below:

[(H)$_3$Os(PPhMe$_2$)$_4$]$^+$CF$_3$SO$_3^-$ (1H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, 20H, Ph), 1.45 (br s, 24H, CH_3), -7.77 (quintet, $^2J_{PH}$ = 9.9 Hz, 3H, Os-H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ -32.7 (s).

[(H)$_3$Os(PPh$_2$Me)$_4$]$^+$CF$_3$SO$_3^-$ (2H$^+$CF$_3$SO$_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, 40H, Ph), 0.93 (br s, 12H, CH_3), -6.82 (quintet, $^2J_{PH}$ = 9.2 Hz, 3H, Os-H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ -19.5 (s).

$[(H_2)(H)Os[PPh(OEt)_2]_4]^+CF_3SO_3^-$ ($3H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.32-7.58 (m, 20H, Ph), 3.44 (m, 8H, CH_2), 3.22 (m, 8H, CH_2), 1.05 (t, $^2J_{HH}$ = 7.2 Hz, 24H, CH_3), -6.80 (br s, 3H, Os-H).

$[(H_2)(H)Os[P(OEt)_3]_4]^+CF_3SO_3^-$ ($4H^+CF_3SO_3^-$): ^1H NMR ($CDCl_3$) δ 3.9 (m, 24H, CH_2), 1.3 (t, $^2J_{HH}$ = 6.2 Hz, 36H, CH_3), -8.23 (br s, 3H, Os-H).

$[(H_2)(H)_3Os(PPhMe_2)_3]^+CF_3SO_3^-$ ($5H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1-7.4 (m, 15H, Ph), 1.78 (br s, 18H, CH_3), -9.68 (br s, 5H, Os-H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ -33.4 (s).

$[(H_2)(H)_3Os(PPh_2Me)_3]^+CF_3SO_3^-$ ($6H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, 30H, Ph), 1.93 (br s, 9H, CH_3), -6.24 (br s, 2H, $Os(H_2)$), -10.96 (br s, 3H, $Os-(H)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ -13.4 (s).

$[CpIr(PPh_3)(H)_3]^+CF_3SO_3^-$ ($7H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3-7.6 (m, 15H, Ph), 5.92 (s, 5H, Cp), -12.39 (d, $^2J_{PH}$ = 7.9 Hz, 3H, $Ir-(H)_3$).

$[CpIr(AsPh_3)(H)_3]^+CF_3SO_3^-$ ($8H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.3-7.6 (m, 15H, Ph), 5.98 (s, 5H, Cp), -12.69 (s, 3H, $Ir-(H)_3$).

$[CpIr[P(OPh)_3](H)_3]^+CF_3SO_3^-$ ($9H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 7.2-7.5 (m, 15H, Ph), 5.50 (s, 5H, Cp), -12.48 (d, $^2J_{PH}$ = 8.5 Hz, 3H, $Ir-(H)_3$).

$[(H)_2Ir(CO)(PPh_3)_3]^+CF_3SO_3^-$ ($10H^+CF_3SO_3^-$): ^1H NMR (CD_2Cl_2) δ 6.8-7.5 (m, 45H, Ph), -9.52 (m, 1H, Ir-H), -11.4 (dtd, $^2J_{PH}$ = 114 Hz, $^2J_{PH}$ = 19.2 Hz, $^2J_{HH}$ = 4.8 Hz, 1H, Ir-H).

The low temperature spectra (see Results) were recorded in CD_2Cl_2 solvent.

RESULTS

Characterization of *cis*-$(H)_2Os(PR_3)_4$ (1-4) and $H_3Os(PR_3)_4^+$ ($1H^+$-$4H^+$)

Complexes **1-4** have previously[10-12] been identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as having *cis*-octahedral structures (eqs 3 and 4). Bordignon et al.,[11] assigned $(H)(H_2)Os[P(OEt)_3]_4^+$ ($4H^+$) a *trans*-octahedral geometry (eq 4) based on its ^1H and $^{31}P\{^1H\}$ NMR spectra; $(H)(H_2)Os(PPh(OEt)_2)_4^+$ ($3H^+$) was assigned,[11] based on the low temperature $^{31}P\{^1H\}$ and ^1H NMR spectra, a distorted *trans*-octahedral structure (eq 4) with two of the *trans* PR_3 ligands bent slightly toward the η^2-dihydrogen (H_2) ligand and the other two *trans* PR_3 ligands bent slightly toward the hydride (H) ligand.

The structure of the related $(H)_3Os(PPh_3)_4^+$ complex, determined by X-ray crystallography,[17] has a distorted tetrahedral arrangement of phosphines (eq 3), while the hydrides, which were not located, were proposed to be capping three of the faces. Seidel et al.[17] noted that $[(H)_3Os(PPh_3)_4^+]$ is fluxional at room temperature as evidenced by a quintet for the hydride resonance in the ^1H NMR spectrum and a singlet in the $^{31}P\{^1H\}$ NMR spectrum; at -70 °C there is a broad singlet for the hydride in the ^1H NMR spectrum and two broad singlets in the $^{31}P\{^1H\}$ NMR spectrum.[17] At room temperature $(H)_3Os(PPh_2Me)_4^+$ ($2H^+$) is also fluxional as indicated by a quintet for the hydride ligands in the ^1H NMR spectrum and a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The fluxionality of $2H^+$ is slowed at -75 °C as suggested by a broad singlet for the hydride in the ^1H NMR spectrum and two broad singlets at -13.8 and -25.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The T_1(min) value (159 ms,-45

°C) for the hydride peak in $2H^+$ is consistent with a classical trihydride structure.[14] The T_1(min) along with the similarities in the low temperature $^{31}P\{^1H\}$ and ^1H NMR spectra of $2H^+$ to those of $(H)_3Os(PPh_3)_4^+$ suggests that $(H)_3Os(PPh_2Me)_4^+$ ($2H^+$) also has a structure similar to that drawn in eq 3.

The hydride signal in the ^1H NMR spectrum of the less sterically crowded complex $(H)_3Os(PPhMe_2)_4^+$ ($1H^+$) occurs as a quintet at room temperature but as a broad singlet at -75 °C. The T_1(min) value (177 ms, -60 °C) for the hydride resonance is consistent with the trihydride structure.[14] Since only a singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum from 20 to -75 °C, it is not possible to establish the geometry. Therefore, it is possible that $1H^+$ has either a geometry similar to that drawn in eq 3 or a *trans*-octahedral geometry in which the phosphines are equivalent in the equatorial plane and the hydride ligands are fluxional. Based on the structure of $(H)_3Os(PPh_3)_4^+$, it seems likely that $1H^+$ also has a structure similar to that shown in eq 3.

Characterization of $(H)_4Os(PR_3)_3$ (5, 6) and $(H)_5Os(PR_3)_3^+$ ($5H^+$, $6H^+$)

Hart and coworkers[18] using neutron diffraction showed that $(H)_4Os(PPhMe_2)_3$ (**5**) has a pentagonal bipyramidal geometry with four hydrides and a $PPhMe_2$ ligand in the equatorial positions (eq 5) and the other two phosphines in the apical positions. The room temperature ^1H NMR spectra of $(H)_4Os(PPhMe_2)_3$ (**5**) and $(H)_4Os(PPh_2Me)_3$ (**6**) indicate that they are both fluxional as suggested by the hydride resonances of both complexes being split into quintets. At lower temperatures (0 to -75 °C) each complex exhibits a broad singlet for the hydride resonance. In the $^{31}P\{^1H\}$ NMR spectra of **5** and **6** from 20 to -70 °C only a singlet is observed; this too indicates that the

complexes are fluxional over this temperature range. Because of the fluxionality of **5** and **6**, it is not possible to establish their structures by NMR spectroscopy in this temperature region; however, it seems likely that **6** has the pentagonal bipyramidal structure established for $H_4Os(PPhMe_2)_3$ (**5**, eq 5).

Structures of the protonated products $\mathbf{5H^+}$ and $\mathbf{6H^+}$ or related derivatives have not been established by X-ray or neutron diffraction. In the ^1H NMR spectrum of $(H_2)(H)_3Os(PPhMe_2)_3^+$ ($\mathbf{5H^+}$) at room temperature, the broad hydride singlet indicates that the compound is fluxional; the singlet in the $^{31}P\{^1H\}$ NMR spectrum supports this conclusion. The hydride peak remains a broad singlet even at -75 °C in the ^1H NMR spectrum; however, the $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{5H^+}$ at -75 °C exhibits a triplet at -18.8 ppm ($^2J_{PP}$ = 19.5 Hz) and a doublet at -23.4 ppm ($^2J_{PP}$ = 19.5 Hz). This doublet and triplet suggest that the phosphines are arranged in a manner similar to those drawn for **5** (eq 5). Caulton et al.,[15a] report the T_1(min) for $\mathbf{5H^+}$ to be 68 ms (-75 °C) and assign it the $(H_2)(H)_3Os(PPhMe_2)_3^+$ structure.

In the $^{31}P\{^1H\}$ NMR spectrum of $(H_2)(H)_3Os(PPh_2Me)_3^+$ ($\mathbf{6H^+}$), a singlet is observed at -13.4 ppm; at -75 °C a doublet at -1.8 ppm ($^2J_{PP}$ = 32.7 Hz) and a broad singlet at -12.5 ppm are observed. Two hydride signals for $(H_2)(H)_3Os(PPh_2Me)_3^+$ ($\mathbf{6H^+}$) are observed in the ^1H NMR spectrum at -6.24 and -10.96 ppm; the integrals of these peaks are in a 2:3 ratio from 20 to -70 °C. The hydride peak at -6.24 ppm in the ^1H NMR spectrum has a T_1(min) value of 30 ms (-55 °C), which is consistent with the dihydrogen (η^2-H_2) assignment; the hydride peak at -10.96 ppm has a T_1(min) value of 70 ms (-55 °C). Therefore, the structure of $\mathbf{6H^+}$ is suggested to be similar to that drawn in eq 5.

Characterization of $CpIr(ER_3)(H)_2$ (7-9) and $CpIr(ER_3)(H)_3^+$ ($7H^+$-$9H^+$)

Complexes **7-9** have the three-legged piano-stool structure (eq 6) as suggested by ^1H NMR spectroscopy.[13] A neutron diffraction study of $[CpIr(PMe_3)(H)_3]BF_4$ indicates that it is a normal trihydride complex;[13,19] therefore, it is likely that complexes **7H⁺-9H⁺** also adopt the four-legged piano stool structure (eq 6) containing classical hydride ligands [T_1 for $CpIr(PPh_3)(H)_3^+$ = 200 ms (minimum not observed, 210K, 500 MHz); $CpIr(AsPh_3)(H)_3^+$ = 210 ms (minimum not observed, 210K, 500 MHz)].[19]

Characterization of $(H)Ir(CO)(PPh_3)_3$ (10) and $(H)_2Ir(CO)(PPh_3)_3$ ($10H^+$)

The structures of both **10**[20a] and **10H⁺**[20b] have been established by X-ray crystallography. In the structure of **10** the hydride and CO ligands are in the axial positions of a trigonal bipyramid as shown in eq 7; **10H⁺** has the *cis*, *mer*-$(H)_2Ir(CO)(PPh_3)_3^+$ structure also shown in eq 7.

Calorimetric Studies

The heats of protonation (ΔH_{HM}) obtained from titrations of complexes **1-10** with CF_3SO_3H in 1,2-dichloroethane (DCE) solvent at 25.0 °C are presented in Table I. Plots of temperature vs amount of acid added were linear, which indicates that the complexes are protonated rapidly and quantitatively. There was no decomposition of either the neutral or the protonated species during the titration as suggested by the normal pre- and post-titration baseline slopes for all of the compounds. It is possible to deprotonate compounds **4H⁺-9H⁺** with 1 equiv of 1,3-diphenylguanidine (ΔH_{HN} = -37.2 kcal/mol);[3] however, only compounds **7-9** can be easily purified by

eluting the sample on a short neutral alumina column with CH_2Cl_2. The osmium compounds **4-6** were separated from the protonated 1,3-diphenylguanidine by extracting the complexes with 3 x 2 mL of benzene and then recrystallizing them from a minimal amount of methanol solvent at -20 °C. Compounds **1H$^+$-3H$^+$** and **10H$^+$** do not deprotonate with 1,3-diphenylguanidine; this was expected, since diphenylguanidine is a weaker base than compounds **1-3** and **10**.

The low dielectric constant ($\varepsilon = 10.46$)[21] for DCE means that the protonated products occur as ion pairs. It has been estimated that dissociation of these ion pairs, autoprotolysis, and dimerization of CF_3SO_3H contribute little to the measured ΔH_{HM} values.[3,7,9b] Thus, we attribute trends and differences in the ΔH_{HM} values to the properties of the reactant and product complexes.

Table I. Enthalpies of Protonation (ΔH_{HM}) of $(H)_2Os(PR_3)_4$, $(H)_4Os(PR_3)_3$, $(H)Ir(CO)(PPh_3)_3$, and $CpIr(ER_3)(H)_2$ Complexes

metal complex	ΔH_{HM},[a,b] kcal/mol
cis-$(H)_2Os(PPhMe_2)_4$ (1)	-43.3 (± 0.3)
cis-$(H)_2Os(PPh_2Me)_4$ (2)	-38.8 (± 0.2)
cis-$(H)_2Os(PPh(OEt)_2)_4$ (3)	-37.2 (± 0.2)
cis-$(H)_2Os(P(OEt)_3)_4$ (4)	-34.2 (± 0.2)
$(H)_4Os(PPhMe_2)_3$ (5)	-27.7 (± 0.1)
$(H)_4Os(PPh_2Me)_3$ (6)	-23.9 (± 0.3)
$CpIr(PPh_3)(H)_2$ (7)	-19.7 (± 0.2)
$CpIr(AsPh_3)(H)_2$ (8)	-19.4 (± 0.1)
$CpIr[P(OPh)_3](H)_2$ (9)	-11.9 (± 0.2)
$(H)Ir(CO)(PPh_3)_3$ (10)	-38.8 (± 0.4)
$CpIr(PPh_3)(CO)$[c]	-30.1(± 0.2)

[a]For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b]Numbers in parentheses are average deviations from the mean of at least four titrations. [c]Reference 4.

DISCUSSION

Comparison of Basicities (ΔH_{HM}) of Complexes with Isoelectronic Ligand Sets: $(H)_2$, CO and PR_3.

As noted in the Introduction, one focus of these studies was to determine the effect of the 2-electron ligand sets $(H)_2$, CO and PR_3 on the basicities of transition metal complexes. A comparison of ΔH_{HM} values (Table I) for $)H)_4Os(PPhMe_2)_3$ (**5**) (-27.7 kcal/mol) and $(H)_2Os(PPhMe_2)_4$ (**1**) (-43.3 kcal/mol) shows that replacement of two hydride ligands in $(H)_4Os(PPhMe_2)_3$ (eq 4) by one $PPhMe_2$ ligand to give $(H)_2Os(PPhMe_2)_4$ (eq 3) increases the basicity of the Os by 15.6 kcal/mol. A slightly smaller increase (14.9 kcal/mol) in basicity occurs when two hydrides in $(H)_4Os(PPh_2Me)_3$ are replaced by one PPh_2Me to give $(H)_2Os(PPh_2Me)_4$. This smaller increase is consistent with PPh_2Me (ΔH_{HP} = -24.7 kcal/mol)[3] being a weaker donor ligand than $PPhMe_2$ (ΔH_{HP} = -28.4 kcal/mol).[3] To illustrate the magnitude of the increase in basicity of the metal (ΔH_{HM}) when $(H)_2$ is replaced by $PPhMe_2$, the equilibruim constant (K_{eq}) for eq 7 can be estimated from $\Delta H_{HM} \cong \Delta G° = -RT\ln K_{eq}$

$$\underset{5H^+}{(H_2)(H)_3Os(PPhMe_2)_3^+} + \underset{1}{(H)_2Os(PPhMe_2)_4} \overset{K_{eq}}{\rightleftharpoons} \underset{5}{(H)_4Os(PPhMe_2)_3} + \underset{1H^+}{(H)_3Os(PPhMe_2)_4^+} \quad (7)$$

(assuming $\Delta S° \cong 0$ e.u., which is a reasonable approximation for protonation of similar neutral complexes).[4] Thus, a 15.6 kcal/mol increase in the basicity of the metal means that $(H)_2Os(PPhMe_2)_4$ is approximately 2.7×10^{11} times more basic than $(H)_4Os(PPhMe_2)_3$.

If the $(H)_2$ ligand set in $CpIr(PPh_3)(H)_2$ (ΔH_{HM} = -19.7 kcal/mol) is substituted by a CO ligand to give $CpIr(PPh_3)(CO)$ (ΔH_{HM} = -30.1 kcal/mol),[4] the basicity of the metal is increased by 10.4 kcal/mol. In terms of a K_{eq} equilibrium constant ($\Delta S° \cong 0$; $\Delta H_{HM} \cong \Delta G° = -RTln\ K_{eq}$), $CpIr(PPh_3)(CO)$ is 4.2×10^7 times more basic than $CpIr(PPh_3)(H)_2$. Thus, the basicity of the metal increases with the isoelectronic ligand sets in the following order: $(H)_2 < CO < PR_3$.

These results indicate that the higher oxidation state, by +2 units, in $M(H)_2$ complexes as compared with that of M(CO) is responsible for the 10.4 kcal/mol (or 4.2×10^7 K_{eq}) lower basicity of $CpIr(PPh_3)(H)_2$ as compared with $CpIr(PPh_3)(CO)$. On the other hand, the 4.2×10^7 factor is small compared to the change in basicity of a metal complex which undergoes a 1-electron oxidation. For example,[22] a 1-electron oxidation of $CpW(CO)_3H$ (pK_a = 16.1) to $CpW(CO)_3H^+$ (pK_a = -3.0) increases the acidity of the hydride ligand by a factor of 10^{19}. Although the metal in $CpIr(PPh_3)(CO)$ is formally oxidized by +2 units in $CpIr(PPh_3)(H)_2$, the Ir basicity changes much less than the W does in a +1 oxidation of $CpW(CO)_3H$.

Effect of PR_3 Ligands on the Basicities (ΔH_{HM}) of $(H)_2Os(PR_3)_4$ and $(H)_4Os(PR_3)_4$ Complexes

Replacement of the PPh_2Me ligands in $(H)_2Os(PPh_2Me)_4$ (**2**) by $PPhMe_2$ increases the basicity (ΔH_{HM}, eq 3) of Os by 4.5 kcal/mol; thus, on average each $PPhMe_2$ ligand increases the basicity of the metal center by 1.1 kcal/mol (4.5/4) over a PPh_2Me ligand. Replacement of the PPh_2Me ligands in $(H)_4Os(PPh_2Me)_3$ (**6**) by $PPhMe_2$ to give $(H)_4Os(PPhMe_2)_3$ (**5**) increases the

basicity (eq 5) of the metal by 3.8 kcal/mol or by 1.3 kcal/mol per PR_3 ligand. Thus, it appears that in both $(H)_2Os(PR_3)_4$ and $(H)_4Os(PR_3)_3$ the replacement of one PPh_2Me by $PPhMe_2$ increases the basicity (ΔH_{HM}) of the metal by ~1.2 kcal/mol. In other systems, the replacement of PPh_2Me by $PPhMe_2$ increases the metal basicity by 0.8 kcal/mol per PR_3 in $W(CO)_3(PR_3)_3$,[5] by 0.9 kcal/mol in $CpIr(PR_3)(CO)$,[4] by 1.8 kcal/mol per PR_3 in $Fe(CO)_3(PR_3)_2$,[4] and by 3.1 kcal/mol per PR_3 in $CpOs(PR_3)_2Br$.[9b] Thus, the effect of replacing PPh_2Me by $PPhMe_2$ on metal basicity depends significantly on the metal and other ligands in the complex.

The basicities ($-\Delta H_{HM}$) of the $(H)_2Os(PR_3)_4$ complexes (eqs 3 and 4) increase with PR_3 in the order: $P(OEt)_3$ (34.2 kcal/mol) < $PPh(OEt)_2$ (37.2 kcal/mol) < PPh_2Me (38.8 kcal/mol) < $PPhMe_2$ (43.3 kcal/mol). This is the same trend as observed for χ values for these ligands obtained for υ(CO) frequencies for $Ni(CO)_3(PR_3)$ complexes.[23]

Basicities (ΔH_{HM}) of $CpIr(ER_3)(H)_2$ Complexes

It was determined that the heats of protonation (ΔH_{HM}, eq 6) of the $CpIr(ER_3)(H)_2$ complexes increase in the order: $P(OPh)_3$ (-11.9 kcal/mol) < $AsPh_3$ (-19.4 kcal/mol) ≈ PPh_3 (-19.7 kcal/mol). The $CpIr(PPh_3)(H)_2$ complex has essentially the same basicity as $CpIr(AsPh_3)(H)_2$, which suggests that the PPh_3 and $AsPh_3$ ligands have similar donor properties. This is in sharp contrast to the free ligand (ER_3) basicities as measured by the gas phase heats of adduct formation of BH_3 with ER_3 [PPh_3 (-36.6 kcal/mol) is 10.0 kcal/mol more basic than $AsPh_3$ (-26.6 kcal/mol)],[24] the pK_b values [PPh_3 (8.57) is 2.03 units more basic than $AsPh_3$ (10.60)],[25] and the heats of protonation of the

phosphorus atom in $(Ph)_2PCH_2CH_2P(Ph)_2(H)^+$ (ΔH_{HP} = -20.2 kcal/mol) which is 12.0 kcal/mol more basic than the As atom in $(Ph)_2AsCH_2CH_2P(Ph)_2(H)^+$ (ΔH_{HAs} = -8.2 kcal/mol).[26] Despite the large differences in PPh_3 and $AsPh_3$ basicities, other complexes containing these ligands also have similar basicities. Thus, *cis*-$Mo(CO)_2(dppe)_2$ (ΔH_{HM} = -27.4 kcal/mol; dppe = $Ph_2PCH_2CH_2PPh_2$) is only 3.6 kcal/mol (1.8 kcal/mol per As donor) more basic than *cis*-$Mo(CO)_2(arphos)_2$ (ΔH_{HM} = -23.8 kcal/mol; arphos = $Ph_2AsCH_2CH_2PPh_2$),[7] and $Fe(CO)_3(dppe)$ (ΔH_{HM} = -23.2 kcal/mol) is only 0.6 kcal/mol more basic than $Fe(CO)_3(arphos)$ (ΔH_{HM} = -22.6 kcal/mol).[6] Therefore, it appears that arsenic donor ligands are a better donors in metal complexes than one would expect based on the basicities of the free arsine ligands.

When PPh_3 in $CpIr(PPh_3)(H)_2$ is substituted by $P(OPh)_3$ to give $CpIr[P(OPh)_3](H)_2$, the basicity of the metal decreases by 7.8 kcal/mol. This large difference in basicities is illustrated by the K_{eq} in eq 8. Assuming

$$\underset{\mathbf{9H^+}}{CpIr[P(OPh)_3](H)_3^+} + \underset{\mathbf{7}}{CpIr(PPh_3)(H)_2} \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{9}}{CpIr[P(OPh)_3](H)_2} + \underset{\mathbf{7H^+}}{CpIr(PPh_3)(H)_3^+} \quad (8)$$

$\Delta S^\circ \cong 0$ e.u., the equilibrium constant for eq 8 is 5.3×10^5. Norton and co-workers observed a similar difference (10^4) between the basicities of $Co(CO)_3(PPh_3)^-$ and $Co(CO)_3[P(OPh)_3]^-$,[27] whose protonated forms have pK_a values in acetonitrile of 15.4 and 11.4, respectively. The large decrease in basicity when a PPh_3 ligand is substituted by $P(OPh)_3$ is consistent with the

lower pK_a value of free $P(OPh)_3$ (-2.01)[23a] as compared with that of PPh_3 (2.73).[23a]

Comparisons of Basicities (ΔH_{HM}) of Complexes with the Isoelectronic Cp and $(PR_3)_2H$ Ligand Sets

Both the Cp ligand and the $(PR_3)_2(H)$ group of ligands contribute five electrons (using the neutral-ligand formalism) to a metal center; two examples of analogous Cp and $(PR_3)_2H$ complexes are $CpIr(PPh_3)(CO)$ and $(PPh_3)_2(H)Ir(PPh_3)(CO)$ (**10**). With the goal of predicting basicities of related complexes, we asked if there is a quantitative and predictable difference between Cp compounds and their $(PR_3)_2(H)$ analogs. In the comparisons listed in Table II, where the formal oxidation state of the metal is the same, substitution of the Cp ligand in $CpIr(PPh_3)(CO)$ (ΔH_{HM} = -30.1 kcal/mol)[4] with $(PPh_3)_2(H)$ to give $(PPh_3)_2(H)Ir(PPh_3)(CO)$ (ΔH_{HM} = -38.8 kcal/mol) increases the basicity of the iridium by 8.7 kcal/mol. Since PPh_2Me is more basic than PPh_3, it is expected that substitution of the Cp ligand by the $(PPh_2Me)_2(H)$ group would result in an even greater increase in basicity than in the iridium system; however, replacement of the Cp ligand in $CpOs(PPh_2Me)_2H$ (ΔH_{HM} = -39.2 kcal/mol)[9] by the $(PPh_2Me)_2(H)$ group to give $(PPh_2Me)_2(H)Os(PPh_2Me)_2(H)$ (ΔH_{HM} = -38.8 kcal/mol) *decreases* the basicity of the metal center by 0.4 kcal/mol.

When a Cp* ligand (Cp* = C_5Me_5), which is more basic than Cp (Cp = C_5H_5), in Cp^*_2Ru (ΔH_{HM} = -19.0 kcal/mol)[7] is replaced by the $(PPh_3)_2(H)$ group to give $Cp^*Ru(PPh_3)_2(H)$ (ΔH_{HM} = -35.2 kcal/mol), the basicity of the metal increases by 16.2 kcal/mol. In the Cp^*_2Os complex (ΔH_{HM} = -26.6 kcal/mol),[7]

replacement of two Cp* ligands by two $(PPhMe_2)_2(H)$ groups to give $(PPhMe_2)_2(H)Os(PPhMe_2)_2(H)$ (ΔH_{HM} = -43.3 kcal/mol) increases the basicity of the metal center by 16.7 kcal/mol; therefore, each $(PPhMe_2)_2(H)$ group increases the basicity by 8.4 kcal/mol. As the basicities of the phosphines in $(PR_3)_2(H)Os(PR_3)_2(H)$ decrease, the basicity of the metal also decreases; thus, the substitution of each Cp* ligand in Cp^*_2Os by different $(PR_3)_2(H)$ ligand sets to give $(PR_3)_2(H)Os(PR_3)_2H$ causes the metal basicity to increase by 3.8 kcal/mol (PR_3 = $P(OEt)_3$) to 8.4 kcal/mol (PR_3 = $PPhMe_2$), (Table II). These studies indicate that the replacement of Cp or Cp* by $(PR_3)_2(H)$ usually increases the basicity of the metal, but the magnitude of the increase is not reliably predictable.

Table II. Effect of Cp and $(PR_3)_2(H)$ Isoelectronic Ligand Sets on Metal Basicity

less basic compound	$\Delta\Delta H_{HM}$ per ligand set, kcal/mol	more basic compound
$CpIr(PPh_3)(CO)$[b]	8.7	**$(PPh_3)_2(H)Ir(PPh_3)(CO)$**
$(PPh_2Me)_2(H)Os(PPh_2Me)_2H$	0.4	**$CpOs(PPh_2Me)_2H$**[e]
Cp^*RuCp^*[c]	16.2	**$Cp^*Ru(PPh_3)_2(H)$**[f]
Cp^*OsCp^*[d]	8.4	**$(PPhMe_2)_2(H)Os(PPhMe_2)_2(H)$**
Cp^*OsCp^*[d]	6.1	**$(PPh_2Me)_2(H)Os(PPh_2Me)_2(H)$**
Cp^*OsCp^*[d]	5.3	**$(PPh(OEt)_2)_2(H)Os(PPh(OEt_2)_2(H)$**
Cp^*OsCp^*[d]	3.8	**$(P(OEt)_3)_2(H)Os(P(OEt)_3)_2(H)$**

[a]Ligands in bold type are the Cp' and $(PR_3)_2(H)$ sets that are being compared. [$\Delta\Delta H_{HM}$ = ΔH_{HM} (less basic compound) -ΔH_{HM} (more basic compound)]/[number of ligand sets]. [b]ΔH_{HM} = -30.1 (± 0.2) kcal/mol, ref. 4. [c]ΔH_{HM} = -19.0 (± 0.1) kcal/mol, ref. 7. [d]ΔH_{HM} = -26.6 (± 0.2) kcal/mol, ref. 7. [e]ΔH_{HM} = -39.2 (± 0.3) kcal/mol, ref. 9. [f]ΔH_{HM} = -35.2 (± 0.2) kcal/mol, ref. 9b.

CONCLUSIONS

Comparisons of $(H)_4Os(PR_3)_3$ vs. $(H)_2Os(PR_3)_4$ and $CpIr(PPh_3)(H)_2$ vs. $CpIr(PPh_3)(CO)$ establish that the basicity (ΔH_{HM}) of the metal increases with its isoelectronic ligands in the order: $(H)_2 < CO < PR_3$. Despite the strong donor ability of an H^- ligand as compared with a halide (X^-), two H ligands reduce the basicity of the metal more than a CO ligand. When substituting a Cp or Cp* ligand with an isoelectronic $(PR_3)_2(H)$ ligand set, the basicity (ΔH_{HM}) of the metal usually increases, but the magnitude of the increase depends greatly on the ligands and the metal. In the series of complexes $(H)_2Os(PR_3)_4$, the basicity of the metal increases with PR_3 in the order: $P(OEt)_3 < PPh(OEt)_2 < PPh_2Me < PPhMe_2$. For the $CpIr(ER_3)(H)_2$ complexes, the basicity of the metal increases with the ER_3 ligand as follows: $P(OPh)_3 << AsPh_3 \approx PPh_3$. It is surprising that the basicities of the $AsPh_3$ and PPh_3 complexes are nearly the same despite the fact that PPh_3 is a much stronger σ-donor than $AsPh_3$.

Acknowledgment

We thank the National Science Foundation (Grant No. CHE-9103948) for support of this work. The loan of OsO_4 and $IrCl_3 \cdot xH_2O$ from Johnson Matthey is greatly appreciated.

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PAPER III. CALORIMETRIC STUDIES OF THE HEATS OF PROTONATION OF THE DANGLING PHOSPHORUS IN η^1-$Ph_2PCH_2PPh_2$ COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

ABSTRACT

Titration calorimetry has been used to determine the heats of protonation (ΔH_{HP}) of $M(CO)_5(\eta^1\text{-dppm})$ (M = Cr, Mo, W) and *fac*-$M(CO)_3(\overset{\frown}{N\ N})(\eta^1\text{-dppm})$ (M = Mo, $\overset{\frown}{N\ N}$ = bipy, phen; M = W, $\overset{\frown}{N\ N}$ = bipy) complexes with CF_3SO_3H in 1,2-dichloroethane solvent at 25.0 °C. Spectroscopic studies show that protonation occurs at the uncoordinated phosphorus atom of the η^1-coordinated dppm ($Ph_2PCH_2PPh_2$) ligand. For dppm, its mono-protonated form ($dppmH^+$), and these complexes, the basicity (ΔH_{HP}) of the dangling phosphorus increases from -14.9 kcal/mol to -23.1 kcal/mol in the order: $dppmH^+ < Cr(CO)_5(\eta^1\text{-dppm}) < Mo(CO)_5(\eta^1\text{-dppm}) < W(CO)_5(\eta^1\text{-dppm}) <$ dppm $\leq$ *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm}) <$ *fac*-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm}) \approx$ *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$. In this series, H^+ is more electron-withdrawing than $M(CO)_5$ (M = Cr, Mo, W); $Mo(CO)_3(\eta^2\text{-phen})$ and $W(CO)_3(\eta^2\text{-bipy})$ actually enhance the basicity of the dangling phosphorus as compared with dppm itself. The basicity (ΔH_{HM}) of *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$, which protonates at the metal center to give a seven coordinate complex, is -18.8 kcal/mol. Thus, the basicity of the dangling phosphorus atom in *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^2\text{-dppm})$ is approximately 4.3 kcal/mol more basic than the metal center.

INTRODUCTION

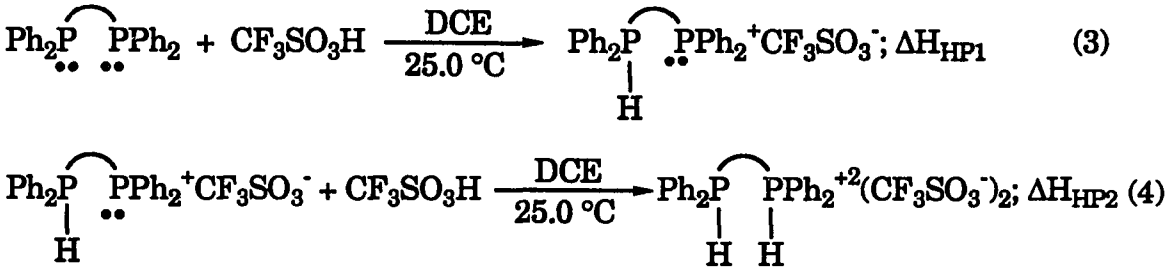
Bidentate phosphine ligands have been widely used as ligands in transition metal complexes.[1] In this research group, we have explored the effects of bidentate ligand structure on the basicity of the metal in the complexes $Fe(CO)_3(\overset{\frown}{P\ P})$,[2] $M(CO)_2(\overset{\frown}{P\ P})_2$ (M = Cr, Mo, W),[3] $CpRu(\overset{\frown}{P\ P})H$ (Cp = C_5H_5)[4] as measured by their heats of protonation with CF_3SO_3H in 1,2-dichloroethane solvent at 25.0 °C (eq 1). In several of these complexes,[2,3] the chelate ring size dramatically alters the basicity of the metal center.

$$ML_n + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HML_n^+CF_3SO_3^-;\quad \Delta H_{HM} \qquad (1)$$

In the present study we sought to understand the effect of a metal complex ML_x on the basicity of the dangling phosphorus of an η^1-coordinated

$$L_xM\text{-}\overset{\frown}{P\ P} + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} L_xM\text{-}\overset{\frown}{P\ PH}^+CF_3SO_3^-;\ \Delta H_{HP} \qquad (2)$$

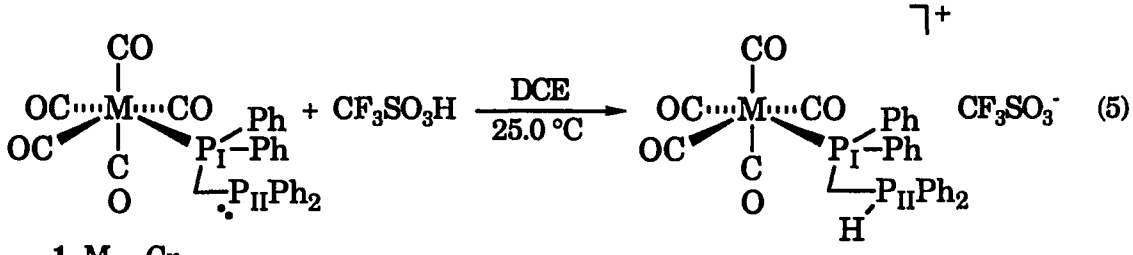
bidentate phosphine ligand by determining heats of protonation (ΔH_{HP}) for reactions of the type in eq 2. Previously, it was established[5] that free bidentate ligands $Ph_2P(CH_2)_nPPh_2$ are protonated in two steps (eqs 3 and 4), and these heats of protonation (ΔH_{HP1} and ΔH_{HP2}) may be substantially different from each other. The largest difference was for dppm ($Ph_2PCH_2PPh_2$), whose ΔH_{HP1} was -22.0 kcal/mol but ΔH_{HP2} was only -14.9 kcal/mol. Thus, protonation of one phosphorus decreases the basicity of the other phosphorus by 7.1 kcal/mol, a large change in donor ability.



$$Ph_2P(\cdot\cdot)\frown(\cdot\cdot)PPh_2 + CF_3SO_3H \xrightarrow[25.0\,^{\circ}C]{DCE} Ph_2P(H)\frown(\cdot\cdot)PPh_2^{+}CF_3SO_3^{-};\ \Delta H_{HP1} \qquad (3)$$

$$Ph_2P(H)\frown(\cdot\cdot)PPh_2^{+}CF_3SO_3^{-} + CF_3SO_3H \xrightarrow[25.0\,^{\circ}C]{DCE} Ph_2P(H)\frown(H)PPh_2^{+2}(CF_3SO_3^{-})_2;\ \Delta H_{HP2} \qquad (4)$$

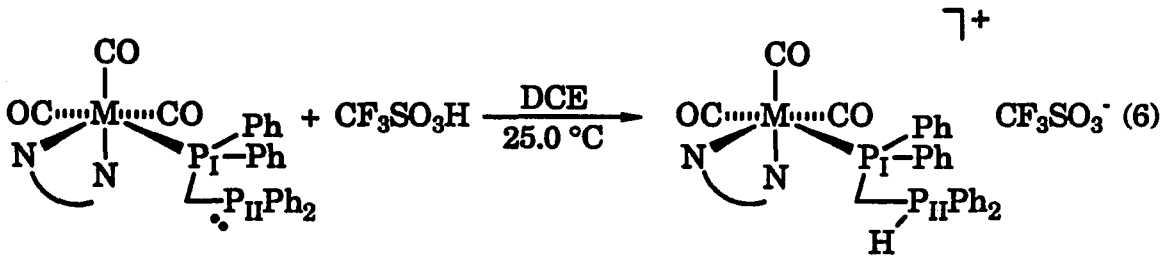
Transition metal complexes, like H^+, would presumably act as Lewis acids when η^1-coordinated to dppm and thereby affect the ΔH_{HP} of the dangling phosphorus. In this investigation, we describe the effects of $M(CO)_5$ (M = Cr, Mo, W) and the more electron-rich $M(CO)_3(\eta^2\text{-bipy})$ (M = Mo, W) and $Mo(CO)_3(\eta^2\text{-phen})$, where bipy is 2,2'-bipyridyl and phen is 1,10-phenanthroline, complexes on the basicity (ΔH_{HP}) of the dangling phosphorus in their η^1-dppm complexes. Thus, ΔH_{HP} values for reactions (5) and (6) were determined under the same conditions as for reactions (3) and (4).



$$OC_4M(CO)(Ph)P_I\text{–}Ph\,P_{II}Ph_2 + CF_3SO_3H \xrightarrow[25.0\,^{\circ}C]{DCE} [OC_4M(CO)(Ph)P_I\text{–}Ph\,P_{II}Ph_2(H)]^{+}\,CF_3SO_3^{-} \qquad (5)$$

1, M = Cr
2, M = Mo
3, M = W

$1H^+CF_3SO_3^-\text{-}3H^+CF_3SO_3^-$



4, M = Mo, N ⌒ N = bipy

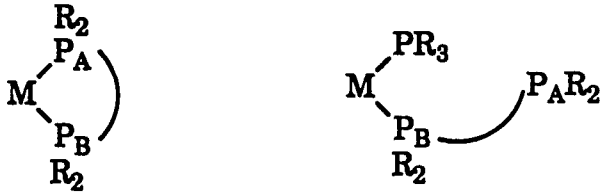
5, M = Mo, N ⌒ N = phen

6, M = W, N ⌒ N = bipy

$4H^+CF_3SO_3^- \cdot 6H^+CF_3SO_3^-$

Another reason to measure ΔH_{HP} for reactions (5) and (6) is to estimate the donor ability of the phosphorus atoms in a dppm chelate complex. Previously,[6] we correlated heats of protonation (ΔH_{HM}) of metal complexes with the basicities (ΔH_{HP}) of their phosphine ligands. For chelating ligands such as dppm, one might assume that the measure of donor ability of the P-atom to be used in these correlations is ΔH_{HP1}. However, it seems likely that the coordination of one P-atom (P_B in Chart I (a)) is going to affect the donor ability of the other (P_A) by withdrawing electron-density through the CH_2 link. An estimate of this effect is ΔH_{HP} for P_A in a complex of type (b) in Chart I.

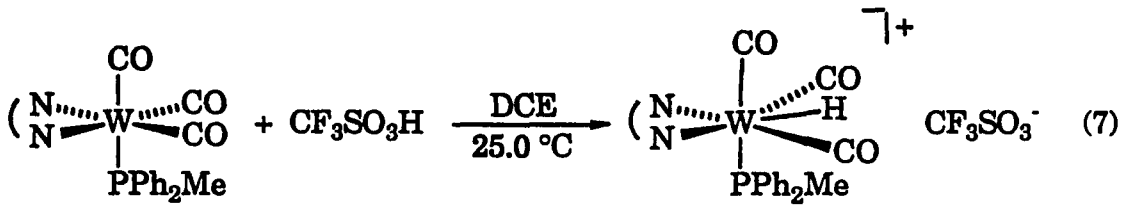
Chart I



(a) (b)

Thus, ΔH_{HP} values for reactions (5) and (6) provide an estimate of the effect that coordination through both P-atoms in dppm has on the donor ability of each phosphorus. The P-donor ability of chelates with longer hydrocarbon links, e.g. $Ph_2PCH_2CH_2PPh_2$ (dppe), will probably be less affected than dppm by coordination of the other end. This is evident from the much smaller difference (2.6 kcal/mol) between ΔH_{HP1} (-22.8 kcal/mol) and ΔH_{HP2} (-20.2 kcal/mol) for dppe (eqs 3 and 4).[5]

In order to compare the basicity of the metal center with that of the dangling phosphorus in eq 6, we also measured the heat of protonation (ΔH_{HM}) of *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) as shown in eq 7.



7, N⌒N = bipy

$7H^+CF_3SO_3^-$

EXPERIMENTAL SECTION

General Procedures

All preparative reactions and solvent purifications were carried out under N_2 atmosphere using standard Schlenk techniques. Hexanes and CH_2Cl_2 were refluxed over CaH_2 and then distilled. Xylenes were deoxygenated with N_2, then stored over molecular sieves for 12 h before use; the 1,2-dichloroethane (99.8%, HPLC Grade purchased from Aldrich) was distilled under argon from P_4O_{10} immediately prior to use. Deuterated solvents (CD_2Cl_2 and $CDCl_3$) were stored over molecular sieves in air. The CF_3SO_3H was purchased from 3M Co. and purified as previously described.[7] The IR spectra were recorded on a Bio-Rad FTS-7 FTIR spectrometer, ^1H NMR spectra were obtained on a Nicolet-NT 300 MHz instrument with TMS (δ = 0.00 ppm) as the internal reference, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer using 85% phosphoric acid (δ = 0.00 ppm) as the external standard.

The complexes $W(CO)_4(\eta^2\text{-bipy})$,[8] $Cr(CO)_5(\eta^1\text{-dppm})$ (1),[9] $Mo(CO)_5(\eta^1\text{-dppm})$ (2),[9] $Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (4),[10] $Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (5)[10] and $W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (6)[11] were prepared as previously described. Ligand abbreviations are bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline, dppm = $Ph_2PCH_2PPh_2$.

Synthesis of $W(CO)_5(\eta^1\text{-dppm})$ (3)

The complex $W(CO)_5(\eta^1\text{-dppm})$ (3) was prepared in a manner similar to that used by Basolo et al.,[12] by vigorously stirring 250 mg (0.71 mmol) of

$W(CO)_6$ and 79 mg (0.71 mmol) of $Me_3NO \cdot 2H_2O$ in 20 mL of CH_2Cl_2 for 15 minutes. To the yellow solution was added 273 mg (0.71 mmol) of dppm; this solution was stirred at room temperature for 3 days with a slow flow of N_2 through the solution. The air-stable white precipitate was filtered off and washed with MeOH, then recrystallized at -20 °C from a minimal amount of CH_2Cl_2 layered with MeOH. Pure, colorless crystals of $W(CO)_5(\eta^1$-dppm) were obtained (210 mg) in 42% yield. The spectral data listed below agree with the previously reported literature values.[9]

Synthesis of *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) (7)

The complex *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) (**7**) was prepared by refluxing 252 mg (0.56 mmol) of $W(CO)_4(\eta^2$-bipy)[8] with 0.104 mL (0.56 mmol) of PPh_2Me in 20 mL of xylenes for 5 h. The precipitate was filtered from the cooled solution and washed with copious amounts of hexanes. The air-stable fine dark purple crystals of *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) (194 mg, 56% yield) were collected and dried in vacuo. Spectral data are listed below.

Protonation Reactions

Compounds **1-7** were protonated for spectroscopic characterization by dissolving ~5 mg of the complex in 0.5 mL of CD_2Cl_2 (or $CDCl_3$) in a 5 mm NMR tube under N_2. To the solution was added 1 equiv of CF_3SO_3H by microliter syringe through a rubber septum. Spectroscopic data collected at room temperature are listed below for compounds **1-7** and **1H$^+$-7H$^+$**. Compounds **1-6** have been previously characterized; the spectroscopic data given in the literature are very similar to those listed below.

$Cr(CO)_5(\eta^1$-dppm) (1): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, Ph), 3.28 (dd, $^2J_{PH}$ = 6.9 and 0.6 Hz, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 47.2 (d, $^2J_{PP}$ = 94 Hz, Cr-P_I), -25.8 (d, $^2J_{PP}$ = 95 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 2067(w), 1939(s).

$Cr(CO)_5[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ (**1H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, Ph), 4.2 (br s, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.3 (s, Cr-P_I), 4.2 (br s, P_{II}). IR (CD_2Cl_2) ν(CO) 2067(w) 1939(s).

$Mo(CO)_5(\eta^1$-dppm) (2): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, Ph), 3.22 (dd, $^2J_{PH}$ = 8.1 and 2.7 Hz, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 28.1 (d, $^2J_{PP}$ = 114 Hz, Mo-P_I), -24.9 (d, $^2J_{PP}$ = 114 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 2072(w), 1945(s).

$Mo(CO)_5[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ (**2H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 7.1-7.3 (m, Ph), 4.2 (br s, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 31.3 (d, $^2J_{PP}$ = 9.2 Hz, Mo-P_I), 6.8 (br s, P_{II}). IR (CD_2Cl_2) ν(CO) 2072(w), 1945(s).

$W(CO)_5(\eta^1$-dppm) (3): ^1H NMR ($CDCl_3$) δ 7.1-7.3 (m, Ph), 3.31 (dd, $^2J_{PH}$ = 8.4 and 2.1 Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 10.4 (d, $^2J_{PP}$ = 106 Hz, $^1J_{PW}$ = 246 Hz, W-P_I), -24.3 (d, $^2J_{PP}$ = 106 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 2071(w), 1934(s).

$W(CO)_5[Ph_2PCH_2P(Ph_2)(H)]^+CF_3SO_3^-$ (**3H$^+$CF$_3$SO$_3^-$**): ^1H NMR ($CDCl_3$) δ 7.2-7.4 (m, Ph), 4.5 (br s, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 11.4 (br s, P_I), 7.7 (br s, P_{II}). IR ($CDCl_3$) ν(CO) 2071(w), 1934(s).

$Mo(CO)_3(\eta^2$-bipy)$(\eta^1$-dppm) (4): ^1H NMR (CD_2Cl_2) δ 9.1 (d, $^2J_{HH}$ = 6.5 Hz, 2H), 8.8 (d, $^2J_{HH}$ = 5.7 Hz, 2H), 8.1 (d, $^2J_{HH}$ = 8.1 Hz, 2H), 7.0-7.8 (m, Ph), 2.64 (dd, $^2J_{PH}$ = 4.4 and 2.1 Hz, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 47.2 (d, $^2J_{PP}$ = 71 Hz, Mo-P_I), -27.9 (d, $^2J_{PP}$ = 71 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 1911(s), 1824(m), 1754(m).

$Mo(CO)_3(\eta^2$-bipy)$[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ (**4H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 9.1 (d, $^2J_{HH}$ = 5.9 Hz, 2H), 8.9 (d, $^2J_{HH}$ = 5.9 Hz, 2H), 8.1 (d, $^2J_{HH}$ =

8.0 Hz, 2H) 7.1-7.8 (m, Ph), 4.0 (br s, CH_2). ^{31}P {^1H} NMR (CD_2Cl_2) δ 30.2 (d, $^2J_{PP}$ = 17 Hz, Mo-P_I), 7.9 (d, $^2J_{PP}$ = 17 Hz, P_{II}). IR (CD_2Cl_2) ν(CO) 1911(s), 1824(m), 1754(m).

$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (**5**): ^1H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 5 Hz, 2H), 8.0 (d, $^2J_{HH}$ = 8.1 Hz, 2H), 6.7-7.4 (m, Ph), 2.66 (dd, $^2J_{PH}$ = 4.5 and 2.0 Hz, CH_2). ^{31}P {^1H} NMR (CD_2Cl_2) δ 28.7 (d, $^2J_{PP}$ = 70 Hz, Mo-P_I), -27.6, (d, $^2J_{PP}$ = 70 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 1906(s), 1826(m), 1781(m).

$Mo(CO)_3(\eta^2\text{-phen})[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ (**5H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 9.1 (d, $^2J_{HH}$ = 4.8 Hz, 2H), 8.9 (d, $^2J_{HH}$ = 4.8 Hz, 2H), 8.2 (d, $^2J_{HH}$ = 7.5 Hz, 2H), 6.9-7.8 (m, Ph), 4.2 (br s, CH_2). ^{31}P {^1H} NMR (CD_2Cl_2) δ 32.1 (d, $^2J_{PP}$ = 17 Hz, Mo-P_I), 8.0 (d, $^2J_{PP}$ = 17 Hz, P_{II}). IR (CD_2Cl_2) ν(CO) 1906(s), 1826(m), 1781(m).

$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (**6**): ^1H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 5.7 Hz, 2H), 8.9 (d, $^2J_{HH}$ = 5.4 Hz, 2H), 8.1 (d, $^2J_{HH}$ = 8.4 Hz, 2H), 7.9 (t, $^2J_{HH}$ = 7.5 Hz, 2H), 7.0-7.5 (m, Ph), 2.22 (dd, $^2J_{PH}$ = 4.5 and 2.1 Hz, CH_2). ^{31}P {^1H} NMR (CD_2Cl_2) δ 20.0 (d, $^2J_{PP}$ = 66 Hz, W-P_I), -27.8 (d, $^2J_{PP}$ = 66 Hz, P_{II}). IR (CH_2Cl_2) ν(CO) 1906(s), 1822(m), 1774(m).

$W(CO)_3(\eta^2\text{-bipy})[Ph_2PCH_2P(Ph)_2(H)]^+CF_3SO_3^-$ (**6H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 9.2 (d, $^2J_{HH}$ = 6.3 Hz, 2H), 8.8 (d, $^2J_{HH}$ = 5.1 Hz, 2H), 8.1 (d, $^2J_{HH}$ = 8.1 Hz, 2H), 7.0-7.9 (m, Ph), 4.2 (br s, CH_2). ^{31}P {^1H} NMR (CD_2Cl_2) δ 19.9 (d, $^2J_{PP}$ = 12 Hz, W-P_I), 8.7 (br d, $^2J_{PP}$ = 12 Hz, P_{II}). IR (CD_2Cl_2) 1906(s), 1822(m), 1774(m).

$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ (**7**): ^1H NMR (CD_2Cl_2) δ 8.9 (d, $^2J_{HH}$ = 5.7 Hz, 2H), 7.8 (d, $^2J_{HH}$ = 8.1 Hz, 2H), 7.2-7.0 (m, Ph), 1.52 (d, $^2J_{PH}$ = 6 Hz, 3H, CH_3). IR (CH_2Cl_2) ν(CO) 1906(s), 1810(m), 1782(m).

$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)(H)^+CF_3SO_3^-$ (**7H$^+$CF$_3$SO$_3^-$**): ^1H NMR (CD_2Cl_2) δ 8.8 (d, $^2J_{HH}$ = 5.4 Hz, 2H), 8.4 (d, $^2J_{HH}$ = 8.1 Hz, 2H), 8.2 (t, $^2J_{HH}$ = 7.8 Hz, 2H), 7.6 (t, $^2J_{HH}$ = 6.3 Hz, 2H), 7.43 (t, $^2J_{HH}$ = 7.5 Hz, 2H), 7.3 (t, $^2J_{HH}$ = 7.5 Hz, 4H), 7.0 (t, $^2J_{HH}$ = 10.5 Hz, 4H), 1.65 (d, $^2J_{PH}$ = 7.2 Hz, 3H, CH_3), -3.0 (d, $^2J_{PH}$ = 30.3 Hz, 1H, W-H). IR (CD_2Cl_2) ν(CO) 2021(s), 1935(s), 1920(s).

Calorimetric Studies

The heats of protonation of complexes **1-7** were measured under an argon atmosphere using a Tronac Model 458 isoperibol calorimeter as originally described[7] and then modified.[6a] A three minute titration period was used for all complexes and was preceded and followed by heat capacity calibrations. During the titration period, approximately 1.2 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 to 50 mL of a 2.6 mM solution of the complex (5-10% excess) in DCE at 25.0 °C.

The ΔH_{HM} values were measured using at least two different standardized acid solutions and are reported as the average of at least four titrations and as many as eight. The heat of dilution of the acid in DCE (-0.2 kcal/mol)[6a] was used to correct the reaction enthalpies.

RESULTS

Characterization of Reactants 1-7 and Protonated Products ($1H^+$-$7H^+$)

Complexes **1-7** are air-stable in the solid state and in solution. Protonations of **1-6** result in complexes that are stable in solution. Complex $7H^+$ is air-sensitive in solution, but is stable under a nitrogen atmosphere.

Complexes **1-3** have previously[9] been assigned octahedral geometries with one phosphorus atom (P_I) of the dppm ligand coordinated to the metal (eq 5) on the basis of their ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR spectra. Since the $^{31}P\{^1H\}$ NMR, ^1H NMR and IR spectra of **1-3** and $1H^+$-$3H^+$ are very similar, only $Mo(CO)_5(\eta^1$-dppm) (**2**) and its protonation will be discussed here. The doublet at -24.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum in **2** was assigned to P_{II} (eq 5) because the chemical shift is so similar to that (-23.4 ppm) of free dppm in CD_2Cl_2; the doublet at 28.1 ppm was therefore assigned to P_I. The doublet of doublets for the methylene protons in the ^1H NMR spectrum also indicates inequivalent phosphorus atoms which is consistent with η^1-coordination of the dppm ligand. Addition of 1 equiv of CF_3SO_3H to **2** results in protonation of the uncoordinated phosphorus atom (P_{II}) as suggested by the $^{31}P\{^1H\}$ NMR resonance for P_{II} moving downfield from -24.9 ppm to 6.8 ppm (br s); the resonance for P_I shifts only slightly downfield to 31.3 ppm (d, $^2J_{PP}$ = 9.2 Hz). A broad singlet at 4.22 ppm is observed for the methylene protons in the ^1H NMR spectrum of $2H^+$. Since protonation of **2** does not occur at the metal, the ν(CO) bands in the IR spectrum of $2H^+$ are the same as those of **2** within experimental error.

Cano et al.,[10,11] used IR spectroscopy to establish the *fac*-geometries for complexes **4-6** (eq 6). Since the $^{31}P\{^1H\}$ NMR, ^1H NMR and IR spectra of **4-6** and **4H$^+$-6H$^+$** are similar, only *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (**4**) and its protonated analog (**4H$^+$**) will be described here. By comparison with the chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of free dppm (-23.4 ppm), the peak for **4** at -27.9 ppm is assigned to the dangling phosphorus atom (P_{II}) (eq 6); therefore, the peak at 47.2 ppm is assigned to P_I (eq 6). The doublet of doublets for the methylene protons in the ^1H NMR spectrum is also consistent with η^1-coordination of dppm. Addition of 1 equiv of CF_3SO_3H to **4** results in protonation of the free phosphorus atom (P_{II}) as suggested by the $^{31}P\{^1H\}$ resonance for P_{II} which shifts downfield from -27.9 ppm to 7.9 ppm upon protonation; the peak assigned to P_I shifts upfield from 47.2 ppm to 30.2 ppm. A broad singlet at 4.0 ppm is observed for the methylene protons in the ^1H NMR spectrum of **4H$^+$**. Since protonation occurs at P_{II} and not at the metal center, the ν(CO) bands for **4** and **4H$^+$** are the same.

The *fac*-geometry is assigned to $W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ (**7**) based on the three strong ν(CO) bands in its IR spectrum; the frequencies of these bands are nearly identical to those previously reported for *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_3)$.[13] In the ^1H NMR spectrum of **7**, a doublet is observed at 1.52 ppm for the methyl group; addition of 1 equiv of CF_3SO_3H results in a downfield shift of the methyl resonance to 1.65 ppm and the appearance of a doublet at -3.0 ppm for the hydride. The IR spectrum of **7H$^+$** has three ν(CO) bands of approximately equal intensity. Since the complex $W(H)(CO)_3[CH_3C(CH_2PPh_2)_3]^+$,[14] which must have 3 mutually *cis* CO ligands as required by the phosphine ligand, was reported to have three ν(CO) bands of

approximately the same intensity, it is likely that $7H^+$ also has three mutually *cis*-CO ligands as drawn in eq 7; details of the structure, such as the position of the hydride ligand, are not known.

Complexes $1H^+$-$7H^+$ are deprotonated rapidly and quantitatively with 1 equiv of 1,3-diphenylguanidine in CH_2Cl_2 or DCE solvent to yield the original complexes **1-7**, which are recovered by passing the solution through a short (~5 cm) neutral alumina column using CH_2Cl_2 as the eluent; the complexes are obtained by evaporating the solutions to dryness. Protonations of $Fe(CO)_4(\eta^1\text{-dppm})$[15] and *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$[16] in CD_2Cl_2 with 1 equiv of CF_3SO_3H result in more than one product as indicated by IR, ^1H NMR and $^{31}P\{^1H\}$ NMR spectroscopy; thus could not be measured in the calorimeter.

Calorimetric Studies

Heats of protonation (ΔH_{HP} and ΔH_{HM}) for complexes **1-7** as determined by titration calorimetry with CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C are listed in Table I. Plots of temperature vs. amount of acid added were linear, which indicates that the complexes are protonated rapidly and quantitatively. There was no decomposition of either the neutral or the protonated species during the titration as evidenced by the normal pre- and post-titration baseline slopes for **1-7**.

The low dielectric constant (ε=10.46)[17] for DCE suggests that the protonated products occur as ion pairs. However, as discussed elsewhere,[3,4,6] there is no evidence that ion-pairing or solvation energies determine trends in ΔH_{HP} or ΔH_{HM}. Thus, we attribute the differences in the ΔH_{HP} (and ΔH_{HM}) values to the properties of the reactant and product complexes.

Table I. Heats of Protonation (ΔH_{HP} and ΔH_{HM}) for $M(CO)_5(\eta^1\text{-dppm})$, *fac*-$M(CO)_3(\eta^2\text{-}\overset{\frown}{N\ N})(\eta^1\text{-dppm})$ and *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ Complexes

metal complex[a]	ΔH_{HP},[b] kcal/mol
$Cr(CO)_5(\eta^1\text{-dppm})$, **1**	-17.1 (± 0.1)
$Mo(CO)_5(\eta^1\text{-dppm})$, **2**	-18.6 (± 0.1)
$W(CO)_5(\eta^1\text{-dppm})$, **3**	-19.1 (± 0.3)
fac-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$, **4**	-22.3 (± 0.2)
fac-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$, **5**	-23.0 (± 0.1)
fac-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$, **6**	-23.1 (± 0.1)
fac-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$, **7**	-18.8 (± 0.2)[c]
$Ph_2PCH_2PPh_2$	-22.0 (± 0.1)[d]
$(H)Ph_2PCH_2PPh_2^+$	-14.9 (± 0.2)[e]

[a]Ligand abbreviations: $Ph_2PCH_2PPh_2$ (dppm), 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen).

[b]For protonation with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. Errors are given as average deviations from the mean of at least 4 titrations.

[c]ΔH_{HM} for protonation at the tungsten with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C.

[d]ΔH_{HP1} according to eq 3; reference 5.

[e]ΔH_{HP2} according to eq 4; reference 5.

DISCUSSION

Effect of the $M(CO)_5$ Group (M = Cr, Mo, W) on the Basicity (ΔH_{HP}, eq 5) of the Dangling Phosphorus Atom (P_{II}) in $M(CO)_5(\eta^1$-dppm)

As noted in the introduction, $(H)Ph_2PCH_2PPh_2^+CF_3SO_3^-$ (ΔH_{HP2} = -14.9 kcal/mol, eq 4) is 7.1 kcal/mol less basic than $Ph_2PCH_2PPh_2$ (ΔH_{HP1} = -22.0 kcal/mol, eq 3), which illustrates the strong electron-withdrawing effect of H^+ through the methylene group in dppm on the basicity of the unprotonated phosphorus. The effect of the $M(CO)_5$ groups (M = Cr, Mo, W) is significantly less as determined by ΔH_{HP} (Table I) for the dangling phosphorus (P_{II}) in the $M(CO)_5(\eta^1$-dppm) complexes; these basicities increase in the order: $(H)Ph_2PCH_2PPh_2^+$ (-14.9 kcal/mol) < $Cr(CO)_5(\eta^1$-dppm) (-17.1 kcal/mol) < $Mo(CO)_5(\eta^1$-dppm) (-18.6 kcal/mol) < $W(CO)_5(\eta^1$-dppm) (-19.1 kcal/mol) < $Ph_2PCH_2PPh_2$ (-22.0 kcal/mol). The order of $M(CO)_5(\eta^1$-dppm) basicities (ΔH_{HP}) is not consistent with either the trend in the Pauling electronegativities, which increase in the order [Cr (1.66) < Mo (2.16) < W (2.36)] or the Allred-Rochow electronegativities [Cr (1.35) < Mo (1.24) < W (1.13)];[18] nor is it consistent with the electron affinities of the elements: Cr (65 kJ/mol) < Mo (100 kJ/mol) > W (60 kJ/mol).[19] It seems likely that the ΔH_{HP} values for $M(CO)_5(\eta^1$-dppm) are a measure of the overall electron-withdrawing ability of the $M(CO)_5$ group, which is determined by σ- and π-bonding between the metal and P_I. This trend suggests that either π-back bonding from the metal to the phosphorus increases in the order: Cr < Mo < W, or that the σ-accepting ability of the metal increases in the reverse order (W < Mo < Cr).

Effect of the $M(CO)_3(\eta^2\text{-}\overset{\frown}{N\ N})$ Group (M = Mo, W) on the Basicity (ΔH_{HP}, eq 6) of the Dangling Phosphorus atom (P_{II}) in *fac*-$M(CO)_3(\eta^2\text{-}\overset{\frown}{N\ N})(\eta^1\text{-dppm})$

The basicity of P_{II} in $W(CO)_5(\eta^1\text{-dppm})$ (ΔH_{HP} = -19.1 kcal/mol) increases by 4.0 kcal/mol when two of the CO ligands are replaced by a bipy ligand to give *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (ΔH_{HP} = -23.1 kcal/mol). When two CO ligands in $Mo(CO)_5(\eta^1\text{-dppm})$ (ΔH_{HP} = -18.6 kcal/mol) are substituted by bipy (pK_{a1} = 4.44)[20] to give *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (ΔH_{HP} = -22.3 kcal/mol) or by the more basic phen ligand (pK_{a1} = 4.84)[20] to give *fac*-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (ΔH_{HP} = -23.0 kcal/mol), the basicity (ΔH_{HP}) of the dangling phosphorus atom (P_{II}) increases by 3.7 and 4.4 kcal/mol, respectively. Thus, replacement of two CO ligands in $M(CO)_5(\eta^1\text{-dppm})$ (M = Mo, W) by bipy or phen ($\overset{\frown}{N\ N}$) to give *fac*-$Mo(CO)_3(\overset{\frown}{N\ N})(\eta^1\text{-dppm})$ (**4, 5, 6**) increases the basicity of the dangling phosphorus atom (P_{II}) by 3.7-4.4 kcal/mol. As observed for the $M(CO)_5(\eta^1\text{-dppm})$ complexes, the tungsten derivative $M(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ is more basic (by 0.8 kcal/mol) than the Mo analog. Summarizing results for dppm and its complexes (**1-6**), the following order of increasing basicity (ΔH_{HP}) of the dangling phosphorus atom (P_{II}) is observed: $(H)Ph_2PCH_2PPh_2^+$ (-14.9 kcal/mol) < $Cr(CO)_5(\eta^1\text{-dppm})$ (-17.1 kcal/mol) < $Mo(CO)_5(\eta^2\text{-dppm})$ (-18.6 kcal/mol) < $W(CO)_5(\eta^1\text{-dppm})$ (-19.1 kcal/mol) < $Ph_2P(CH_2)PPh_2$ (-22.0 kcal/mol) ≤ *fac*-$Mo(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (-22.3 kcal/mol) < *fac*-$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (-23.0 kcal/mol) ≈ *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (-23.1 kcal/mol). Of particular interest is the result that *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (ΔH_{HP} = -23.1 kcal/mol) is 1.1 kcal/mol *more* basic than $Ph_2PCH_2PPh_2$ itself (ΔH_{HP1} = -22.0 kcal/mol). Similarly, *fac*-

$Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$ (ΔH_{HP1} = -23.0 kcal/mol) is more basic than dppm. A simple Lewis acid-base σ-bond between the metal and phosphorus would require that P_I donate some electron density to the metal which would make P_{II} *less* basic than dppm itself. These results therefore suggest that the $M(CO)_3(\overset{\frown}{N\ \ N})$ groups actually donate electron-density *to* the dppm ligand. This donation would presumably occur by π-back-bonding from the metal to P_I.

Based on these results, the effect of coordinating P_B (Chart I) on the donor ability of P_A in a dppm chelate complex can vary from decreasing the donor ability of P_A by 4.9 kcal/mol (in $Cr(CO)_5(\eta^1\text{-dppm})$) to actually increasing its donor ability by 1.1 kcal/mol (in *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$) depending on the metal and its other ligands.

Comparison of the Basicities (ΔH_{HM} and ΔH_{HP}) of *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) and *fac*-$W(CO)_3(\eta^2$-bipy)(η^1-dppm).

In order to estimate the basicity of the metal in *fac*-$W(CO)_3(\eta^2\text{-bipy})(\eta^1$-dppm) (**6**), the ΔH_{HM} of the analogous complex, *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$, (**7**), without a dangling phosphorus, was determined (eq 7). Its basicity (ΔH_{HM} = -18.8 kcal/mol) is probably somewhat higher than that of tungsten in **6** because PPh_2Me (ΔH_{HP1} -24.7 kcal/mol) is a better donor than dppm (ΔH_{HP1} = -22.0 kcal/mol). However, assuming that ΔH_{HM} of **7** is a high estimate for the basicity of the metal in **6**, the dangling P_{II} in **6** is at least 4.3 kcal/mol more basic than the tungsten atom. This difference in basicities (4.3 kcal/mol) of these two sites can be expressed in the form of the equilibrium constant (K_{eq}) for reaction (8). Assuming that ΔS^o is zero for this reaction, which means

$$7 + 6H^+ \overset{K_{eq}}{\rightleftharpoons} 7H^+ + 6 \qquad (8)$$

that $\Delta G°$ is 4.3 kcal/mol, K_{eq} is calculated ($\Delta G° = -RTlnK_{eq}$) to be 1.4×10^3. This large value accounts for the observation that *fac*-$W(CO)_3(\eta^2$-bipy)(η^1-dppm) is protonated at the dangling phosphorus (P_{II}) rather than at the metal.

Comparison of the Basicities (ΔH_{HM}) of *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) and *fac*-$W(CO)_3(PPh_2Me)_3$

The substitution of two PPh_2Me ligands in *fac*-$W(CO)_3(PPh_2Me)_3$ (ΔH_{HM} = -15.1 kcal/mol) by a bipy ligand to give *fac*-$W(CO)_3(\eta^2$-bipy)(PPh_2Me) (ΔH_{HM} = -18.8 kcal/mol) results in a 3.7 kcal/mol increase in the basicity of the metal. That the bipy complex **7** is more basic than *fac*-$W(CO)_3(PPh_2Me)_3$ is somewhat surprising since bipy ($pK_a = 4.44$)[20] is less basic than PPh_2Me ($pK_a = 4.59$). In previous studies of metal phosphine complexes,[5,6] we have noted linear correlations between metal complex basicity (ΔH_{HM}) and the basicities of the phosphine ligands as measured by ΔH_{HP}. If the pK_a of bipy is converted to ΔH_{HN} for protonation with CF_3SO_3H in DCE at 25.0 °C using a correlation

$$-\Delta H_{HN} = 1.64\ pK_a + 21.0;\ \text{in kcal/mol} \qquad (9)$$

(eq 9) of pK_a with ΔH_{HN} for other nitrogen bases,[3] bipy (ΔH_{HN} = -28.3 kcal/mol) is more basic than PPh_2Me whose ΔH_{HP} is -24.7 kcal/mol. Thus, using ΔH_{HN} and ΔH_{HP} as measures of the donor abilities of bipy and PPh_2Me allows one to

account for the higher basicity of the metal in *fac*-$W(CO)_3(\eta^2\text{-bipy})(PPh_2Me)$ as compared with that of *fac*-$W(CO)_3(PPh_2Me)_3$.

CONCLUSIONS

The basicity (ΔH_{HP}) of the dangling phosphorus (P_{II}) in $Ph_2PCH_2PPh_2$ (dppm) and its η^1-coordinated complexes increases in the order: $dppmH^+$ < $Cr(CO)_5(\eta^1$-dppm), **1** < $Mo(CO)_5(\eta^1$-dppm), **2** < $W(CO)_5(\eta^1$-dppm), **3** < dppm ≤ *fac*-$Mo(CO)_3(\eta^2$-bipy)$(\eta^1$-dppm), **4** < *fac*-$Mo(CO)_3(\eta^2$-phen)$(\eta^1$-dppm), **5** ≈ *fac*-$W(CO)_3(\eta^2$-bipy)$(\eta^1$-dppm), **6**. The proton (H^+) reduces the basicity of P_{II} more than any of the metal complexes. In fact, the basicity of the dangling phosphorus in **5** and **6** is actually higher than that of dppm itself, which indicates that the $W(CO)_3(\eta^2$-bipy) group is a net electron donor to the dppm, perhaps via π-back-bonding from the metal to the phosphorus. It is not surprising that **6** is protonated at the dangling phosphorus rather than at the tungsten since the metal, as estimated by the ΔH_{HM} for $W(CO)_3(\eta^2$-bipy)(PPh_2Me) **7**, is at least 4.3 kcal/mol less basic than the phosphorus in **6**. The basicity of the metal in **7** is higher than that in *fac*-$W(CO)_3(PPh_2Me)_3$ which is consistent with the donor abilities of the bipy and PPh_2Me ligands.

ACKNOWLEDGMENT

We thank the National Science Foundation (Grant CHE-9103948) for support of this work. We are also grateful to Diana Mayer, an Ames Laboratory (DOE) Summer Research Fellow, for exploratory studies on this project.

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SUMMARY

This research has shown that the basicity (ΔH_{HM}) of a transition metal complex can be systematically controlled by altering the ligands and/or the metal. In general, the basicities of the metals are increased as the basicities of the phosphine ligands are increased. The $CpOs(PPh_3)_2X$ (X = I, Br, Cl, H) system, the basicities of the metals increase as the gas phase proton affinities of the X ligands increase. The Cp* ligand increases the basicity (ΔH_{HM}) of complex by 5.5 - 9.0 kcal/mol more than those with the Cp ligand, and Os complexes are 6.0 - 8.5 kcal/mol more basic than the analogous Ru complexes. By comparison of $(H)_4Os(PR_3)_3$ vs $(H)_2Os(PR_3)_4$ and $CpIr(PPh_3)(H)_2$ vs $CpIr(PPh_3)(CO)$ complexes, it has been established that the basicity (H_{HM}) of the metal increases with its isoelectronic ligands in the order: $(H)_2$ < CO < PR_3. The basicity (ΔH_{HM}) of the dangling phosphorus atom in $L_nM(\eta^1$-dppm) complexes was found to be decreased more by H^+ (i.e., $(H)Ph_2PCH_2PPh_2^+$) than $M(CO)_5$ (M = Cr, Mo, W), while $Mo(CO)_3(\eta^2$-phen) and $W(CO)_3(\eta^2$-bipy) actually enhance the basicity of the dangling phosphorus more than free dppm.

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