

1987

Determination of phosphine basicity and study of nucleophilic addition to $[\pi]$ -hydrocarbon ligands

Russell C. Bush
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Bush, Russell C., "Determination of phosphine basicity and study of nucleophilic addition to $[\pi]$ -hydrocarbon ligands " (1987).
Retrospective Theses and Dissertations. 8621.
<https://lib.dr.iastate.edu/rtd/8621>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a 17" × 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or 6" × 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.



300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA



Order Number 8805051

**Determination of phosphine basicity and study of nucleophilic
addition to π -hydrocarbon ligands**

Bush, Russell C., Ph.D.

Iowa State University, 1987

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106



Determination of phosphine basicity and study of
nucleophilic addition to π -hydrocarbon ligands

by

Russell C. Bush

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

1987

TABLE OF CONTENTS

	Page
DEDICATION	iv
PREFACE	v
SECTION 1. PROTONATION OF MONO- AND DINUCLEAR COMPLEXES OF Fe, Ru, AND Os	1
INTRODUCTION	2
PROTONATION OF ANIONIC COMPLEXES	3
PROTONATION OF NEUTRAL ZEROVALENT COMPLEXES	8
PROTONATION OF HIGHER VALENT DERIVATIVES	14
PROTONATION OF NEUTRAL DINUCLEAR COMPLEXES	20
CONCLUDING REMARKS	24
REFERENCES	25
SECTION 2. PROTONATION ENTHALPIES OF PHOSPHINES DETERMINED BY TITRATION CALORIMETRY WITH TRIFLUOROMETHANESULFONIC ACID IN 1,2-DICHLOROETHANE. A NEW MEASURE OF PHOSPHINE DONOR ABILITY	31
INTRODUCTION	32
EXPERIMENTAL SECTION	35
RESULTS	40
DISCUSSION	44
CONCLUSION	57
REFERENCES	58
SECTION 3. METAL CARBONYL $\nu(\text{CO})$ FORCE CONSTANTS AS PREDICTORS OF π -ETHYLENE AND π -BENZENE COMPLEX REACTIVITY WITH NUCLEOPHILES	62
INTRODUCTION	63

METHOD	66
RESULTS	71
DISCUSSION	74
CONCLUSIONS	98
REFERENCES	99
SECTION 4. SYNTHESIS AND STRUCTURE OF [1-5- η -6- <u>exo</u> -Re(CO) ₅ - C ₇ H ₈]Mn(CO) ₃ . THE FIRST EXAMPLE OF METAL CARBONYL ANION ADDITION TO A COORDINATED CYCLIC π -HYDROCARBON	105
COMMUNICATION	106
REFERENCES	112
SUPPLEMENTARY MATERIAL	115
SUMMARY	120
ACKNOWLEDGMENTS	121

iv

DEDICATION

To Mom, Dad, and Carol

PREFACE

The research described in this dissertation addresses two quite different aspects of organometallic chemistry. The first topic is the determination of phosphine basicity. Phosphines are employed as ligands in a vast array of organometallic complexes, and the properties of such complexes are often strongly related to the basicities of the phosphine ligands. Although estimates of phosphine pK_a 's in H_2O have been available for many years, there was a need for a more direct measure of their basicity. Thus, a new method for gauging phosphine basicity was developed, based on the measurement of protonation enthalpies with a solution calorimeter.

The second area of research interest is the activation of π -hydrocarbon ligands to nucleophilic attack. This type of reaction is commonly exploited in organometallic synthesis. A method for predicting whether complexes would be reactive toward the desired nucleophile could be a useful tool for synthetic chemists. Such a method, based on simple force constant calculations, is described in the present work. A new application of the nucleophilic addition reaction is also described.

The dissertation consists of four sections, with the first comprising a literature survey of protonation reactions of basic mono- and dimetallic Fe, Ru, and Os complexes. The remaining sections are articles, as submitted for journal publication, covering the research topics noted above. Each section contains references, tables, figures, and equations pertinent only to the particular article.

SECTION 1. PROTONATION OF MONO- AND DINUCLEAR
COMPLEXES OF Fe, Ru, AND Os

INTRODUCTION

Anionic or low valent organo-transition metal complexes may possess a substantial degree of electron-donating ability associated with the metal center; which may be manifested in nucleophilic reactivity,¹ propensity to undergo oxidative addition of polar substrates,² or basicity toward protonic or Lewis acids.³ Of these, the basicity toward protonic acids is perhaps the most important; in that study of this most simple electron donor/acceptor interaction can lead to enhanced understanding of donor behavior in the other more complex cases.

Protonation reactions have been reported for a wide variety of metal complexes. However, examples from the Fe, Ru, Os triad stand out from the others in both variety of base structure and degree of basicity exhibited, with proton binding ability in some cases rivaling that of such strong bases as alkoxides.⁴ The reactions of complexes from this triad with various protonic acids are the subject of the present survey.

Over 100 mono- and dinuclear iron triad complexes that give simple protonation products are listed in the tables that follow. In every case, protonation was determined to occur either at a metal center or at a metal-metal bond. Basicity trends and relationships are discussed for many of the compounds.

Complexes of higher nuclearity may also act as bases; in fact, examples of this behavior are quite numerous. However, these compounds are not covered in this survey in order to provide detailed coverage of the more fundamental cases of protonation at a single metal atom or a single metal-metal bond.

PROTONATION OF ANIONIC COMPLEXES

Acid-base studies of the iron group anionic complexes have appeared in the literature for more than 30 years; some of these compounds are among the strongest metal bases known. Anionic complexes of Fe, Ru, and Os that undergo protonation are listed in Table 1.1.

The cyclopentadienyl complexes $\text{CpFe}(\text{CO})_2^-$ and $\text{Cp}^*\text{Fe}(\text{CO})_2^-$ are protonated readily by the weak acid $\text{CH}_3\text{CO}_2\text{H}$. The former complex and its ruthenium analog, $\text{CpRu}(\text{CO})_2^-$, are even protonated in H_2O . The facile decomposition of $\text{CpFe}(\text{CO})_2\text{H}$ (eq. 1) noted in early work with cyclopentadienyl derivatives of Fe¹⁹ has probably limited basicity study



of $\text{CpFe}(\text{CO})_2^-$, although recent reports⁵ have indicated that the hydride is more stable than previously believed. Metal hydrides formed from a few other anions of Fe and Ru also have rather limited stability. Protonation of $\text{Fe}(\text{CO})_3\text{NO}^-$ gives $\text{HFe}(\text{CO})_3\text{NO}$, which decomposes violently above -45°C (the phosphine analog, $\text{HFe}(\text{PF}_3)\text{NO}$, is more well-behaved).⁸ The metal hydrides $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{H}_2\text{Ru}(\text{CO})_4$ are reported to decompose even at 0°C ,¹⁶ thus addition of acid to a methanol solution of $[\text{PPN}][\text{HFe}(\text{CO})_4]$ (PPN = bis(triphenylphosphine)iminium ion) at ambient temperature or simple dissolution of the ruthenium analog in a protic solvent, again at ambient temperature, reportedly gives the anions $\text{HM}_3(\text{CO})_{11}^-$ (M = Fe, Ru).²⁰

Despite the instability of the $\text{H}_2\text{M}(\text{CO})_4$ species, some quantitative basicity information is available for the conjugate bases of the Fe and Os

Table 1.1. Protonation of anionic mono- and dinuclear complexes of Fe, Ru, and Os^a

Complex	Acid	Reference
$\text{CpFe}(\text{CO})_2^-$ ^b	$\text{CH}_3\text{CO}_2\text{H}; \text{H}_2\text{O}$	3a, 5
$\text{Cp}^*\text{Fe}(\text{CO})_2^-$ ^c	$\text{CH}_3\text{CO}_2\text{H}$	6
$\text{Fe}(\text{CO})_3\text{NO}^-$ ^d	$\text{HCl}/\text{Et}_2\text{O}$	7
$\text{Fe}(\text{PF}_3)_3\text{NO}^-$	H_2SO_4 (50%)	8
$\text{Fe}(\text{CO})_4^{2-}$	HCl (aq.) ^e	9, 10, 11
$\text{HFe}(\text{CO})_4^-$	HCl (aq.), $\text{CH}_3\text{CO}_2\text{H}$	10a, 11
$\text{Fe}(\text{PF}_3)_4^{2-}$	$\text{H}_2\text{O};^f \text{H}_3\text{PO}_4^e$	12
$\text{Fe}_2(\text{CO})_8^{2-}$	$\text{CH}_3\text{CO}_2\text{H}$	13
$\text{Fe}(\text{CO})_3(\mu\text{-Ph}_2\text{PC}(\text{H})\text{PPh}_2)\text{Fe}(\text{CO})_3^-$	$\text{CF}_3\text{CO}_2\text{H}$	14
$\text{CpRu}(\text{CO})_2^-$	H_2O	3a
$\text{Ru}(\text{CO})_4^{2-}$	MeOH	15
$\text{HRu}(\text{CO})_4^-$	H_3PO_4	16
$\text{Ru}(\text{PF}_3)_2^-$	$\text{H}_2\text{O};^f \text{H}_3\text{PO}_4^e$	12

^aProduct is that resulting from monoprotection unless otherwise noted.

^bCp = $\eta\text{-C}_5\text{H}_5$.

^cCp* = $\eta\text{-C}_5\text{Me}_5$.

^dProtonated form decomposes violently above -45°C .

^eDiprotection occurs with two equivalents (or more) of acid.

^fIn the presence of $[\text{Fe}(\text{o-phenanthroline})_3]\text{SO}_4$.

Table 1.1. Continued

Complex	Acid	Reference
$\text{Os}(\text{CO})_4^{-2}$	H_3PO_4 ; ^e MeOH; $\text{CF}_3\text{CO}_2\text{H}$ ^g	15, 17
$\text{Os}(\text{PF}_3)_4^{2-}$	H_3PO_4 ^e	12
$\text{HOs}_2(\text{CO})_8^-$	$\text{CF}_3\text{CO}_2\text{H}$	18

^gOne equivalent of acid.

derivatives ($\text{H}_2\text{Os}(\text{CO})_4$ is quite stable thermally). Potentiometric titrations of aqueous solutions of $\text{K}_2\text{Fe}(\text{CO})_4$ and $\text{KHF}(\text{CO})_4$ have been reported^{10a} with values of 4×10^{-5} and 4×10^{-14} determined for the first and second acid dissociation constants, respectively, at 17.5°C (values of $K_1 = 3.6 \times 10^{-5}$ and $K_2 = 1 \times 10^{-14}$ were obtained at 0°C in a separate study).^{10b} These data indicate that $\text{Fe}(\text{CO})_4^{2-}$ is on par with OH^- in base strength (a 0.18 M solution of $\text{K}_2\text{Fe}(\text{CO})_4$ is approximately 35% hydrolyzed in H_2O). The pK_1 's for $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{H}_2\text{Os}(\text{CO})_4$ in MeOH solution reveal a tremendous difference in strength of the conjugate bases on moving from a 3d to a 5d metal, with $\text{pK}_1 = 6.8$ for the Fe complex⁴ and $\text{pK}_1 = 15.2$ for the Os analog.²⁰ Qualitative information suggests that $\text{Ru}(\text{CO})_4^{2-}$ is also much more basic than $\text{Fe}(\text{CO})_4^{2-}$. Good yields of $\text{HRu}(\text{CO})_4^-$ are obtained simply by dissolving $\text{Na}_2\text{Ru}(\text{CO})_4$ in the very weak acid MeOH at -78°C ¹⁵ (also successful for $\text{Na}_2\text{Os}(\text{CO})_4$), but salts of $\text{Fe}(\text{CO})_4^{2-}$ may be prepared in alcohols.⁴ The finding of increased basicity for the heavier metals is evident in many other comparisons of iron group complexes and is consistent with behavior observed for basic complexes of other metal groups.²¹

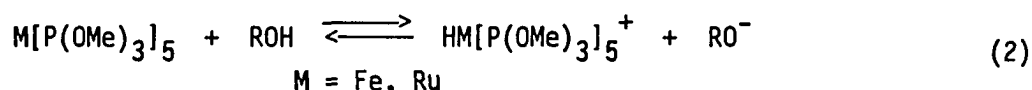
Infrared studies of deprotonation of $\text{H}_2\text{Os}(\text{CO})_4$ and $\text{H}_2\text{Os}_2(\text{CO})_8$ with amines in CH_3CN have yielded quantitative comparisons of basicity for their corresponding mono-anions. The difference in basicity between the mono- and dinuclear anions is very slight, with $\text{pK}_a = 20.8$ and 20.4 for the respective conjugate acids of $\text{HOs}(\text{CO})_4^-$ and $\text{HOs}_2(\text{CO})_8^-$.¹⁸

Both of these complexes are less basic than CH_3CO_2^- in the CH_3CN solvent ($\text{pK}_a = 22.3$). In contrast, $\text{HOs}(\text{CO})_4^-$ is considerably more basic than CH_3CO_2^- in MeOH ($\text{pK}_a = 9.6$ for CH_3CO_2^- , 15.2 for $\text{HOs}(\text{CO})_4^-$).²⁰

PROTONATION OF NEUTRAL ZEROVALENT COMPLEXES

The neutral complexes listed in Table 1.2 exhibit a broad range of basic behavior. The binary metal carbonyls $M(\text{CO})_5$ ($M = \text{Fe}, \text{Ru}, \text{Os}$) require strongly acidic media ($\text{BF}_3 \cdot \text{H}_2\text{O}/\text{CF}_3\text{CO}_2\text{H}$, 98% H_2SO_4) for protonation. As expected, substitution of CO with stronger electron donors enhances the basicity of complexes: $\text{Fe}(\text{CO})_2(\text{PMe}_3)_2$ reacts with NH_4^+ , and $\text{Ru}[\text{P}(\text{OMe})_3]_5$ is protonated by alcohols.

Quantitative basicity measurements are largely lacking for neutral zerovalent complexes. Preliminary studies of the heat of reaction of iron group complexes with $\text{CF}_3\text{CO}_2\text{H}$ give confirmation that phosphine substitution for CO or a change in central metal atom can have a substantial effect on basicity. Protonation of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ is 8 kcal mol^{-1} more exothermic than $\text{Os}(\text{CO})_4\text{PPh}_3$, and an increase in exothermicity of approximately 8 kcal mol^{-1} is likewise noted on going from $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ to $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$.²⁴ Qualitative differences have been noted for the pair of compounds $\text{Fe}[\text{P}(\text{OMe})_3]_5$ and $\text{Ru}[\text{P}(\text{OMe})_3]_5$. The equilibrium in eq. 2 lies substantially further toward the protonated form



for $M = \text{Ru}$; salts of $\text{HRu}[\text{P}(\text{OMe})_3]^+$ can be isolated from alcohols,³³ whereas $\text{Fe}[\text{P}(\text{OMe})_3]_5$ is only protonated to a slight extent in MeOH .³⁸ The basicity of the iso-nitrile complex $\text{Fe}[\text{CN}(\text{t-Bu})]_5$ exceeds that of $\text{HOs}(\text{CO})_4^-$, as $\text{H}_2\text{Os}(\text{CO})_4$ serves as an acid in the reaction shown in eq. 3.

Table 1.2. Protonation of mononuclear derivatives of zero-valent Fe, Ru, and Os

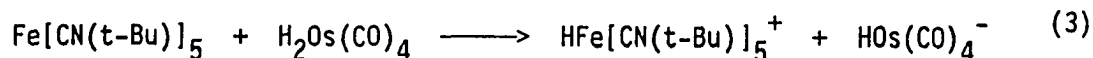
Complex	Acid	Reference
Fe(CO) ₅	BF ₃ H ₂ O/CF ₃ CO ₂ H; HCl(x)	22, 23
Fe(CO) ₄ PPh ₃	H ₂ SO ₄ (98%)	22
Fe(CO) ₄ AsPh ₃	H ₂ SO ₄ (98%)	22
Fe(CO) ₃ (PPh ₃) ₂	H ₂ SO ₄ (98%); CF ₃ SO ₃ H	22, 23
Fe(CO) ₃ (AsPh ₃) ₂	H ₂ SO ₄ (98%)	22
Fe(CO) ₂ (PMe ₃) ₃	NH ₄ PF ₆	25
Fe(CO)(PMe ₃) ₄	NH ₄ PF ₆	25
Fe(PMe ₃) ₂ [P(OMe) ₃] ₃	NH ₄ PF ₆	25
Fe(PMe ₃) ₃ [P(OMe) ₃] ₂	NH ₄ PF ₆	25
Fe[P(OMe) ₃] ₅	NH ₄ PF ₆	26
Fe[CN(t-Bu)] ₅	HMn(CO) ₅ ; H ₂ Os(CO) ₄ ; HBF ₄ •2 Et ₂ O	27
Fe(η^4 -norbornadiene)(CO) ₃	FSO ₃ H/SO ₂	28
Ru(CO) ₅	H ₂ SO ₄ (98%)	29
Ru(CO) ₄ PPh ₃	H ₂ SO ₄ (98%)	29
Ru(CO) ₃ (PPh ₃) ₂	HPF ₆ (60%)	30
Ru(CO) ₂ (triphos) ^a	HCl(g)	31
Ru(CO) ₂ (PPh ₃) ₂ (PH ₂ Ph)	HClO ₄	32
Ru[P(OMe) ₃] ₅	MeOH	33
Os(CO) ₅	H ₂ SO ₄ (98%)	34

^aTriphos: 1,1,1-tris[(diphenylphosphino)methyl]ethane.

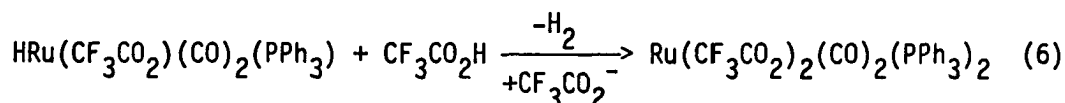
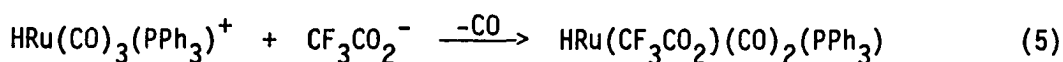
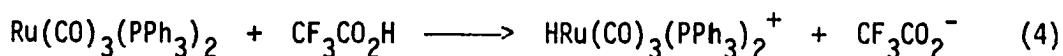
Table 1.2. Continued

Complex	Acid	Reference
$\text{Os}(\text{CO})_4\text{PPh}_3$	$\text{CF}_3\text{SO}_3\text{H}$; $\text{CF}_3\text{CO}_2\text{H}$	24, 35
$\text{Os}(\text{CO})_3(\text{PPh}_3)_2$	$\text{HCl}(\text{g})$; $\text{HBr}(\text{g})$; HClO_4 (70%) HBF_4 (48%); HPF_6 (65%); $\text{CF}_3\text{CO}_2\text{H}$; $\text{CF}_3\text{SO}_3\text{H}$	24, 36
$\text{Os}(\text{NO})_2(\text{PPh}_3)_2^{\text{b}}$	"strong acids"	37

^bThough $\text{Os}(\text{NO})_2(\text{PPh}_3)_2$ is not formally zerovalent, it is most similar to the complexes in this group.



Protonation of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ is achieved with HPF_6 , but reaction with $\text{CF}_3\text{CO}_2\text{H}$ gives the bis acetate complex, $\text{Ru}(\text{CF}_3\text{CO}_2)_2(\text{CO})_2(\text{PPh}_3)_2$.³⁹ This type of behavior is observed for other complexes of this class in reactions with acids possessing coordinating anions.⁴⁰ The proposed mechanism for the $\text{CF}_3\text{CO}_2\text{H}$ reaction noted above is shown in eqs. 4-6.



Careful choice of acid is thus required to avoid these secondary reactions when the initial protonated complex is relatively labile.

The protonation energies of the $\text{M}(\text{CO})_5$ compounds ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) have been examined through MO calculations with values of 195.0, 200.9, and 210.9 kcal mol^{-1} calculated for the Fe, Ru, and Os complexes, respectively.²¹ The value for $\text{Fe}(\text{CO})_5$ is in good agreement with the experimentally determined gas-phase proton affinity, $204 \pm 4 \text{ kcal mol}^{-1}$.⁴¹ In the theoretical study, the differences in protonation energies were largely attributed to increasingly favorable overlap of the metal carbonyl's donor orbital (after reorganization from trigonal-bipyramidal to square-pyramidal geometry) with the 1s acceptor orbital of

H⁺. This view is consistent with the observed enhanced basicity of Os relative to Fe in experimental work.

Arene complexes comprise a large portion of the neutral zerovalent complexes of the iron group (Table 1.3). Reactions of compounds in this class have been reviewed by Werner,^{3d} whose group is primarily responsible for the reported chemistry. The only iron complex in this series, (η -C₆H₅Me)Fe[P(OMe)₃]₂, reacts with the strong acid HBF₄ to give the corresponding hydride cation. The remaining Ru and Os derivatives once again reveal the dependence of basicity on ligands and metal. The complexes (C₆H₆)Ru(PMe₃)L, L = phosphine or phosphite, and (C₆H₆)Ru(PMe₂Ph)₂ are protonated at -78°C with NH₄PF₆.⁴³ The reaction mixture must be warmed to room temperature to effect protonation of (C₆H₆)Ru(PMePh₂), and the PPh₃ derivative in addition requires the stronger acid, CF₃CO₂H. The compounds (C₆H₆)Ru(PMe₃)(η -C₂H₄) and (C₆Me₆)Ru(PMe₃)CO must also be reacted with stronger acids, such as HBF₄ or CF₃CO₂H, whereas the Os analogs, (C₆H₆)Os(PMe₃)(η -C₂H₄) and (C₆H₆)Os(PMe₃)CO, can be protonated with NH₄PF₆.

Table 1.3. Protonation of zerovalent π -arene complexes of Fe, Ru, and Os

Complex	Acid	Reference
$(\eta\text{-C}_6\text{H}_5\text{Me})\text{Fe}[\text{P}(\text{OMe})_3]_2$	HBF_4	42
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_2\text{Ph})_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMePh}_2)_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)_2$	$\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)(\text{PPh}_3)$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)[\text{P}(\text{OMe})_3]$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)(\eta\text{-C}_2\text{H}_4)$	HBF_4 (50%)/ $(\text{EtCO})_2\text{O}$; $\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	44, 45
$[\text{p}-(i\text{-Pr})\text{C}_6\text{H}_4\text{Me}]\text{Ru}(\text{PMe}_3)_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\text{PMe}_3)_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\text{PMe}_3)(\text{CO})$	$\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	43
$(\eta\text{-C}_6\text{H}_6)\text{Os}(\text{PPh}_3)_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Os}[\text{P}(\text{OMe})_3]_2$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\eta\text{-C}_2\text{H}_4)$	NH_4PF_6	44
$(\eta\text{-C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\text{CO})$	NH_4PF_6	43
$(\eta\text{-C}_6\text{H}_6)\text{Os}(\text{PMe}_3)(\text{CNR})$		
R = Me; t-Bu; p-tolyl; Ph	NH_4PF_6	46

PROTONATION OF HIGHER VALENT DERIVATIVES

It is perhaps surprising that organometallic derivatives of the M(II) (M = Fe, Ru, Os) metal ions can act as bases, but the compounds in Table 1.4 provide clear examples of such behavior. Ferrocene (Cp_2Fe) and several alkyl derivatives are protonated by strong acids, but the basicity of [m]-ferrocenophanes (complexes in which the cyclopentadienyl ligands are bridged by m methylene groups) appear to be enhanced if the bridge is short enough to significantly tilt the ligand rings ([2]-ferrocenophane reacts with H_2SO_4 in EtOH at concentrations lower than 0.1% v/v).⁵¹ The phosphoferrocenes, $(\eta\text{-PC}_5\text{R}_4)_2\text{Fe}$, decompose in $\text{CF}_3\text{SO}_3\text{H}$ after a short time, but the corresponding onium ions are observable by NMR spectroscopy.^{52,53} Qualitatively, these appear to be less basic than the simple ferrocenes.⁵²

Ferrocene was originally proposed to be a stronger base than ruthenocene and osmocene on the basis of NMR observations,⁴⁷ an apparent reversal of the usual trends. However, measurements of the Hammett acidity function (H_0) at half neutralization for ferrocene and ruthenocene (determined from phase-transfer equilibria) show the Ru analog to be more basic than ferrocene.⁵⁴ This order is also found in the gas phase, where proton affinities of ruthenocene ($220 \pm 3 \text{ kcal mol}^{-1}$) and ferrocene ($213 \pm 5 \text{ kcal mol}^{-1}$) have been measured.⁴¹

The half-sandwich compounds of Ru and Os (Table 1.4) react readily with acids; the phosphine ligands imparting considerable basicity to the complexes as expected. The Ru(II) complex, $\text{Cp}^*\text{Ru}(\text{PMe}_3)_2\text{Cl}$, is sufficiently basic to be protonated with NH_4PF_6 .

Table 1.4. Protonation of metallocenes and other π -hydrocarbon derivatives of Fe(II), Ru(II), and Os(II)

Complex	Acid	Reference
Cp_2Fe^a	$\text{BF}_3 \cdot \text{H}_2\text{O}$; $\text{BF}_3 \cdot \text{H}_2\text{O}/\text{CF}_3\text{CO}_2\text{H}$; $\text{CF}_3\text{SO}_3\text{H}$	47, 48, 49
$(\eta\text{-C}_5\text{H}_4\text{R})\text{CpFe}$ R = Me; Et	$\text{BF}_3 \cdot \text{H}_2\text{O}$	49
$(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Fe}$ R = Me; Et	$\text{BF}_3 \cdot \text{H}_2\text{O}$	49
$(\eta\text{-C}_5\text{H}_4\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{Fe}$ n = 1, 2, 3	$\text{BF}_3 \cdot \text{H}_2\text{O}$	50
n = 0	H_2SO_4	51
$(\eta\text{-PC}_4\text{H}_3\text{R})_2\text{Fe}$ R = H; 2-Me; 3-Me	$\text{CF}_3\text{SO}_3\text{H}$	52
$(\eta\text{-PC}_4\text{H}_2\text{R}_2)_2\text{Fe}$ $\text{R}_2 = 3,4\text{-Me}_2$; 2,5-Ph ₂	$\text{CF}_3\text{SO}_3\text{H}$	52
$(\eta\text{-PC}_4\text{H}_2\text{R}_2)\text{CpFe}$ $\text{R}_2 = \text{H}_2$; 3,4-Me ₂ ; 2,5-Ph ₂	$\text{CF}_3\text{SO}_3\text{H}$	53
$(\eta\text{-PC}_4\text{Ph}_4)\text{CpFe}$	$\text{CF}_3\text{SO}_3\text{H}$	53
Cp_2Ru	$\text{BF}_3 \cdot \text{H}_2\text{O}$; H_2SO_4 (90-96%); $\text{H}_2\text{SO}_4/\text{CF}_3\text{CO}_2\text{H}$; $\text{BF}_3 \cdot \text{H}_2\text{O}/\text{CF}_3\text{CO}_2\text{H}$	47, 54

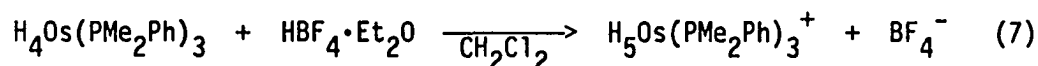
^aCp = $\eta\text{-C}_5\text{H}_5$.

Table 1.4. Continued

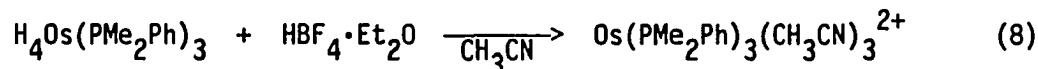
Complex	Acid	Reference
Cp^*_2Ru^b	$\text{CF}_3\text{CO}_2\text{H}; \text{HPF}_6$	55
$\text{CpRu}(\text{PMe}_3)_2\text{Cl}$	$\text{HPF}_6 \cdot \text{Et}_2\text{O}$	56
$\text{Cp}^*\text{Ru}(\text{PMe}_3)_2\text{Cl}$	NH_4PF_6	57
Cp^*_2Os	$\text{CF}_3\text{CO}_2\text{H}; \text{HPF}_6$	55
$\text{CpOs}(\text{PMe}_3)_2\text{Br}$	$\text{HPF}_6 \cdot \text{Et}_2\text{O}$	56
$\text{CpOs}(\text{PPh}_3)_2\text{Br}$	$\text{HBF}_4 \cdot \text{Me}_2\text{O}$	56
$(\eta\text{-6-exo-RC}_6\text{H}_6)\text{Os}(\text{PMe}_3)_2\text{I}$		
R = Me; n-Bu; t-Bu	$\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	58

^b $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$.

The hydride containing complexes in Table 1.5 comprise a particularly interesting group, in that they might be expected to undergo the acidolysis reaction noted previously in eq. 6. Although this reaction is observed in some cases,^{59b,66,68} stable protonated hydrido complexes of the iron group metals are fairly common. The bis-chelate dihydride complexes of Fe and Ru react with strong acids, although the protonated forms of $\text{H}_2\text{Ru}(\text{dppe})_2$ and $\text{H}_2\text{Ru}(\text{dppb})_2$ are not very stable.^{59a,60} The compounds $\text{H}_2\text{Ru}(\text{PMe}_3)_4$ and $\text{H}_2\text{Os}(\text{PMe}_3)_4$ react with NH_4PF_6 . Substitution of three phosphines by C_6Me_6 reduces the basicity so that $(\text{C}_6\text{Me}_6)\text{Ru}(\text{PMe}_3)\text{H}_2$ reacts only with stronger acids, although the related $(\text{C}_6\text{H}_6)\text{Os}[\text{P}(\text{i-Pr})_3]\text{H}_2$ has been protonated with NH_4PF_6 . Protonic basicity is also noted for H_4OsL_3 ($\text{L} = \text{PMe}_2\text{Ph}, \text{PEt}_2\text{Ph}$). In CH_2Cl_2 , the reaction of $\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ proceeds as shown in eq. 7.⁶⁶ When the reaction is carried out



in CH_3CN under similar conditions, a completely different product is obtained (eq. 8). The product in eq. 8 was shown to form by a sequence of



protonation/ H_2 elimination steps, illustrating the influence of solvent in the decomposition of simple protonation products.

Table 1.5. Protonation of hydride complexes of Fe, Ru, and Os

Complex	Acid	Reference
$\text{H}_2\text{Fe}(\text{dppe})_2^{\text{a}}$	$\text{HBF}_4 \cdot \text{Et}_2\text{O}$; $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$	59
$\text{H}_2\text{Ru}(\text{PMe}_3)_4$	NH_4PF_6	3d
$\text{H}_2\text{Ru}(\text{PMe}_2\text{Ph})_4$	HPF_6	60
$\text{H}_2\text{Ru}(\text{L}_2)_2$		
$\text{L}_2 = \text{dppe}$	HPF_6 ; $\text{HBF}_4 \cdot \text{Et}_2\text{O}$	59a, 60
$\text{L}_2 = \text{dppp}$, dppb^{b}	HPF_6	60
$\text{CpRu}(\text{PPh}_3)_2\text{H}^{\text{c}}$	$\text{HC}_5(\text{CO}_2\text{Me})_5$	61
$\text{CpRu}(\text{PPh}_3)(\text{t-BuNC})\text{H}$	HPF_6	62
$(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\text{PMe}_3)\text{H}_2$	$\text{HBF}_4 \cdot \text{Et}_2\text{O}$	63
$(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\text{PPh}_3)\text{H}_2$	$\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	63
$(\eta\text{-C}_6\text{H}_6)\text{Ru}[\text{P}(\text{i-Pr})_3]\text{H}_2$	$\text{CF}_3\text{CO}_2\text{H}/\text{NH}_4\text{PF}_6$	63
$\text{H}_2\text{Os}(\text{PMe}_3)_4$	NH_4PF_6	64
$\text{H}_2\text{Os}(\text{PEt}_2\text{Ph})_4$	$\text{HCl}(\text{MeOH})$	65
$\text{H}_4\text{Os}(\text{PMe}_2\text{Ph})_3$	$\text{HCl}(\text{MeOH})$; $\text{HBF}_4 \cdot \text{Et}_2\text{O}$	66, 67
$\text{H}_4\text{Os}(\text{PEt}_2\text{Ph})_3$	$\text{HCl}(\text{MeOH})$	66
$\text{HOs}(\text{NO})(\text{PPh}_3)_3$	$\text{CF}_3\text{CO}_2\text{H}$	68
$\text{HOs}(\text{L}_2)(\text{PPh}_3)_2\text{CO}^+$		
$\text{L}_2 = \text{bpy}$; $4,4'\text{-Me}_2\text{bpy}$; $5,5'\text{-Me}_2\text{bpy}^{\text{d}}$	$\text{CF}_3\text{SO}_3\text{H}$; $\text{CF}_3\text{CO}_2\text{H}$	69

^adppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

^bdppp = $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$; dppb = $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$.

^cCp = $\eta\text{-C}_5\text{H}_5$.

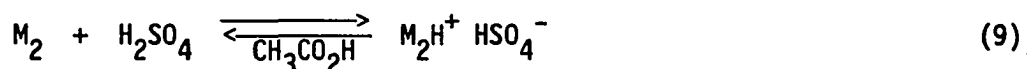
Table 1.5. Continued

Complex	Acid	Reference
$\text{CpOs}(\text{PPh}_3)_2\text{H}$	HCl (aq.); HBr (aq.); HI (aq.); $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$; $d\text{-}(+)\text{-campho-10-sulfonic acid}$	70
$(\eta\text{-C}_6\text{H}_6)\text{Os}[\text{P}(i\text{-Pr})_3]_2\text{H}_2$	NH_4PF_6	3d

PROTONATION OF NEUTRAL DINUCLEAR COMPLEXES

In 1962, the dinuclear complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{CpFeMn}(\text{CO})_7$, and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ were found to form stable solutions in 98% H_2SO_4 .⁷⁸ Since that time, several reports have appeared on this interesting class of organometallic bases (Table 1.6), in which the electron density available for binding protons is generally associated with the metal-metal bond.

Equilibrium studies with of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$, and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ gave estimates of the equilibrium constants for the reactions in eq. 9 (M_2 = dinuclear complex).⁷² For $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $K = 10^{-0.8}$, but



only a lower limit of $K \approx 100$ could be estimated for the Ru and $\text{P}(\text{OMe})_3$ complexes. Thus the basicities of metal-metal bonds also appear to follow the trend of increasing basicity on going to heavier metals within a triad.

Studies of complexes of the general formula $\text{Fe}_2(\mu\text{-A})(\mu\text{-A}')(\text{CO})_4\text{L}_2$ give further insight into the effect of ligands on metal-metal bond basicity.^{73,74} Qualitative differences were noted based on whether protonation was reversible or irreversible in MeOH with 60% HClO_4 (eq. 10). When $\text{A} = \text{A}' = \text{SMe}$ or SPh , the reaction is irreversible for $\text{L} = \text{PMe}_3$

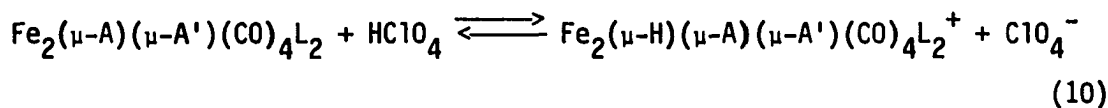


Table 1.6. Protonation of neutral bimetallic complexes of Fe, Ru, and Os

Complex	Acid	Reference
$\text{Cp}_2\text{Fe}_2(\text{CO})_4^{\text{a}}$	H_2SO_4 (98%); $\text{HBF}_4 \cdot \text{Me}_2\text{O}$	22, 71, 72
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$	H_2SO_4 (98%)	72
$\text{CpFeMn}(\text{CO})_7$	H_2SO_4 (98%)	22
$\text{Fe}_2(\mu\text{-SMe})_2(\text{CO})_4\text{L}_2$		
L = PMe_3 ; PMe_2Ph	H_2SO_4 (conc.)	73
L = PMePh_2 ; PPh_3	H_2SO_4 (conc.); $\text{CF}_3\text{CO}_2\text{H}$	73
$\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_4\text{L}_2$		
L = PMe_3 ; PMe_2Ph	HClO_4 (60%)	74
L = PMePh_2	$\text{CF}_3\text{CO}_2\text{H}$	74
$\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_4\text{L}_2$		
L = PMePh_2	HClO_4 (60%)	74
L = PPh_3	$\text{CF}_3\text{CO}_2\text{H}$	74
$\text{Fe}_2(\mu\text{-PMe}_2)_2(\text{CO})_4(\text{PPh}_3)_2$	HClO_4 (60%)	74
$\text{Fe}_2(\mu\text{-SPh})(\mu\text{-PPh}_2)(\text{CO})_4\text{L}_2$		
L = PMe_3 ; PMe_2Ph ; PMePh_2	HClO_4 (60%)	74
L = PPh_3	$\text{CF}_3\text{CO}_2\text{H}$	74
$\text{Fe}_2(\text{CO})_6[\mu\text{-CHC}(\text{Ph})\text{NEt}](\mu\text{-PPh}_2)$	$\text{HBF}_4 \cdot \text{Et}_2\text{O}$	75
$\text{Cp}_2\text{Ru}_2(\text{CO})_4$	H_2SO_4 (98%)	22, 72
$\text{Cp}^*_2\text{Ru}_2(\text{CO})_4^{\text{b}}$	HBF_4	76

^aCp = $\eta\text{-C}_5\text{H}_5$.

^bCp* = $\eta\text{-C}_5\text{Me}_5$.

Table 1.6. Continued

Complex	Acid	Reference
$\text{Ru}_2(\text{CO})_6[\mu\text{-CHC}(\text{Ph})\text{NEt}](\mu\text{-PPh}_2)$	$\text{HBF}_4 \cdot \text{Et}_2\text{O}$	75
$\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2^{\text{C}}$ R = Me; i-Pr	H_2SO_4 ; HPF_6 ; $\text{HBF}_4 \cdot \text{Et}_2\text{O}$	77
$\text{Ru}_2(\text{CO})_5[\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2]_2^{\text{C}}$	HPF_6 ; $\text{HBF}_4 \cdot \text{Et}_2\text{O}$	78
$\text{Os}_2(\text{CO})_6[\mu\text{-CHC}(\text{Ph})\text{NEt}](\mu\text{-PPht})$	$\text{HBF}_4 \cdot \text{Et}_2\text{O}$	75

^CIn the protonated complex, the hydride ligand is terminally bonded to only one Ru atom.

and PMe_2Ph , but reversible for $\text{L} = \text{PMePh}_2$ and PPh_3 . Replacement of one or both bridges by PPh_2 makes the reaction irreversible for $\text{L} = \text{PMePh}_2$, but not PPh_3 . However, replacement of the bridges with the still more electron-donating PMe_2 group gives irreversible protonation even with $\text{L} = \text{PPh}_3$.

CONCLUDING REMARKS

The foregoing examples demonstrate that protonation reactions of Fe, Ru, and Os compounds indeed represent a fruitful area of research. Although a good deal of qualitative observations on trends in basicity within this group have been made, there is a great need for more systematic and quantitative investigations. Information derived from such studies will lead to an enhanced understanding of the reactivities of these and other organometallic bases.

REFERENCES

1. King, R. B. Accounts Chem. Res. 1970, 3, 417.
2. Collman, J. P.; Roper, W. R. Adv. Organomet. Chem. 1968, 7, 53.
3. a) Shriver, D. F. Accounts Chem. Res. 1970, 3 231.
b) Schunn, R. A. in "Transition Metal Hydrides. The Hydrogen Series"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971, Chap. 5.
c) Kotz, J. C.; Pedrotty, D. G. Organomet. Chem. Rev. 1969, 4, 479.
d) Werner, H. Angew. Chem. Int. Ed. Engl. 1983, 22, 927.
4. Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. J. Am. Chem. Soc. 1979, 101, 7428.
5. a) Whitesides, T. H.; Shelly, J. J. Organomet. Chem. 1975, 92, 215.
b) Fergusson, S. B.; Sanderson, L. B. J.; Shackleton, T. A.; Baird, M. C. Inorg. Chim. Acta 1984, 83, L45.
6. Angerer, W.; Fiederling, K.; Grötsch, G.; Malisch, W. Chem. Ber. 1983, 116, 3947.
7. Hieber, W.; Buetner, H. Z. Anorg. Allg. Chem. 1963, 320, 101.
8. Kruck, T.; Lang, W. Chem. Ber. 1966, 99, 3794.
9. Blanchard, A. A.; Coleman, G. W. Inorg. Synth. 1946, 2, 243.
10. a) Krumholz, P.; Stettiner, H. M. A. J. Am. Chem. Soc. 1949, 71, 3035.
b) Hieber, W.; Hübel, W. B. Z. Elektrochem. 1953, 57, 235.
11. Fiegl, F.; Krumholz, P. Z. Anorg. Allg. Chem. 1933, 215, 242.
12. Kruck, T.; Kobelt, R. Chem. Ber. 1972, 105, 3765.

13. a) Hieber, W.; Brendel, G. Z. Anorg. Allg. Chem. 1958, 289, 324.
b) Sumner, C. E.; Collier, J. A.; Pettit, R. Organometallics 1982, 1, 1350.
14. Dawkins, G. M.; Green, M.; Jeffrey, J. C.; Stone, F. G. A. J. Chem. Soc., Chem. Commun. 1980, 1120.
15. Walker, H. W.; Ford, P. C. J. Organomet. Chem. 1981, 214, C43.
16. Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. J. Chem. Soc. A 1968, 2162.
17. Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. Inorg. Chem. 1982, 21, 3955.
18. Jordan, R. F.; Norton, J. R. J. Am. Chem. Soc. 1982, 104, 1255.
19. Green, M. L. H.; Street, C. N.; Wilkinson, G. Z. Naturforsch. B 1959, 14B, 738.
20. Walker, H. W.; Pearson, R. G.; Ford, P. C. J. Am. Chem. Soc. 1983, 105, 1179.
21. Ziegler, T. Organometallics 1985, 4, 675.
22. Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. J. Chem. Soc. 1962, 3653.
23. Iqbal, Z.; Waddington, T. C. J. Chem. Soc. A 1968, 2958.
24. Bush, R. C.; Angelici, R. J., unpublished results, Department of Chemistry, Iowa State University, 1986.
25. Karsch, H. H. Chem. Ber. 1977, 110, 2222.
26. Muetterties, E. L.; Rathke, J. W. J. Chem. Soc., Chem. Commun. 1974, 850.

27. Basset, J.-M.; Farrugia, L. J.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1980, 1789.
28. Falkowski, D. R.; Hunt, D. F.; Lillya, C. P.; Rausch, M. D. J. Am. Chem. Soc. 1967, 89, 6387.
29. Yarrow, P.; Ford, P. C. J. Organomet. Chem. 1981, 214, 115.
30. Johnson, B. F. G.; Segal, J. A. J. Chem. Soc., Dalton Trans. 1973, 478.
31. Hommeltoft, S. I.; Baird, M. C. Organometallics 1986, 5, 190.
32. Bohle, S. D.; Roper, W. R. Organometallics 1985, 5, 1607.
33. Jesson, J. P.; Cushing, M. A.; Ittel, S. D. Inorg. Synth. 1980, 20, 79.
34. Deeming, A. J.; Johnson, B. F. G.; Lewis, J. J. Chem. Soc. A 1970, 1967.
35. Doyle, R. A.; Angelici, R. J., unpublished results, Department of Chemistry, Iowa State University, 1985.
36. Laing, K. R.; Roper, W. R. J. Chem. Soc. A 1969, 1889.
37. Grundy, K. R.; Laing, K. R.; Roper, W. R. J. Chem. Soc., Chem. Commun. 1970, 1500.
38. Ittel, S. D.; English, J. D.; Tolman, C. A.; Jesson, J. P. Inorg. Chim. Acta 1979, 33, 101.
39. Collman, J. P.; Roper, W. R. J. Am. Chem. Soc. 1965, 87, 4008.
40. Burt, R.; Cooke, M.; Green, M. J. Chem. Soc. A 1969, 2645.
41. Stevens, A. E.; Beauchamp, J. L. J. Am. Chem. Soc. 1981, 103, 190.
42. Ittel, S. D.; Tolman, C. A. J. Organomet. Chem. 1979, 172, C49.
43. Werner, R.; Werner, H. Chem. Ber. 1982, 115, 3781.

44. Werner, R.; Werner, H. Chem. Ber. 1983, 116, 2074.
45. Werner, H.; Werner, R. J. Organomet. Chem. 1979, 174, C63.
46. Werner, H.; Weinand, R. Z. Naturforsch. B 1983, 38B, 1518.
47. Curphey, T. J.; Santer, J. O.; Rosenblum, M.; Richards, J. H. J. Am. Chem. Soc. 1960, 82, 5249.
48. Roberts, R. M. G.; Silver, J.; Ranson, R. J.; Morrison, I. E. G. J. Organomet. Chem. 1981, 219, 233.
49. Bitterwolf, T. E.; Ling, A. C. J. Organomet. Chem. 1972, 40, 197.
50. Bitterwolf, T. E.; Ling, A. C. J. Organomet. Chem. 1981, 215, 77.
51. Lentzner, H. L.; Watts, W. E. J. Chem. Soc., Chem. Commun. 1970, 26.
52. Roberts, R. M. G.; Silver, J.; Wells, A. S. Inorg. Chim. Acta 1986, 119, 1.
53. Roberts, R. M. G.; Silver, J.; Wells, A. S. Inorg. Chim. Acta 1986, 118, 135.
54. Cerichelli, G.; Illuminati, G.; Ortaggi, G.; Giuliani, A. M. J. Organomet. Chem. 1977, 127, 357.
55. Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. Organometallics 1986, 5, 2321.
56. Bruce, M. I.; Tomkins, I. B.; Wong, F. S.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 1982, 687.
57. Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. Organometallics 1984, 3, 274.
58. Werner, R.; Werner, H. Chem. Ber. 1984, 117, 161.

59. a) Morris, R. H.; Sawyer, J. A.; Shiralian, M.; Zubkowski, J. D. J. Am. Chem. Soc. 1985, 107, 5581.
b) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. Inorg. Chem. 1986, 25, 3412.
60. Ashworth, T. V.; Singleton, E. J. Chem. Soc., Chem. Commun. 1976, 705.
61. Bruce, M. I.; Wallis, R. C.; Williams, M. L.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 1983, 2183.
62. Conroy-Lewis, F. M.; Simpson, S. J. J. Chem. Soc., Chem. Commun. 1986, 506.
63. Werner, H.; Kletzin, H. J. Organomet. Chem. 1983, 243, C59.
64. Werner, H.; Gotzig, J. Organometallics 1983, 2, 547.
65. Bell, B.; Chatt, J.; Leigh, G. J. J. Chem. Soc., Dalton Trans. 1973, 997.
66. Douglas, P. G.; Shaw, B. L. J. Chem. Soc. A 1970, 334.
67. Bruno, J. W.; Huffman, J. C.; Caulton, K. G. J. Am. Chem. Soc. 1984, 106, 1663.
68. Boyer, E. B.; Dobson, A.; Robinson, S. D.; Haymore, B. L.; Huffman, J. C. J. Chem. Soc., Dalton Trans. 1985, 621.
69. Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. Inorg. Chem. 1987, 26, 1247.
70. Wilczewski, T. J. Organomet. Chem. 1986, 317, 307.
71. Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. Organometallics 1983, 2, 1238.
72. Harris, D. C.; Gray, H. B. Inorg. Chem. 1975, 14, 1215.

73. Fauvel, K.; Mathieu, R.; Poilblanc, R. Inorg. Chem. 1976, 15, 976.
74. Arabi, M. S.; Mathieu, R.; Poilblanc, R. J. Organomet. Chem. 1979, 177, 199.
75. Cherkas, A. A.; Hoffman, D.; Taylor, N. J.; Carty, A. J. Organometallics 1987, 6, 1466.
76. Stasunik, A.; Malisch, W. J. Organomet. Chem. 1984, 270, C56.
77. Field, J. S.; Haines, R. J.; Sampson, C. N.; Sundermeyer, J. J. Organomet. Chem. 1987, 327, C18.
78. Field, J. S.; Haines, R. J.; Sampson, C. N.; Sundermeyer, J.; Moodley, K. G. J. Organomet. Chem. 1987, 322, C7.

SECTION 2. PROTONATION ENTHALPIES OF PHOSPHINES DETERMINED
BY TITRATION CALORIMETRY WITH TRIFLUOROMETHANESULFONIC
ACID IN 1,2-DICHLOROETHANE. A NEW MEASURE OF
PHOSPHINE DONOR ABILITY

INTRODUCTION

A casual examination of the current literature of transition metal complexes is all that is required to gauge the importance of phosphines as ligands in organometallic and coordination chemistry. Developing an understanding of the effects of phosphines on metal complexes is a major goal of inorganic research.

The ability of phosphines to bind to transition metals is usually described in terms of steric and electronic properties. Quantitative determination of these binding characteristics has been the aim of a number of studies,¹ leading to parameters such as Tolman's cone angles (θ) and $\nu(\text{CO})$ values (for the A_1 vibration in $\text{Ni}(\text{CO})_3\text{PR}_3$) for describing steric and electronic effects, respectively, of phosphorus ligands. These parameters have often been employed in investigations of reactions involving phosphines.^{1c-d,2} Attempts to further dissect electronic effects have led to the development of a method for quantitatively analyzing reactions in terms of the σ -bonding, π -bonding, and steric properties of phosphines.³ Application of this method to data for ligand-dependent substitutions and reactions of phosphine-containing complexes has shown that, although π -bonding is important in some cases,^{3b} most of the data can be explained in terms of steric properties and σ -bonding alone.^{3a}

In view of the importance of phosphine σ -bonding in determining reactivity, a reliable measure of σ -bonding ability is critical to the interpretation of reactivity data. The values of ΔG or ΔH for reactions of phosphines with protonic or Lewis acids are the most obvious choices

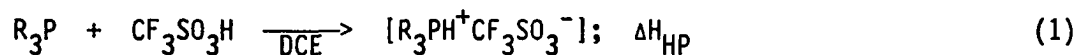
for such a measure. Free energies and enthalpies of phosphine adduct formation with group 13 Lewis acids (BH_3 , BF_3 , BMe_3 , and GaMe_3 , among others) have been measured,⁴ as have reaction enthalpies (and some free energies) with mercury dihalides⁵ and silver salts.⁶ Gas phase proton affinities have also been determined for a few phosphines;⁷ the results in some cases contrast sharply with what is observed in solution studies.^{7d}

The basicities of phosphines toward protonic acids in solution are the most commonly encountered measures of σ -bonding ability in metal complexes. A few pK_a 's have been evaluated for phosphines in aqueous EtOH ,⁸ but the most systematic investigation was that reported by Streuli for potentiometric measurements in polar aprotic media.⁹ The pK_a 's (referenced to aqueous solution) were estimated from the potential, measured with a glass electrode, at half neutralization in titrations of the phosphines in CH_3NO_2 with 0.1 N HCl. The basicities determined in this manner are consistent with the expectations for substituent effects from organic chemistry, i.e., higher pK_a 's for phosphines with more electron donating alkyl groups than with aryl groups, and a correlation was noted between the pK_a 's and Taft's σ^* substituent parameters¹⁰ (designed to gauge electronic effects of substituents bound to carbon). These pK_a 's, and others similarly determined,¹¹ are the basis for many mechanistic investigations in organo-transition metal chemistry.

Our particular interest in measures of phosphine basicity stems from a desire to study how phosphines contribute to the basicities of transition metals in complexes. Numerous phosphine complexes are known to undergo protonation at the metal center;¹² one would expect the basicity

in a series of $M'PR_3$ (M' = particular metal-ligands fragment; PR_3 = various phosphines) complexes to vary linearly with the basicity of PR_3 . In order to make correlations of phosphine basicity with metal-phosphine complex basicity as direct as possible, a system for measuring the basicities of phosphines in a reliable way, that would also be suitable for metal complexes, was desired. The development of such a system and its application to phosphine basicity measurement is the subject of the present study.

The basicity measure employed is the protonation enthalpy (ΔH_{HP}) of a phosphine, as determined by calorimetric titration with CF_3SO_3H in 1,2-dichloroethane (eq. 1). This acid/solvent system gives rapid and



complete protonation even of weakly basic phosphines. The ΔH_{HP} values for 12 tertiary phosphines are reported, and comparisons of the results with other measures of basicity are discussed.

EXPERIMENTAL SECTION

Purification of Reagents

Inert gases employed in this study were dried using the following procedures. Argon used in solvent distillation was dried by passage through a 45 cm column of activated CaSO_4 ,¹³ while Ar used to maintain an inert atmosphere in the calorimeter reaction vessel was dried with a 20 cm column of activated 4A molecular sieves¹³ and a -78°C trap. Nitrogen was passed through a 40 cm column of activated CaSO_4 , then through a liquid N_2 trap.

The solvent 1,2-dichloroethane (DCE) was purified using the procedure outlined by Perrin, Armarego, and Perrin,¹⁴ by washing with conc. H_2SO_4 , 5% NaOH , and then distilled H_2O . The solvent was predried over MgSO_4 , stored in amber bottles over molecular sieves for at least 12 h, then distilled from P_2O_5 under Ar immediately before use.

Trifluoromethanesulfonic acid (Aldrich) was fractionally distilled under N_2 at ambient pressure. Trifluoroacetic acid was refluxed over, then fractionally distilled from, P_2O_5 under N_2 after the method of Perrin et al.¹⁴ The acids were distilled (typically 4 to 8 mL) directly into a graduated reservoir (similar to Kontes model K-288630), which allowed for delivery of a known volume of acid with minimal exposure to the atmosphere during preparation of acid solutions.

Triphenylphosphine was recrystallized twice from hexanes, then from EtOH by dissolving in the hot solvent, filtering, and allowing the filtrate to cool to 0°C ; the crystals were then stored under N_2 . Tricyclohexylphosphine was dissolved in hexanes and filtered, with

evaporation of the solvent by a flow of N_2 , or purified by preparing and recrystallizing the CS_2 adduct, then regenerating the phosphine.¹⁵ The phosphines Et_3P and $MePh_2P$ (Aldrich) were distilled prior to use, and Me_3P was generated by heating $Me_3P \cdot AgI$ (Aldrich) under vacuum. The remaining phosphines, $(p-C_6H_4)_3P$, $(p-FC_6H_4)_3P$, $(p-MeOC_6H_4)_3P$, $(t-Bu)_3P$ (Strem), $(p-MeC_6H_4)_3P$, $(o-MeC_6H_4)_3P$ (Pressure Chemical), and Me_2PhP (Aldrich), were used as received.

1,3-Diphenylguanidine $((PhNH)_2CNH$, hereafter referred to as DPG) was available as a primary standard from GFS Chemicals. The compound was dried in an oven at $110^\circ C$ for 3 to 6 h, then stored in a desiccator over P_2O_5 .

Preparation and Standardization of Acid Solutions

A volume of acid (CF_3SO_3H or CF_3CO_2H) corresponding to approximately 10 mmol was added directly to 100 mL of freshly distilled DCE with use of the graduated acid reservoir. After mixing, 50 mL of solution was transferred via Teflon cannula to a titration buret under N_2 . The acid solution was then standardized by titration against a DCE solution of DPG (~1.5 mmol) in air, using bromophenol blue as indicator.¹⁶ This procedure generally gave concentrations reproducible to $\pm 0.2\%$.

Apparatus

The protonation enthalpies were measured with a Tronac Model 458 isoperibol calorimeter equipped with a motor-driven (4 rpm) buret for delivery of titrant. A 50 mL silvered Dewar flask was used as the reaction vessel. Thermistor output was recorded with an Apple II+

computer using the ADALAB instrument interface card (Interactive Microwave, Inc.). Operation of the system was checked by measuring the heat of protonation of tris(hydroxymethyl)aminomethane (THAM) with aq. HCl. Our value of $-11.2 \pm 0.3 \text{ kcal mol}^{-1}$ is in good agreement with the literature value of -11.33 .¹⁷

Experimental Procedure

Glassware was dried in an oven at 140°C for at least 4 h and allowed to cool in a desiccator over P_2O_5 . The Dewar flask and buret plunger were also stored in a P_2O_5 -dried desiccator for at least 12 h before a sequence of runs; the Dewar flask was returned to the desiccator between runs.

In a typical experiment, a solution of $\text{CF}_3\text{SO}_3\text{H}$ in DCE (generally near 0.1 M) was loaded into the calorimeter buret (2 mL capacity) with use of a Teflon tube. The empty Dewar flask was then attached to the calorimeter's insert assembly, and the insert was lowered into the 25.0°C bath. The reaction vessel was flushed with Ar for 20-40 min. A 5 ml aliquot of a freshly prepared solution of the phosphine in DCE (approximately 0.033 M) was injected into the reaction vessel via syringe, followed by 45 mL of DCE. The phosphine was kept in slight excess (approximately 10%) of the total amount of acid to be added. The temperature of the reaction vessel contents was adjusted to give a voltage reading below the set point of 0.00 mV (25.0°C) by electrical heating with the calibration heater or cooling with a flow of Ar. The starting point of each experiment was chosen so that the mid-point of the titration curve would coincide as nearly as possible with the thermistor set-point. This minimizes errors due to differences in titrant/titrate temperatures during an experiment.

Each run consists of an initial heat capacity determination, titration, and final heat capacity determination, each preceded by a baseline acquisition period. Heat capacities were evaluated by resistance heating. Titrations were generally set for 3 to 3.5 min at a buret delivery rate of $0.398 \pm 0.001 \text{ mL min}^{-1}$. Tronac specifications list a typical instrument sensitivity of $35 \text{ mV } ^\circ\text{C}^{-1}$. The recorded voltages for the experiments generally spanned about 15 mV, so the overall temperature change during each run was approximately 0.4°C , and the temperature change during titration was less than 0.2°C .

The thermistor output voltages were recorded at the rate of 1 s^{-1} . The voltage/time data were stored on diskette for each run. The data were then analyzed by linear regression for each segment of the experiment: calculated slopes (corrected for baseline heat effects) and intersection points were used to determine heat capacities and total reaction heat, using the general method outlined by Eatough et al.¹⁷ The reaction enthalpies were corrected for the heat of dilution of the acid solution with DCE, resulting in the values of ΔH_{HP} . Four experimental runs were used to determine ΔH_{HP} for all phosphines except Ph_3P (5 runs), $(t\text{-Bu})_3\text{P}$ (5 runs), and $(c\text{-C}_6\text{H}_{11})_3\text{P}$ (3 runs).

Measurement of the heat of dilution was complicated by interference from protonation of traces of H_2O in the titrate vessel. This interference could not be eliminated, but was minimized by rinsing the Dewar flask with anhydrous Et_2O , flushing with Ar for 10 min, then leaving the Dewar in a P_2O_5 -dried dessicator for 4 h. This procedure allowed determination of the dilution heat by extrapolation of the data from the

final one-third of the titration segment, giving a value of $-0.32 \text{ kcal mol}^{-1}$.

In some ΔH_{HP} runs, a slight depression of reaction heat was noted at the beginning of the titration segment. This randomly observed depression was most likely due to traces of H_2O in the titrant delivery tube which converted some of the CF_3SO_3H in the first titrant portion to the weaker acid, $(H_3O)(O_3SCF_3)$. In these instances, the first one-third of the titration data were neglected in the ΔH_{HP} calculation.

RESULTS

The enthalpies of protonation determined for 12 common phosphine ligands are listed in Table 2.1. The error limits represent the average deviation from the mean of the experimental runs for the phosphines. The titration curves of the phosphines listed exhibited no evidence of incomplete reaction. Neat $\text{CF}_3\text{SO}_3\text{H}$ is one of the strongest acids known,¹⁸ and the titration behavior observed in this study indicates that a 0.1 M solution of $\text{CF}_3\text{SO}_3\text{H}$ in DCE is a strongly acidic medium as well, completely protonating even the weak base $(p\text{-ClC}_6\text{H}_4)_3\text{P}$ ($\text{pK}_a = 1.03$). The ΔH_{HP} values have been corrected for the heat of dilution of the acid solution, which was found to be $-0.32 \text{ kcal mol}^{-1}$ for a 0.1011 M solution. As the range of acid concentrations varied only from 0.0951 to 0.1148 M, we consider a correction of $0.3 \text{ kcal mol}^{-1}$ valid for all of the experimental runs with $\text{CF}_3\text{SO}_3\text{H}$ in DCE.

Our reference base for the evaluation of the solvent/acid system was DPG ($\text{pK}_a = 10.1$),¹⁹ and its protonation enthalpy with $\text{CF}_3\text{SO}_3\text{H}$ was found to be $-37.2 \pm 0.4 \text{ kcal mol}^{-1}$. To compare the strength of $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{CO}_2\text{H}$, the protonation enthalpies of DPG and Et_3P were also determined with the latter acid. The values obtained (corrected for the heat of dilution of 0.1 M $\text{CF}_3\text{CO}_2\text{H}$, $0.3 \text{ kcal mol}^{-1}$) were $-23.5 \pm 0.3 \text{ kcal mol}^{-1}$ for DPG and $-12.9 \pm 0.1 \text{ kcal mol}^{-1}$ for Et_3P , both substantially less exothermic ($> 10 \text{ kcal mol}^{-1}$) than the ΔH values with the stronger acid $\text{CF}_3\text{SO}_3\text{H}$.

For some of the compounds studied, there was evidence of heat contributions from other reactions. The experimental data for $(t\text{-Bu})_3\text{P}$

Table 2.1. ΔH_{HP} and pK_a (aq.) values for tertiary phosphines

	PR_3	$-\Delta H_{HP}$ (kcal mol ⁻¹) ^a	pK_a
1	(p-ClC ₆ H ₄) ₃ P	17.9 (0.2) ^b	1.03 ^c
2	(p-FC ₆ H ₄) ₃ P	19.6 (0.2)	1.97 ^c
3	Ph ₃ P	21.2 (0.1)	2.73 ^d
4	(o-MeC ₆ H ₄) ₃ P	22.6 (0.2)	3.08 ^c
5	(p-MeC ₆ H ₄) ₃ P	23.2 (0.3)	3.84 ^c
6	(p-MeOC ₆ H ₄) ₃ P	24.1 (0.2)	4.57 ^c
7	MePh ₂ P	24.7 (0.0)	4.59 ^e
8	Me ₂ PhP	28.4 (0.2)	6.50 ^d
9	Me ₃ P	31.6 (0.2)	8.65 ^d
10	(c-C ₆ H ₁₁) ₃ P	33.2 (0.4)	9.70 ^d
11	Et ₃ P	33.7 (0.3)	8.69 ^d
12	(t-Bu) ₃ P	36.6 (0.3)	11.4 ^c

^aFor protonation with CF₃SO₃H in DCE solvent at 25.0°C.

^bNumbers in parentheses are average deviations.

^cReference 11.

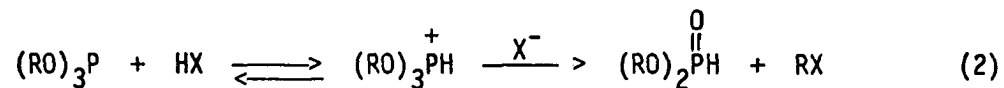
^dReference 9.

^eReference 3a.

show a roughly 2-fold increase in slope for the baseline preceding and following titration, when compared to runs for the other phosphines in Table 2.1. This could be attributed to oxidation of the extremely air-sensitive $(t\text{-Bu})_3\text{P}$ by adventitious oxygen, and would be expected to contribute to the overall heat of reaction. However, since the side reaction appears to proceed to the same extent before and after titration, the heat of this reaction will be subtracted from the ΔH_{HP} value by normal baseline correction. This, coupled with the observation that the increase in baseline slope is only 3% of the titration slope, leads us to believe that the ΔH_{HP} for $(t\text{-Bu})_3\text{P}$ is reliable.

For other compounds where side reactions were evident, ΔH_{HP} measurements were not judged to be as reliable. The phosphine $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{P}$ did not exhibit clean protonation; a highly exothermic secondary reaction was apparent after addition of the acid, making estimation of ΔH_{HP} impossible. The data for the phosphite $(i\text{-PrO})_3\text{P}$ revealed an endothermic process after titration. Calculation of ΔH_{HP} in the normal manner gives a value of $-23.6 \text{ kcal mol}^{-1}$, a reasonable value based on the reported $\text{p}K_{\text{a}}$ of 4.08^{3b} (see Discussion for relation of ΔH_{HP} to $\text{p}K_{\text{a}}$). However, the observed decrease in baseline slope amounts to 12% of the titration slope, so the actual ΔH_{HP} could be 2-3 kcal mol^{-1} more exothermic. The reverse behavior is noted for $(\text{MeO})_3\text{P}$, with an exothermic secondary process occurring after addition of acid. Analysis of the baseline slopes suggests that the actual ΔH_{HP} could be 2-3 kcal mol^{-1} less exothermic than the measured value of $-21.3 \text{ kcal mol}^{-1}$. Side reactions in the protonation of alkyl phosphites are well-known, with acids reacting to give dialkylphosphonates

as shown in eq. 2.²⁰ We suspect that the complications noted for (i-PrO)₃P and (MeO)₃P arise from this type of reaction.

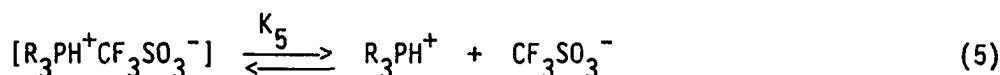
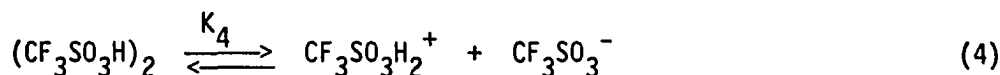


The phosphite (PhO)₃P exhibits different behavior, with normal baseline slopes but an exothermic jump at the beginning of the titration, occurring to a different degree in 3 runs. We suspect that, as in the dilution studies, H₂O in the titrate causes the deviations. Analysis of the second half of the titration data gives a consistent value of $\Delta H_{HP} = -7.25 \pm 0.08$, however, as some other reaction may be causing the deviation, this value should not be considered definitive.

DISCUSSION

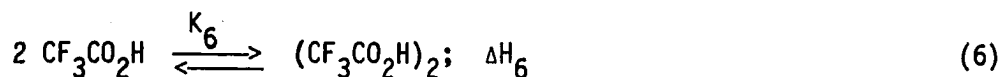
Evaluation of Possible Errors in the Interpretation of ΔH_{HP} Values

Although the heat of protonation (ΔH_{HP}) of phosphines has been discussed in terms of the reaction shown in eq. 1, one needs to consider the possibility that other processes (such as the reactions in equations 3-5) may contribute to ΔH_{HP} . Equations 3 and 4 describe the dimerization



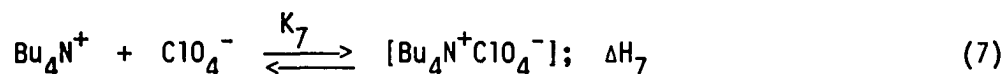
and autoprotolysis of $\text{CF}_3\text{SO}_3\text{H}$, and eq. 5 the dissociation of phosphonium triflate ion pairs. Thermodynamic data for these reactions in DCE have not been reported. However, estimates of their contributions to ΔH_{HP} can be made from data on related systems.

The reactions shown in equations 3 and 4 have been studied by means of conductivity measurements in CH_2Cl_2 .²¹ The overall equilibrium constant, K_3K_4 , was found to be 9×10^{-8} at -15°C . The authors estimate K_3 to be between 1 and 0.01, so K_4 should be no larger than 10^{-5} . Assuming similar values for K_3 and K_4 in DCE, only dimerization need be considered at the total acid concentrations typical of the ΔH_{HP} runs. It is perhaps more instructive at this point to consider the dimerization of $\text{CF}_3\text{CO}_2\text{H}$ (eq. 6), for which thermodynamic data in DCE are known ($K_6 = 1.5$ 1



mol^{-1} ; $\Delta H_6 = -7 \text{ kcal mol}^{-1}$)²². At a total acid concentration of $3 \times 10^{-3} \text{ M}$ (a typical value after dilution of the original 0.1 M solution in the ΔH_{HP} studies), the concentration of $(\text{CF}_3\text{CO}_2\text{H})_2$ is $2.2 \times 10^{-5} \text{ M}$. The heat required to dissociate this quantity of dimer is $0.05 \text{ kcal mol}^{-1}$. From the estimated K_3 noted above, the concentration of $(\text{CF}_3\text{SO}_3\text{H})_2$ can be assumed to be near or less than that determined for $(\text{CF}_3\text{CO}_2\text{H})_2$. From studies of carboxylic acid association in aprotic solvents, there is a rough correlation of less exothermic association enthalpies with increasing acidity.²³ The association enthalpy of $\text{CF}_3\text{SO}_3\text{H}$ would thus be expected to be less than that of $\text{CF}_3\text{CO}_2\text{H}$, and the heat associated with dimer dissociation in $3 \times 10^{-3} \text{ M}$ $\text{CF}_3\text{SO}_3\text{H}$ in DCE should be less than $0.05 \text{ kcal mol}^{-1}$. This contribution is less than 0.2% of most ΔH_{HP} values and, therefore, is negligible, according to these estimates.

The enthalpy contribution of the ion-pair dissociation (eq. 5) can be estimated from data available for $[(n\text{-Bu})_4\text{N}](\text{ClO}_4)$ in DCE (eq. 7) with $K_7 = 6.41 \times 10^3 \text{ l mol}^{-1}$ ²⁴ and $\Delta H_7 = 1.3 \text{ kcal mol}^{-1}$ (calculated from data



of Abraham et al.)²⁵ At a total salt concentration of $3 \times 10^{-3} \text{ M}$ (approximately the final concentration in the ΔH_{HP} experiments), 20% of the salt is dissociated, and the heat evolved in this process is -0.26

kcal mol⁻¹. The (n-Bu)₄N⁺ ion should be similar in size to most of the phosphonium ions produced in this study, and there is evidence that R₃PH⁺ species do not form strong hydrogen bonds²⁶ (CF₃SO₃⁻ is likewise a poor hydrogen bond acceptor²⁷), so the heat contribution due to ion-pair dissociation in the present study should be of comparable magnitude to -0.26 kcal mol⁻¹. In addition, the total heat of solution of [(n-Bu)₄N](ClO₄) at 2.5 x 10⁻³ M in DCE is only -0.45 kcal mol⁻¹.²⁵ If ΔH_{solution} were comparably small for the phosphonium triflates in eq 1, the heat contributions from all solvent interactions with the product salt would be less than 2% of the ΔH_{HP} values.

Thus, the measured ΔH_{HP} values predominantly represent the heat evolved when R₃P reacts with monomeric CF₃SO₃H to form the R₃PH⁺CF₃SO₃⁻ ion pair, with only minor contributions from acid dimerization and ion-pair dissociation.

General Trends in ΔH_{HP}

As expected, the ΔH_{HP} values in Table 1 become more exothermic as electron donating substituents are substituted on phosphorus; thus, the trialkylphosphines give ΔH_{HP}'s approximately 10 kcal mol⁻¹ more negative than those of the triarylphosphines. The series Me_xPh_{3-x}P shows a very consistent increase in basicity as methyl replaces phenyl, with differences of 3.2, 3.7, and 3.5 kcal mole noted between the respective pairs Me₃P-Me₂PhP, Me₂PhP-MePh₂P, and MePh₂P-Ph₃P. The change on substitution thus appears to be additive, and, unless steric properties (such as C-P-C angles) vary regularly through this series, the ΔH_{HP} differences should be due to electronic rather than steric factors (the

cone angles do not show regular variation, with differences of 4, 14, and 9°, respectively, for the above pairs, suggesting that the ΔH_{HP} differences in the $Me_xPh_{3-x}P$ series are indeed not due to steric effects).

Consistent differences in ΔH_{HP} are also noted in the isosteric series $(p-XC_6H_4)_3P$ ($X = Cl, F, H, Me, MeO$) (Table 2.1). The ΔH_{HP} values give an excellent correlation with Hammett σ_{para} substituent parameters²⁸ (r , the correlation coefficient, is 0.992), with $-\Delta H_{HP}$ decreasing in the order $X = MeO > Me > H > F > Cl$ (Fig. 2.1).

Comparison of ΔH_{HP} with Other Protonic Basicity Measures

The ΔH_{HP} values show a strong linear correlation with the reported pK_a 's (from the half-neutralization potentials (ΔHNP 's) in CH_3NO_2 noted previously), as seen in the plot of $-\Delta H_{HP}$ vs. pK_a (Fig. 2.2). Linear least-squares regression gives eq. 8 as the best fit for the data

$$-\Delta H_{HP} = 1.82 pK_a + 16.3 \text{ (kcal mol}^{-1}\text{)} \quad (8)$$

($r = 0.994$). The most significant deviation from the correlation is observed for Et_3P ($pK_a = 8.69$), whose ΔH_{HP} value of $-33.7 \text{ kcal mol}^{-1}$ indicates a difference of $1.6 \text{ kcal mol}^{-1}$ (more exothermic) from the best fit line. The origin of this deviation is not entirely clear; however, it is possible that the original pK_a value for this phosphine is slightly in error. Streuli measured the pK_a 's of several phosphines by extrapolation of data from titrations in aqueous $MeOH$,⁹ and these were compared to values obtained from the ΔHNP method. The differences in pK_a were 0.2 pK units or less for the tertiary phosphines studied, except for Et_3P , where

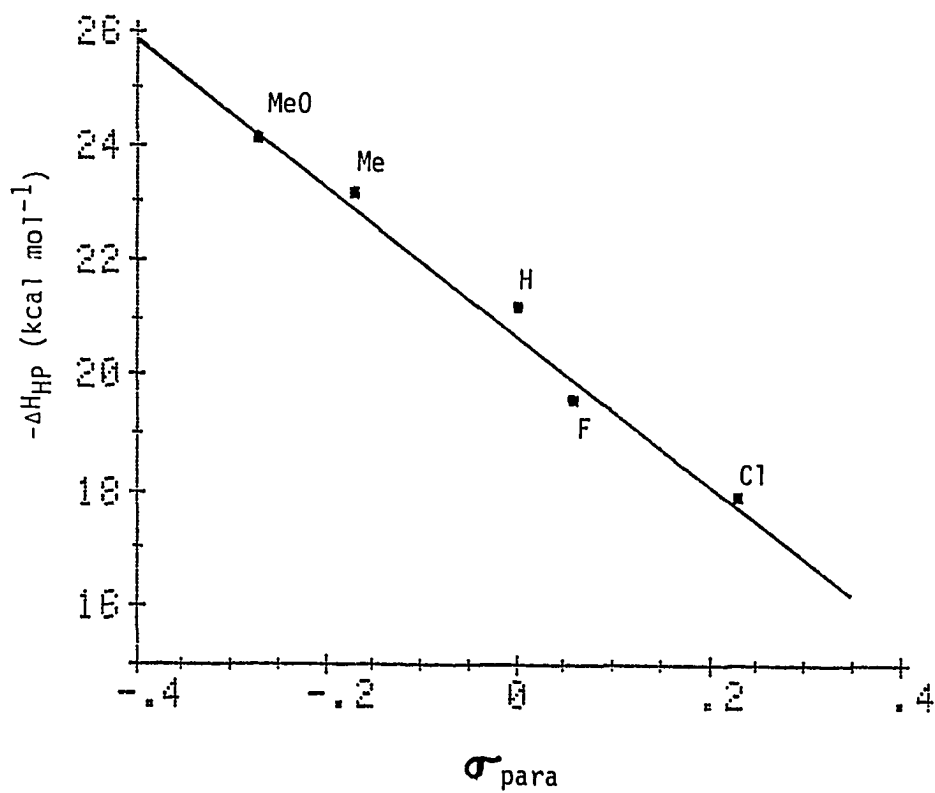


Figure 2.1. Plot of $-\Delta H_{\text{HP}}$ (at 25.0°C in DCE) vs. Hammett σ_{para} parameters for the series $(p\text{-XC}_6\text{H}_4)_3\text{P}$

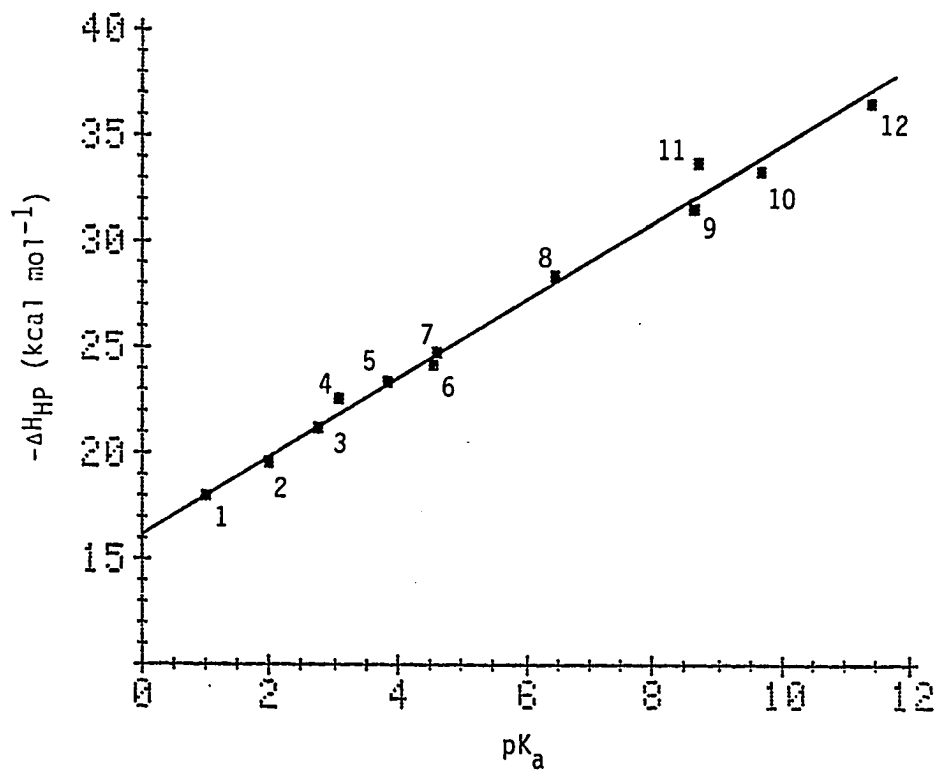


Figure 2.2. Plot of $-\Delta H_{HP}$ in DCE vs. pK_a 's from ΔH_{NP} measurements in CH_3NO_2 . Numbers refer to Table 2.1

the pK_a from aqueous MeOH data was 9.10 (a difference of 0.41). This higher pK_a value is in better accord with the ΔH_{HP} value.

Considering the vastly different properties of the solvents employed in the ΔH_{HP} and pK_a determinations, it is perhaps surprising that the values correlate so well. Other linear ΔH - ΔG relationships have been noted for protonation enthalpies of amines and pyridines in organic solvents with aqueous pK_a 's.²⁹ In Arnett's study of amine protonation in FSO_3H and H_2SO_4 ,^{29b} the conditions leading to such relationships are clearly discussed. In these protonations, free energy changes ($\Delta\Delta G$) for a series of compounds in one solvent (CH_3NO_2) may be proportional to enthalpy changes ($\Delta\Delta H$) in another (DCE), provided $\Delta\Delta G_{CH_3NO_2}$ is proportional to $\Delta\Delta G_{DCE}$ and $\Delta\Delta S_{DCE}$ is either proportional to $\Delta\Delta H_{DCE}$ or equal to 0. However, from the available data, it is not possible to say which condition is satisfied for the correlation between ΔH_{HP} and pK_a .

Arnett's calorimetric studies of N-donor molecules in neat FSO_3H have been extended to cover O-, S-, and a few P-donor bases,^{26,30} with a linear correlation ($r = 0.986$) observed between ΔH_i (defined as the difference between ΔH of solution in FSO_3H and ΔH of solution in an inert solvent, such as CCl_4) and aqueous pK_a 's for over 50 bases (eq. 9). The similarity

$$-\Delta H_i = 1.77 pK_a + 28.1 \text{ (kcal mol}^{-1}\text{)} \quad (9)$$

of the slopes for equations 8 and 9 is perhaps fortuitous, but a comparison of the intercepts clearly shows that neat FSO_3H is a stronger protonating medium than CF_3SO_3H in DCE. This increased strength is also

evident in the ΔH_i values of the two tertiary phosphines, Ph_3P ^{29b} and Me_3P ,²⁶ included in Arnett's studies. The ΔH_i values for Ph_3P and Me_3P are -28.7 and -44.6 kcal mol⁻¹, respectively (compare with $\Delta H_{\text{HP}} = -21.2$ kcal mol⁻¹ for Ph_3P and $\Delta H_{\text{HP}} = -31.6$ kcal mol⁻¹ for Me_3P (Table 2.1)). The difference in ΔH_i for Ph_3P and Me_3P (15.9 kcal mol⁻¹) suggests that the slope of a $-\Delta H_i$ vs $\text{p}K_a$ plot for phosphines will be different (larger) than the value of 1.77 observed for other bases (eq. 9). Arnett et al.³⁰ have noted that particular classes of compounds would probably show deviations from eq. 9 if more data were available; this appears to be true for the tertiary phosphines. A similar variation in basicity relationships between types of bases is noted in the comparison of protonation enthalpies in $\text{CF}_3\text{CO}_2\text{H}/\text{DCE}$ with ΔH_{HP} values in $\text{CF}_3\text{SO}_3\text{H}/\text{DCE}$. The enthalpies obtained in this study (in kcal mol⁻¹) are -33.7 ($\text{CF}_3\text{SO}_3\text{H}$) and -12.9 ($\text{CF}_3\text{CO}_2\text{H}$) for Et_3P , and -37.3 ($\text{CF}_3\text{SO}_3\text{H}$) and -23.2 ($\text{CF}_3\text{CO}_2\text{H}$) for $(\text{PhNH})_2\text{CNH}$ (DPG). The difference between enthalpies measured with the two acids (14.1 kcal mol⁻¹ for DPG, 20.8 kcal mol⁻¹ for Et_3P) shows a sizeable change in acid strength on going from $\text{CF}_3\text{SO}_3\text{H}$ to $\text{CF}_3\text{CO}_2\text{H}$. These differences also indicate that the relationship between protonation enthalpies measured with $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{CO}_2\text{H}$ will not be the same for N- and P-donor bases.

As noted in the Introduction, basicity trends of phosphines in the gas phase are, in some cases, in contrast to trends observed in solution. Table 2.2 lists gas phase proton affinities and ΔH_{HP} values (from Table 2.1) for Ph_3P , MePh_2P , Me_2PhP , and Me_3P . The gas phase values are in the opposite order of $-\Delta H_{\text{HP}}$ and $\text{p}K_a$, with Me_3P exhibiting the

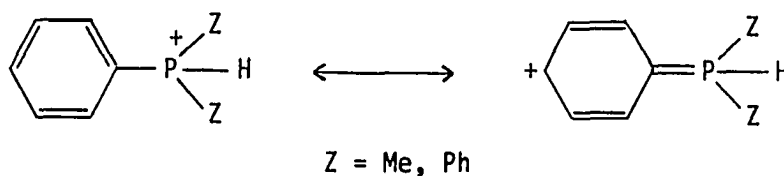
Table 2.2. Gas phase proton affinities and solution ΔH_{HP} 's for the series $\text{Me}_x\text{Ph}_{3-x}\text{P}$

R_3P	PA (kcal mol^{-1}) ^a	$-\Delta H_{HP}$ (kcal mol^{-1}) ^b
Ph_3P	226.7	21.2
MePh_2P	226.7	24.7
Me_2PhP	226.0	28.4
Me_3P	223.5	31.6

^aReference 7d. Estimated errors are $\pm 0.2 \text{ kcal mol}^{-1}$ except for Ph_3P , where the error is $> \pm 0.2 \text{ kcal mol}^{-1}$.

^bThis work is in DCE solvent.

lowest proton affinity. The gas phase basicities also run counter to the results of several reactivity studies of phosphine complexes, where data are successfully analyzed using the solution basicities as a measure of σ -bonding ability.³ One of the arguments made in explaining the gas phase proton affinity order was that phenyl-substituted phosphonium ions could be stabilized by aryl π - to phosphorus d -donation, as depicted in Scheme I. However, there is no conclusive evidence for such a π -bonding



Scheme I

interaction. As mentioned above, the correlation of ΔH_{HP} with σ_{para} is excellent; but a poor correlation ($r = 0.887$) is found between ΔH_{HP} and σ^+ parameters²⁸ (these measure the effect of resonance donor substituents in direct conjugation with the reaction center, as would be the case in Scheme I). This indicates that the phenyl ring π -system does not interact significantly with the phosphorus d -orbitals in the phosphonium ion. A similar conclusion was reached in a photoelectron spectroscopy study of para-substituted triarylphosphines.³¹ In light of these results, a re-evaluation of the factors leading to the reversal of the solution basicity order for the series $Me_xPh_{3-x}P$ in the gas phase may be warranted.

Correlations of ΔH_{HP} with Taft σ^* and Kabachnik σ^{ph} Parameters

The pK_a 's of phosphines were originally shown to be linearly related to Taft's σ^* parameters,³² with a different line (of approximately equal slope) for tertiary, secondary, and primary phosphines.¹⁰ A set of substituent parameters was later developed specifically for groups bound to phosphorus.³³ These constants, denoted σ^{ph} , were applied to the phosphine pK_a data, giving a linear correlation for all three phosphine classes on the same line, with a higher correlation coefficient. As the σ^{ph} parameters could have useful predictive value if they are truly superior to σ^* for substituents bound to phosphorus, correlations with ΔH_{HP} values were tested for both sets of parameters. The results are given in eqs. 10 and 11. For the tertiary phosphines examined σ^{ph} gives no better fit than σ^* . In fact, the data in the σ^{ph} correlation

$$-\Delta H_{HP} = - 5.83 \Sigma \sigma^* + 31.1 \text{ (kcal mol}^{-1}\text{)} \quad (10)$$

(r = 0.966, 8 data points)

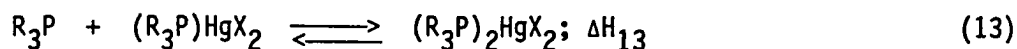
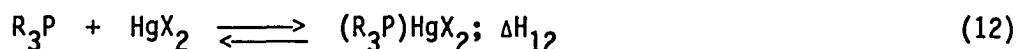
$$-\Delta H_{HP} = - 5.44 \Sigma \sigma^{ph} + 13.4 \text{ (kcal mol}^{-1}\text{)} \quad (11)$$

(r = 0.961, 11 data points)

show somewhat random deviations, but only one point (for $(p\text{-MeOC}_6\text{H}_4)_3\text{P}$) in the σ^* correlation is significantly out of line. Thus, for tertiary phosphines such as those used in the present study, σ^{ph} does not appear to offer better predictive ability than σ^* .

Correlation of ΔH_{HP} with ΔH of $R_3P-HgCl_2$ Adduct Formation

Enthalpies for the reactions of phosphines with Lewis acids may serve as measures of phosphine σ -donor ability. The stepwise reactions (eqs. 12 and 13) of phosphines with mercury dihalides in benzene solution have been studied by calorimetry.⁵ Heats of the respective reactions are plotted



vs. ΔH_{HP} in Figure 2.3. For ΔH_{12} vs. ΔH_{HP} , linear regression shows a fair correlation ($r = 0.977$) for the 5 phosphines (ΔH_{HP} for $(n-Bu)_3P$ estimated from eq. 8), but $(c-C_6H_{11})_3P$ is obviously out of line. The correlation with the point for $(c-C_6H_{11})_3P$ removed is practically perfect ($r = 1.000$). The deviation of $(c-C_6H_{11})_3P$ can be attributed to specific steric hindrance ($\theta = 170^\circ$ for this phosphine)^{1d} to adduct formation (there may also be some contribution from a repulsive π -interaction between $(c-C_6H_{11})_3P$ (which can act as a π -donor)³ and the filled d orbitals of $HgCl_2$). The values of ΔH_{13} are not correlated well with ΔH_{HP} 's ($r = 0.910$). For this reaction, steric effects would be expected to be more important; this, coupled with the now variable electronic properties of the acceptor, $(R_3P)HgCl_2$, eliminates any expectation of a linear correlation with ΔH_{HP} .

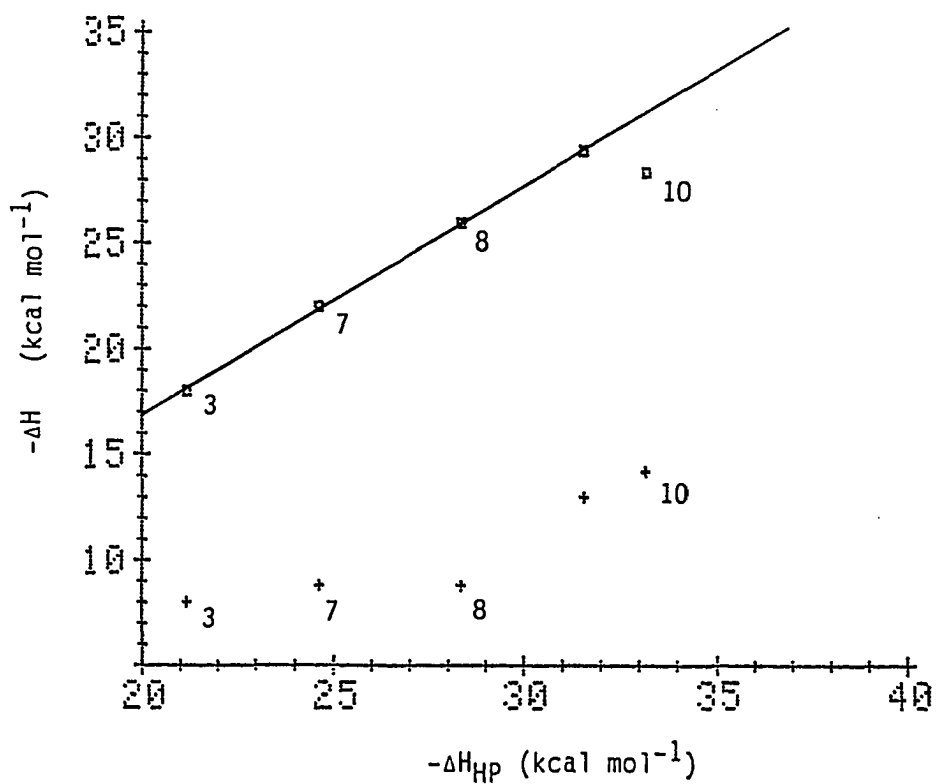


Figure 2.3. Plot of $-\Delta H_{12}$ (squares) for reaction of R_3P with $HgCl_2$ in C_6H_6 and $-\Delta H_{13}$ (crosses) for reaction of R_3P with $(R_3P)HgCl_2$ in C_6H_6 vs. $-\Delta H_{HP}$ for R_3P . Numbers refer to Table 2.1, points not numbered are for $(n-Bu)_3P$

CONCLUSION

The present study demonstrates that protonation enthalpies (ΔH_{HP} 's, determined by calorimetric titration with CF_3SO_3H in DCE) are valid and consistent measures of phosphine basicity and are directly related to the electron donating ability of phosphines in other solution media. The protonation reactions are highly exothermic ($-\Delta H_{HP} \geq 18 \text{ kcal mol}^{-1}$ for the phosphines studied); thus, errors due to secondary reactions (such as acid dimerization or ion pair dissociation) are not significant in the ΔH_{HP} measurements. The method described also offers the ability to measure basicity for a wide range of base strengths under the same conditions. The ΔH_{HP} values should prove to be extremely useful tools for investigations of reactivity in transition metal chemistry; such studies aimed at determining the relationship between phosphine and metal-phosphine complex basicity are in progress in our laboratories.

REFERENCES

1. a) Strohmeier, W.; Müller, F.-J. Chem. Ber. 1967, 100, 2812.
b) Tolman, C. A. J. Am. Chem. Soc. 1970, 92, 2953.
c) Tolman, C. A. J. Am. Chem. Soc. 1970, 92, 2956.
d) Tolman, C. A. Chem. Rev. 1977, 77, 313.
2. a) Burke, N. E.; Singhal, A.; Hintz, M. J.; Leg, J. A.; Hui, H.; Smith, L. R.; Blake, D. M. J. Am. Chem. Soc. 1979, 101, 74.
b) Schenkluhn, H.; Scheidt, W.; Weimann, B.; Zähres, M. Angew. Chem., Int. Ed. Engl. 1979, 18, 401.
c) Nolan, S. P.; Hoff, C. D. J. Organomet. Chem. 1985, 290, 365.
d) See references cited in 3a.
3. a) Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. Organometallics 1985, 4, 1981.
b) Rahman, Md. M.; Hong, Y. L.; Prock, A.; Giering, W. P. Organometallics 1987, 6, 650.
4. a) Stone, F. G. A. Chem. Rev. 1958, 58, 101.
b) Graham, W. A. G.; Stone, F. G. A. J. Inorg. Nuc. Chem. 1956, 3, 164.
5. a) Farhangi, Y.; Graddon, D. P. Aust. J. Chem. 1973, 26, 983.
b) Gallagher, M. J.; Graddon, D. P.; Sheikh, A. R. Aust. J. Chem. 1976, 29, 759.
6. Hultén, F.; Persson, I. Inorg. Chim. Acta 1987, 128, 43.
7. a) Holtz, D.; Beauchamp, J. L.; Euler, J. R. J. Am. Chem. Soc. 1970, 92, 7045.

- b) McDaniel, D. H.; Coffman, N. B.; Strong, J. M. J. Am. Chem. Soc. **1970**, 92, 6697.
- c) Staley, R. H.; Beauchamp, J. L. J. Am. Chem. Soc. **1974**, 96, 6252.
- d) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddenphatt, R. J. J. Am. Chem. Soc. **1982**, 104, 5899.
8. a) Davies, W. C.; Addis, H. W. J. Chem. Soc. **1937**, 1622.
b) Goetz, H.; Sidhu, A. Justus Liebigs Ann. Chem. **1965**, 682, 71.
9. Streuli, C. A. Anal. Chem. **1960**, 32, 985.
10. Henderson, W. A.; Streuli, C. A. J. Am. Chem. Soc. **1960**, 82, 5791.
11. Allman, T.; Goel, R. G. Can. J. Chem. **1982**, 60, 716.
12. For a few examples, see a) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. J. Chem. Soc. **1962**, 3653.
b) Laing, K. R.; Roper, W. R. J. Chem. Soc., A **1969**, 1889.
c) Collman, J. P.; Vastine, F. D.; Roper, W. R. J. Am. Chem. Soc. **1968**, 90, 2282.
d) Oliver, A. J.; Graham, W. A. G. Inorg. Chem. **1970**, 9, 2653.
e) Arabi, M. S.; Mathieu, R.; Poilblanc, R. J. Organomet. Chem. **1976**, 104, 323.
f) Werner, R.; Werner, H. Chem. Ber. **1982**, 115, 3781.
g) Werner, H.; Gotzig, J. Organometallics **1986**, 5, 1337.
h) Hommeltoft, S. I.; Baird, M. C. Organometallics **1986**, 5, 190.
13. Activated by heating at 350°C for 12 h under vacuum.
14. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; 2nd ed.; Pergamon: New York, 1980.

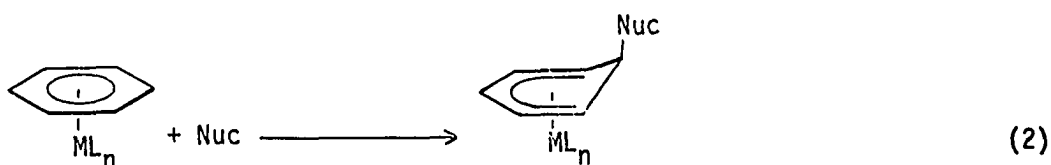
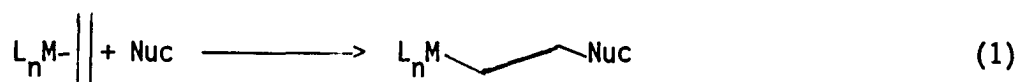
15. Isslieb, K.; Brack, A. Z. Anorg. Allg. Chem. 1954, 277, 258.
16. Huber, W. "Titrations in Nonaqueous Solvents"; Academic Press: New York, 1967.
17. Eatough, D. J.; Christensen, J. J.; Izatt, R. M. "Experiments in Thermometric and Titration Calorimetry"; Brigham Young University Press: Provo, Utah, 1974.
18. Howells, R. D.; McCown, J. D. Chem. Rev. 1977, 77, 69.
19. Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965.
20. a) Weiss, R.; Vande Griend, L. J.; Verkade, J. G. J. Org. Chem. 1979, 44, 1860.
b) Olah, G. A.; McFarland, C. W. J. Org. Chem. 1971, 36, 1374.
21. Chmelir, M.; Cardona, N.; Schulz, G. V. Makromol. Chem. 1977, 178, 169.
22. Milne, J. B. in "The Chemistry of Nonaqueous Solvents", Lagowski, J. J., Ed.; Academic Press: New York, 1978; Vol. VB; p. 1.
23. Davis, M. M. "Acid-Base Behavior in Aprotic Solvents"; NBS Monograph 105; U.S. Government Printing Office: Washington, D.C., 1968; p. 31.
24. Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc., Faraday Trans. 1 1976, 72, 955.
25. Abraham, M. H.; Danil de Namor, A. F.; Schulz, R. A. J. Solution Chem. 1976, 5, 529.
26. Arnett, E. M.; Wolf, J. F. J. Am. Chem. Soc. 1973, 95, 978.
27. Leucks, M.; Zundel, G. Can. J. Chem. 1980, 58, 311.

28. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; 2nd ed.; Harper and Row: New York, 1981.
29. a) Mead, T. E. J. Phys. Chem. 1962, 66, 2149.
b) Arnett, E. M.; Quirk, R. P.; Burke, J. J. J. Am. Chem. Soc. 1970, 92, 1260.
30. Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. J. Am. Chem. Soc. 1974, 96, 3875.
31. Weiner, M. A.; Lattman, M.; Grim, S. O. J. Org. Chem. 1975, 40, 1292.
32. Taft, R. W. in "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956, p. 556.
33. Kabachnik, M. I. Russian Chem. Rev. 1969, 38, 795.

SECTION 3. METAL CARBONYL $\nu(\text{CO})$ FORCE CONSTANTS AS PREDICTORS
OF π -ETHYLENE AND π -BENZENE COMPLEX REACTIVITY
WITH NUCLEOPHILES

INTRODUCTION

Nucleophilic attack on unsaturated hydrocarbons which are coordinated to transition metals has been studied extensively and continues to be a subject of considerable interest.¹ Two reactions of this type involving attack on π -ethylene and π -benzene ligands are shown in eqs. 1 and 2.

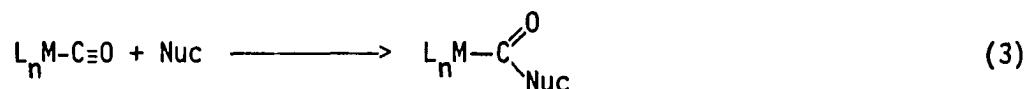


Such reactions are important in certain industrial processes, such as the Wacker acetaldehyde synthesis,² and are also useful in a variety of laboratory scale syntheses.³ In attempts to understand better the reactivities of unsaturated ligands in these complexes, several theoretical studies have been carried out. Through the application of simple Hückel MO theory, Davies, Green, and Mingos^{1b} developed a useful qualitative scheme for predicting the site of attack on organotransition metal cations containing unsaturated hydrocarbon ligands; however, their approach was not designed to determine which complexes were susceptible to attack and which were not. Their simple set of rules has been successfully applied, though not without exception, to a number of organometallic reactions. Several researchers have also applied more quantitative MO techniques to explore the factors which contribute to the

activation of alkenes, arenes, and other unsaturated hydrocarbon ligands in various organometallic complexes.⁴

An empirical correlation of reactivity with some readily obtainable experimental quantity would be desirable, yet attempts to do this with various experimental observables have met with little success. For various benzene complexes, there is no useful correlation between ¹³C and ¹H NMR shifts of the arene ligand and its reactivity with nucleophiles.⁵ Similarly, there is no correlation with C(1s) energies from XPS measurements.⁵ However, a correlation has been noted between the reduction potentials and relative rates of phosphine attack on a series of π-hydrocarbon complexes,^{1c,5} but this type of electrochemical data is not routinely obtainable for many compounds. Kane-Maguire et al.^{1c} have also reported parameters, called electrophilic transferability (T_E) numbers, which reflect the activating ability of metal-ligand fragments bound to π-hydrocarbons. The T_E numbers are useful in predicting the reactivity of triene and dienyl complexes; however, values for only a few ML_n fragments are available.

Several years ago publications by Darensbourg and Darensbourg^{6a} and from this laboratory^{6b,c,d} reported correlations between C-O stretching force constants, k_{CO}, and the susceptibility of CO ligands to nucleophilic attack (eq. 3). This method was based on the assumption that k_{CO} is a



measure of the electron withdrawing ability of the ML_n metal-ligands

fragment: the higher k_{CO} , the more electron-withdrawing the ML_n unit. An electron-withdrawing ML_n group makes the CO carbon more positive and more susceptible to nucleophilic attack. Therefore, the higher k_{CO} , the more susceptible to nucleophilic attack is the CO carbon in the complex. It was found that primary alkyl amines react with CO groups having k_{CO} values greater than approximately 17.0 mdynes/Å; alkyl lithium reagents (LiR) react with CO ligands having k_{CO} values higher than 15.3 mdynes/Å.

In the present paper, k_{CO} values are used to measure the electron-withdrawing ability of the ML_n fragment in complexes with unsaturated hydrocarbon ligands. For example, the electron-withdrawing ability of the ML_n group in the π -ethylene complex $ML_n(C_2H_4)$ is measured by the k_{CO} value of the analogous CO complex, $ML_n(CO)$. As demonstrated in this paper, k_{CO} values are very useful for correlating a large number of literature reports of the reactivity or non-reactivity of π -ethylene and π -benzene complexes with various nucleophiles.

METHOD

Approach

As noted above, carbonyl stretching force constants, k_{CO} , have been used as an indicator of the positive charge on a CO carbon and the reactivity of a CO ligand with nucleophiles (eq. 3).⁶ MO calculations by Hall and Fenske⁷ have established that k_{CO} can be correlated with the carbonyl lone pair orbital and π^* -antibonding orbital occupations in several metal-carbonyl complexes. Increasing the σ -donor strength of CO results in an increase in k_{CO} and a decrease in electron density at the carbonyl carbon. A decrease in metal-to-carbonyl back-bonding has a similar effect. If one considers the Dewar-Chat model for a π -ethylene bond to a transition metal, the factors that increase positive charge on carbon in CO should also increase positive charge on carbon in ethylene; that is, increased σ -donation from ethylene and decreased back donation from the metal to the π^* -orbitals both decrease electron density at carbon, resulting in an increased positive charge. These parallels in bonding between CO and π -ethylene suggest that electronic changes in the ML_n group of $ML_n(C_2H_4)$ will be reflected in properties of the CO ligand in the analogous $ML_n(CO)$.

As noted in the Introduction (eq. 3), k_{CO} for the CO group in $ML_n(CO)$ has been used as a measure of the electron-withdrawing ability of the ML_n fragment. In this study, it is assumed that k_{CO} is also a measure of the electron-withdrawing ability of the ML_n group in the analogous $ML_n(C_2H_4)$ complex, and also that k_{CO} is a measure of the susceptibility of the ethylene to nucleophilic attack. Similarly, the k_{CO} of the 3 CO groups in

the complex, $ML_n(CO)_3$, is a measure of the electron-withdrawing ability of the ML_n group in the analogous $ML_n(C_6H_6)$ π -benzene complex.

EHMO calculations carried out by Eisenstein and Hoffmann^{4a} indicate that ethylene activation is not necessarily due to positive charge buildup on the carbon atoms. Some complexes for which they calculate negative charges on the ethylene carbons nevertheless undergo nucleophilic addition. They propose that the olefin is activated by a slippage toward an η^1 -configuration with concomitant enhancement of the LUMO coefficient on the carbon farthest from the metal. However, they also conclude that the more positively charged η^2 -olefins were more activated in the slipped configuration; thus the use of k_{CO} as a gauge of the relative activation of ethylene could still be valid. However, it should be noted that the present approach cannot and makes no attempt to address the question of whether nucleophilic addition reactions are charge or frontier orbital controlled. This study simply notes that $\nu(CO)$ force constants are useful predictors of π -ethylene and π -benzene reactivity with nucleophiles.

In this paper, the k_{CO} for CO group(s) replacing π -ethylene or π -benzene ligands is labelled k_{CO}^* . In the general case, k_{CO}^* is the average k_{CO} for the CO's replacing a π -hydrocarbon ligand maintaining the same formal electron count at the metal and occupying approximately the same coordination sites as the π -hydrocarbon. For ethylene complexes, k_{CO} and k_{CO}^* have the same value. For example, the k_{CO}^* value for $CpFe(CO)_2(C_2H_4)^+$ is equal to k_{CO} for the CO groups in $CpFe(CO)_3^+$. For benzene complexes, k_{CO}^* is an average of the three k_{CO} values. Thus, the k_{CO}^* value for $(C_6H_6)Mn(CO)_3^+$ ($C_6H_6 = \eta-C_6H_6$) is equal to the average k_{CO}

of the three fac CO groups in $\text{Mn}(\text{CO})_6^+$, which in this case are all equivalent. For complexes in which the CO groups are not equivalent, k_{CO}^* is the weighted average of the different k_{CO} values. An example of this situation is the complex fac- $\text{RuCl}_2(\text{PPh}_3)(\text{CO})_3$, which has two k_{CO} values, k_{CO}^1 (trans-Cl) and k_{CO}^2 (trans-PPh₃). The k_{CO}^* value for this complex is equal to $(2 k_{\text{CO}}^1 + k_{\text{CO}}^2)/3$.

Force Constants

Carbonyl stretching force constants were, wherever possible, either taken from the literature or calculated from literature IR data using approximate energy-factored force field methods, such as the Cotton-Kraihanzel (C-K) approximation.⁸ However, in many cases the IR spectrum of the desired carbonyl analog was unavailable. For these situations, the method outlined by Timney⁹ was employed to estimate force constants. This procedure is based on C-K force constants and involves calculating k_{CO} for the CO ligand in a complex $\text{ML}_n(\text{CO})$ using individual ligand and metal contributions. The formula used for these calculations (eq. 4) contains a parameter, k_d , that is dependent only on the number of valence d electrons

$$k_{\text{CO}} = k_d + \sum \epsilon_L^\theta + n\epsilon_C \quad (4)$$

of a transition metal in a particular row. The ligand effect constant, ϵ_L^θ , gives the contribution of a particular ligand in a given geometry. These constants are calculated from k_{CO} values in a series of complexes and are estimated to have standard deviations of up to ± 0.03 mdyne/Å. The factor $n\epsilon_C$ accounts for charge effects on k_{CO} (n =the net charge of the

species, $\epsilon_C = 197 \pm 10$ N/m). The formula is used as shown for pseudo-octahedral complexes and for other complexes with carbonyls and only one other type of ligand. Slight modifications are made for other situations.

An example of the use of this equation for $\text{fac-Ru(PMe}_3)_3(\text{CO})_3^{2+}$ is shown in eq. 5. Thus, k_{CO} for this compound is equal to 1824 N/m,

$$\begin{aligned} k_{\text{CO}} &= k_d + 2\epsilon_{\text{CO}}^{\text{cis}} + 2\epsilon_{\text{PMe}_3}^{\text{cis}} + \epsilon_{\text{PMe}_3}^{\text{trans}} + 2\epsilon_C & (5) \\ &= 1389 + 2(33.5) + 2(-27.7) + 29.8 + 2(197) = 1824 \text{ N/m} \end{aligned}$$

or 18.24 mdyne/Å. Timney has compiled a list of ligand effect constants for over 30 common ligands in different geometries. Others can be calculated by combining his formula with k_{CO} values calculated from IR data. Additional ϵ_L^θ values calculated for use in this study are $\epsilon_{\text{C}_6\text{H}_6} = 40$ N/m and $\epsilon_{\text{C}_5\text{Me}_5}^{\text{td}} = 86$ N/m.

Reaction Data

Information on reactions of π -coordinated hydrocarbon complexes was taken from the literature. In many cases, the adducts resulting from nucleophilic addition to the π -hydrocarbon were isolated and fully characterized. In others, the products were not isolable; then, reasonable spectral evidence for the formation of an adduct was considered sufficient. Some compounds are stated to undergo reactions other than addition to the π -hydrocarbon or they are reported to not react at all. This information is given in the Results and Discussion sections and listed in the tables.

This treatment assumes the mechanism of these reactions is direct nucleophilic addition to the coordinated hydrocarbon, and kinetic studies^{1c} indicate that this is the preferred mechanism in the overwhelming majority of such reactions. However, in a few cases the situation may be more complicated than this. Two modes of nucleophilic addition to Pt(II) and Pd(II) olefin complexes have been observed, direct attack on the olefin to give overall trans addition and initial attack on the metal followed by insertion to give overall cis addition. Recent results^{2,10} indicate that the direct attack mechanism occurs in the reactions of amines with Pd(II) olefin and Pt(II) olefin complexes. MO calculations by Bäckvall et al.^{4f} suggest that insertion of ethylene into the metal-nucleophile bond may occur for nucleophiles with high energy HOMO's (such as Me⁻), but is highly unfavorable for N- and O-donor nucleophiles with lower-lying HOMO's.

RESULTS

Results of the investigation are summarized in Tables 3.1 and 3.2 for ethylene and benzene, respectively. The compounds are listed in order of decreasing k_{CO}^* . References to $\nu(CO)$ data and reactions are also given in these tables. Nucleophiles which are reported to add to the arene or olefin are highlighted in bold type. Those nucleophiles given in regular type do not add to the hydrocarbon; either they react at another site in the complex, which is indicated by a superscript to a footnote, or they do not react at all, in which case there is no footnote superscript.

As will be discussed in greater detail in the next section, a given nucleophile adds to the ethylene (or benzene) ligand only when k_{CO}^* is above a certain value, which we call the threshold value. The threshold value (Table 3.3) is defined as the highest k_{CO}^* corresponding to a complex that was reported not to react with a specific nucleophile. Threshold k_{CO}^* values are for cases where no reaction of any kind was reported; examples where side-reactions occurred were not taken as defining a threshold value because the side-reaction could simply be faster than attack at the unsaturated hydrocarbon. For some nucleophiles there are no reports of failed reactions. In these instances, the value corresponding to the lowest k_{CO}^* of a reacting complex is listed, in parentheses, in Table 3.3. The following discussion of the tables makes use of force constants calculated from IR data wherever possible; those calculated by Timney's method will be denoted by a "T" superscript.

As noted in the tables, reactions of π -hydrocarbon complexes with nucleophiles may lead to products other than those resulting from

nucleophilic addition to the π -hydrocarbon. Reduction, especially with carbon-centered nucleophiles, attack on other ligands, and displacement of the olefin or arene are the predominant side reactions. These processes are often accompanied by extensive decomposition of the starting material as well, and products resulting from these side reactions are in many cases observed concurrently with the desired nucleophilic addition product.

Fairly polar solvents such as MeOH, acetone, MeCN, and MeNO₂ are often used in these reactions. Recent calculations^{4b} for nucleophilic addition to (C₆H₆)Cr(CO)₃ suggest that attack at the hydrocarbon is favored as the solvent polarity increases. Thus, the solvent may play a role in favoring or disfavoring the reactions shown in equations 1 and 2.

These reactions are nearly always performed at or below ambient temperature, with many in the range of -20° to 0°C. Kinetic studies of Kane-Maguire et al.^{1c} show that, in general, activation energies are low (< 40 KJmol⁻¹) and entropies of activation are large and negative. Thus, elevated temperatures would not be very useful in promoting nucleophilic addition to the unsaturated hydrocarbon.

It should be noted that while the force constants calculated from IR data are accurate to approximately ± 0.04 mdyne/Å within the CK approximation, comparisons must be made with larger errors in mind. The spectral data used for the determination of force constants were obtained in several different solvents, and solvent shifts of IR bands could cause variations in k_{C-O}^* of up to 0.1 mdyne/Å. Other factors, which are not taken into consideration in this treatment, could play some role.

Temperature, concentrations and solvents vary widely in the reactions that have been reported. Also, steric properties of the attacking nucleophiles and the ligands around the metal are not considered in this treatment. Therefore, the threshold k_{CO}^* values must be considered not as firm cut-offs, but as approximate guidelines for predicting which π -ethylene or π -benzene complexes will react with specific nucleophiles and which will not.

DISCUSSION

Nucleophilic Addition to π -Ethylene Complexes

Table 3.1 lists data pertaining to reactions (eq. 1) involving nucleophilic addition to π -ethylene complexes. References to all literature results are given in the tables.

Phosphine nucleophiles

When PPh_3 is the attacking nucleophile, addition to ethylene has been observed for the following complexes: $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$ ($\text{C}_6\text{H}_6=\eta\text{-C}_6\text{H}_6$) with $k_{\text{CO}}^* = 17.72^{\text{T}}$, $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ (17.71), $\text{CpW}(\text{CO})_3(\text{C}_2\text{H}_4)^+$ (16.88), and $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_4)^+$. The reaction does not occur for $\text{CpFe}[\text{P}(\text{OPh})_3]_2(\text{C}_2\text{H}_4)^+$ (16.82^T). Since we find no reports of successful addition below this value of k_{CO}^* , the threshold value for PPh_3 attack on π -ethylene is 16.8.

There are some examples (Table 3.1) in which ethylene is displaced by PPh_3 , even though addition might be expected on the basis of the k_{CO}^* value. In these cases, ethylene displacement is presumably faster than nucleophilic addition to the olefin. The present method cannot predict when displacement is faster than addition; it only indicates when addition is a possible pathway. One example of ethylene displacement is the reaction of $\text{CpFe}(\text{CO})(\text{CNMe})(\text{C}_2\text{H}_4)^+$ with PPh_3 in refluxing acetone. The k_{CO}^* value for this complex is 17.10, certainly large enough to expect addition based on the threshold value of 16.8. Many of the tetra-coordinate Pt complexes with k_{CO}^* values above 16.8 also undergo displacement of ethylene by phosphines. For square planar Pt(II) and

Table 3.1. Correlation of k_{CO}^* with nucleophilic addition to π -ethylene ligands^a

Compound [$L_nM(C_2H_4)$]	$\nu_{\text{CO}}(\text{cm}^{-1})$ [$L_nM(\text{CO})$]	k_{CO}^* ^b	k_{CO}^* ^c	PR_3
$(C_2H_4)Ir(H)Cl(CO)(Ph_3P)_2^+$			18.41	
<u>trans</u> - $(C_2H_4)PtCl_2(py)$	2133 ¹²	18.39		
$(C_2H_4)Rh(PMe_3)_2Cp^{2+}$			18.26	Me₃P, i-Pr₃P, (MeO)₃P
<u>trans</u> - $(C_2H_4)PtCl_2(NH_2CH(Me)Ph)$	2126 ¹⁷	18.27		
<u>trans</u> - $(C_2H_4)PtCl_2(n-PrNH_2)$	2125 ¹⁷	18.25		
$(C_2H_4)Pd(Ph_3P)Cp^+$	2113 ¹⁸	18.05		
<u>cis</u> - $(C_2H_4)PtCl_2(Ph_3P)$	2108 ¹⁹	17.96		
<u>cis</u> - $(C_2H_4)PtCl_2(n-Bu_3P)$	2101 ²²	17.84		
$(C_2H_4)Ru(PMe_3)_2(C_6H_6)^{2+}$			17.72	Me₃P, Ph₃P, i-Pr₃P, (PhO)₃P, (MeO)₃P
$(C_2H_4)Fe(CO)_2Cp^+$	2125 ²³ 2079	17.71 ²³	17.58	Ph₃P, n-Bu₃P, (EtO)₃P

^aBold type denotes successful addition.

^bCalculated by C-K method.

^cCalculated by Timney approximation.

^dOlefin displacement only.

^eDecomposition or reduction occurs.

^fAttack on other ligand observed.

NR ₃	Carbanions	Others	References
		Re(CO) ₅ ⁻	11
py			13, 14, 15
Et ₃ N		SCN ⁻	16
Ph(Me)CHNH ₂			14
n-PrNH ₂			14
Et ₂ NH ^d , py ^d	CH(COMe) ₂ ⁻	OMe ⁻ , i-PrO ⁻	10a
Me ₂ NH, Et ₂ NH, n-Bu ₂ NH, NH ₃			20, 21
Me ₂ NH, Et ₂ NH, n-Bu ₂ NH, NH ₃			20, 21
Et ₃ N			16
Me ₂ NH, MeNH ₂ , Me ₃ N, py, NH ₃ , NH ₂ NH ₂	MeLi ^e , PhLi, MeMgX ^e PhMgCl, CH ₂ NO ₂ ⁻ , CH(CO ₂ Et) ₂ ⁻ , CMe(CO ₂ Et) ₂ ⁻ , Ph ₃ PCH(CO ₂ Et), Ph ₃ PCH ₂ ^d ,	OMe ⁻ , t-BuS ⁻ , N ₃ ⁻ ^f , CpFe- (CO)(Ph ₃ P)H[H ⁻], CN ⁻ , CpFe(CO) ₂ - (σ-allyl)	24, 25, 26 27, 28, 29

Table 3.1. Continued

Compound $[L_nM(C_2H_4)]$	$\nu_{CO}(cm^{-1})$ $[L_nM(CO)]$	$k_{CO}^*{}^b$	$k_{CO}^*{}^c$	PR_3
$(C_2H_4)Fe(CO)_2Cp^+$ (continued)				
$(C_2H_4)Ru(CO)_2Cp^+$	2125 ³⁰ 2075	17.62	17.60	
$(C_2H_4)Ni(Me_2PhP)Cp^+$	2086 ¹⁸	17.59		$R_3P^{d,g}$
$(C_2H_4)Rh(Me_3P)MeCp^+$			17.28	Me_3P
$(C_2H_4)PtCl(acac)$	2066 ³²	17.25		
$(C_2H_4)Fe(CO)(CNMe)Cp^+$	2078 ²³ 2038	17.10 ²³	17.00	Ph_3P^d
$(C_2H_4)W(CO)_3Cp^+$	2118 ³⁴ 2034 2010	16.88 ²³		Ph_3P
$(C_2H_4)Fe[(PhO)_3P]_2Cp^+$			16.82	Ph_3P
$(C_2H_4)Ru(Me_3P)Me(\eta^6-C_6H_6)^+$			16.7	Me_3P
$(C_2H_4)RuCl_2(PhMe_2P)_2(CO)$	2058 ³⁶ 1994	16.60		$PhMe_2P^h$, Ph_2MeP^h , $PhMe_2As$, $Ph(MeO)_2P$
$(C_2H_4)Fe(CO)(Ph_3P)Cp^+$	2055 ²³ 2010	16.68 ²³		
$(C_2H_4)Fe(CO)_4$	2023 ³⁹ 2000	16.56		

^gR-group unspecified.

^hFinal product has one halide displaced by a second molecule of phosphine.

ⁱUncharacterized products.

NR ₃	Carbanions	Others	References
	various enamines		
NH ₃			31
			18
			16
n-PrNH ₂ , Et ₂ NH py ^d			14
			33
Me ₂ NH, MeNH ₂ , py, Me ₃ N, NH ₃		Re(CO) ₅ ⁻ , CpW(CO) ₃ ⁻	24, 35
NH ₃ , NR ₃ ^g		CN ⁻	24
			16
PhCH ₂ NH ₂ , 4-Mepy, PhMe ₂ N		OMe ⁻ , SMe ₂ , CN ⁻ ⁱ	37
	Ph ₃ PCH ₂	OP(OMe) ₂ ⁻	38
	CH(CO ₂ Me) ₂ ⁻		40

Table 3.1. Continued

Compound $[L_nM(C_2H_4)]$	$\nu_{CO}(cm^{-1})$		
	$[L_nM(CO)]$	k_{CO}^{*b}	k_{CO}^{*c} PR_3
$(C_2H_4)W(CO)_2(Ph_3P)Cp^+$			
$(C_2H_4)WMeCp_2^+$	1960 ⁴¹	15.53	$Me_3P, PhMe_2P$

NR ₃	Carbanions	Others	References
		Re(CO) ₅ ⁻ ,	35
		CpW(CO) ₃ ⁻	42

Pd(II) complexes, nucleophilic attack at the metal might be expected to be especially favorable, leading to ethylene-displaced products. It is possible that in some cases, addition to the olefin occurs at low temperature, but at higher temperatures only olefin-substituted products are observed. This has been reported for the reaction of $\text{CpRu}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$ and SCN^- , in which an olefin adduct is formed at 25°C , but warming of the solution results in loss of ethylene. NMR evidence suggests the same behavior for attack by I^- as well. Nevertheless, olefin substitution is the end result and is a possible side reaction in all complexes, even when the olefin is susceptible to attack as indicated by its k_{CO}^* value.

The more nucleophilic trialkylphosphines⁴³ also add to several olefin complexes. $\text{CpRh}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$ ($k_{\text{CO}}^*=18.26^{\text{T}}$) and $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$ (17.72^{T}) undergo addition with PMe_3 and $\text{P}(i\text{-Pr})_3$; $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$ (17.71) adds $\text{P}(n\text{-Bu})_3$; and PMe_3 reacts with $\text{CpRh}(\text{PMe}_3)\text{Me}(\text{C}_2\text{H}_4)^+$ (17.28^{T}), $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)\text{Me}(\text{C}_2\text{H}_4)^+$ (16.7^{T}), and $\text{Cp}_2\text{W}(\text{Me})(\text{C}_2\text{H}_4)^+$ (15.53). The mixed alkyl-aryl phosphine PMe_2Ph is also quite reactive, successfully adding to ethylene in $\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{CO})(\text{C}_2\text{H}_4)$ (16.60) and in $\text{Cp}_2\text{W}(\text{Me})(\text{C}_2\text{H}_4)^+$ (15.53). Since there are no reports of no-reaction with these phosphines, it is not possible to estimate a k_{CO}^* threshold value. Nevertheless, the observed reactivity indicates that the k_{CO}^* threshold is below 15.53 .

Amine nucleophiles

Quite a number of complexes in Table 3.1 react with amine nucleophiles. Reactions of aliphatic amines include Et_3N addition to $\text{CpRh}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)^{2+}$ ($k_{\text{CO}}^*=18.26^{\text{T}}$), $\text{Ph}(\text{Me})\text{CHNH}_2$ reaction with trans- PtCl_2 -

(Ph(Me)CHNH₂)(C₂H₄) (18.27), n-PrNH₂ with trans-PtCl₂(n-PrNH₂)(C₂H₄) (18.25) and dimethyl, diethyl, and dibutyl amines with both cis-PtCl₂(PPh₃)(C₂H₄) (17.96) and cis-PtCl₂(n-Bu₃P)(C₂H₄) (17.84). Also, CpFe(CO)₂(C₂H₄)⁺ (17.71) reacts with Me₃N, Me₂NH, and MeNH₂; Pt(acac)Cl(C₂H₄) (17.25) adds n-PrNH₂ and Et₂NH; and CpW(CO)₃(C₂H₄)⁺ (16.88) reacts with tri-, di-, and monomethyl amine. Amines do not add to ethylene in CpFe[P(OPh)₃]₂(C₂H₄)⁺ (16.82^T), and benzylamine and N,N-dimethylaniline fail to add to RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60); thus, the k_{CO}^* threshold value for alkylamine reactions is roughly the same as in the PPh₃ reactions, i.e., approximately 16.8. One apparent exception to this threshold value is the failure of (C₆H₆)Ru(PMe₃)₂(C₂H₄)²⁺ (17.72^T) to react with Et₃N. This is the only example in this paper where k_{CO}^* does not correctly predict the reaction or non-reaction of a system. While the bulkiness of Et₃N may account for its lower reactivity, it is remarkable that steric effects need not be considered in any other system including those involving the sterically dissimilar primary, secondary, and tertiary amines.

Pyridine adds to ethylene in trans-PtCl₂(py)(C₂H₄) (18.39), CpFe(CO)₂(C₂H₄)²⁺ (17.71), and CpW(CO)₃(C₂H₄)⁺ (16.88), but coordinates to Pt in PtCl(acac)(C₂H₄) to give a five-coordinate complex.¹⁴ The more basic 4-methylpyridine fails to react with RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60); thus, pyridine and 4-methyl-pyridine appear to be similar in reactivity to the aliphatic amines (k_{CO}^* threshold = 16.8).

Other nucleophiles

Most of the other nucleophiles in Table 3.1 have not been studied sufficiently to allow an estimate of threshold k_{CO}^* values. Reactions of carbon-centered nucleophiles have been carried out primarily on $CpFe(CO)_2(C_2H_4)^+$ (17.71). Although reduction and displacement of the olefin complicate these reactions, Grignard reagents, ester enolates, phosphorus ylides, and enamines have all been successfully added to ethylene in this complex. Reactions of ketone and ester enolates show that a threshold value of k_{CO}^* will be relatively low for these nucleophiles, probably below 16.6.

Addition of $CH(COMe)_2^-$ occurs for $CpPd(PPh_3)(C_2H_4)^+$ (18.05); $CH(CO_2Et)_2^-$ and $CMe(CO_2Et)_2^-$ add to ethylene in $CpFe(CO)_2(C_2H_4)^+$ (17.71), and even the neutral $Fe(CO)_4(C_2H_4)$ complex (16.56) reacts with $CH(CO_2Me)_2^-$. Unsuccessful attempts at addition have not been reported for these enolates.

Alkoxide and cyanide reactions have also been investigated for a few different complexes. Methoxide and isopropoxide ions attack ethylene in $CpPd(PPh_3)(C_2H_4)^+$ (18.05), and cyanide and methoxide ions react with $CpFe(CO)_2(C_2H_4)^+$ (17.71). Cyanide ion also reacts with $CpFe[P(OPh)_3]_2(C_2H_4)^+$ (16.82^T). Reaction of OMe^- and $RuCl_2(PMe_2Ph)_2(CO)(C_2H_4)$ (16.60) fails, and the product of the CN^- reaction with this complex was not characterized. Based on these observations, the threshold k_{CO}^* for OMe^- is about 16.60, but the CN^- value is not as well defined.

Another class of nucleophiles capable of adding to ethylene are the metal carbonyl anions. $CpW(CO)_3^-$ and $Re(CO)_5^-$ form olefin adducts with

$\text{CpW}(\text{CO})_3(\text{C}_2\text{H}_4)^+$ (16.88) as well as the monophosphine-substituted complex $\text{CpW}(\text{CO})_2(\text{PPh}_3)(\text{C}_2\text{H}_4)^+$. Instances of no-reaction have not been reported.

In comparing various nucleophiles, one observes that many exhibit threshold k_{CO}^* values in the range of 16.6-16.8; these include PPh_3 , various alkyl amines, pyridine, and methoxide ion. Carbon-centered nucleophiles and tri-alkylphosphines, for which reactions have been observed with complexes with k_{CO}^* values of 16.56 and 15.53, respectively, are more reactive.

Nucleophilic Addition to π -Benzene Complexes

Nucleophilic attack on a π -benzene ligand gives an η^5 -6-exo-substituted cyclohexadienyl complex, as shown in eq. 2. Several studies^{1c} have established that the product of kinetically controlled attack is the exo adduct. The reactions being considered in this section are summarized in Table 3.2.

Phosphine nucleophiles

The reaction of PPh_3 with $(\text{C}_6\text{H}_6)_2\text{Fe}^{2+}$ ($k_{\text{CO}}^*=18.88^{\text{T}}$) results in the formation of a cyclohexadienylphosphonium complex. The reaction also occurs for the ruthenium and osmium analogs (18.90^{T} and 18.82^{T} , respectively). PPh_3 does not add to $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33) or $(\text{C}_6\text{H}_6)\text{Ru}(\text{PEt}_3)\text{Cl}_2$ (17.04^{T}). Although kinetic studies^{1c} show that PPh_3 is more reactive than alkyl phosphites, there are not sufficient data in the literature to distinguish these nucleophiles by the k_{CO}^* approach. The phosphites, $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$, add to $(\text{C}_5\text{Me}_4\text{Et})\text{Rh}(\text{C}_6\text{H}_6)^{2+}$ (19.27^{T}), and $\text{P}(\text{O-Bu})_3$ adds to the $(\text{C}_6\text{H}_6)_2\text{M}^{2+}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) complexes. $\text{P}(\text{OEt})_3$ fails to

Table 3.2. Correlation of k_{CO}^* with nucleophilic addition to π -benzene ligands^a

Compound [$L_nM(C_6H_6)$]	$\nu_{CO}(cm^{-1})$		PR_3
	$[L_nM(CO)_3]$	k_{CO}^* ^b	
$(C_6H_6)CoCp^{2+}$		19.55	Ph_3P^e
$(C_6H_6)CoCp^{*2+}$		19.42	$n-Bu_3P$
$(C_6H_6)IrCp^{*2+}$		19.36	
$(C_6H_6)Rh(C_5Me_4Et)^{2+}$		19.27	$n-Bu_3P, PhMe_2P$ $(MeO)_3P^g,$ $(EtO)_3P^g,$ $(PhO)_3P$
$(C_6H_6)_2Ru^{2+}$		18.90	$Ph_3P, n-Bu_3P,$ $(n-BuO)_3P$
$(C_6H_6)_2Fe^{2+}$		18.88	$Ph_3P, n-Bu_3P,$ $(n-BuO)_3P$
$(C_6H_6)_2Os^{2+}$		18.82	$Ph_3P, n-Bu_3P,$ $(n-BuO)_3P$

^aBold type denotes successful addition.

^bCalculated by C-K method.

^cEstimated by Timney approximation.

^dR = alkyl or aryl, M = alkali metal.

^eDecomposition or reduction occurs.

^fDisplacement of C_6H_6 .

^gProduct is that resulting from Michaelis-Arbuzov rearrangement of attacking phosphite.

R-M ^d and R-MgX	Stabilized Carbanions	Others	References
NaCp, MeLi ^e , MeMgI ^e	LiCH ₂ CN ^e , LiCMe ₂ CN ^e , LiCMe(CO ₂ Et) ₂ ^e	OMe ⁻ , NaBH ₄ ^e , LiBEt ₃ H ^e , CN ^{-e} , OH ^{- e}	44 45
MeLi	CH ₂ NO ₂ ⁻	NaBH ₄ , OMe ⁻ NEt ₃ , py ^f , NHEt ₂ Li[AlH(t-BuO) ₃] OMe ^{- e} , CN ^{- e}	46
PhLi			5, 47
		NaBH ₄	5, 48, 49
			5, 48

Table 3.2. Continued

Compound $[L_nM(C_6H_6)]$	$\nu_{CO}(cm^{-1})$			PR ₃
	$[L_nM(CO)_3]$	$k_{CO}^*{}^b$	$k_{CO}^*{}^c$	
$(C_6H_6)Mn(CO)_3^+$	2101 ⁵⁰	18.33 ⁵⁰	18.44	n-Bu ₃ P, Ph ₃ P (EtO) ₃ P
$(C_6H_6)Re(CO)_3^+$	2085 ⁵⁶	18.09	18.38	n-Bu ₃ P
$(C_6H_6)Ru(PMe_3)_2CH_3CN^{2+}$ ^h			18.12	Me ₃ P
$(C_6H_6)Ru(PMe_3)(PPh_3)Cl^+$ ⁱ			17.71	Me ₃ P, PhMe ₂ P
$(C_6H_6)Ru(PMe_2Ph)(bipy)^{2+}$			17.70	R ₃ P ^j
$(C_6H_6)Co(\eta-C_4Ph_4)^+$			17.69	
$(C_6H_6)Ru(PMe_3)_2Cl^+$ ^k			17.67	Me ₃ P
$(C_6H_6)FeCp^+$	2125 ¹⁹ 2079	17.71 ¹⁹	17.58	
$(C_6H_6)RuCp^+$	2125 ²² 2075	17.62	17.60	R ₃ P ^j , (MeO) ₃ P

^hStarting material is $[(C_6H_6)Ru(CH_3CN)_3]^{2+}$, assume $[(C_6H_6)Ru(PMe_3)_2(CH_3CN)]^{2+}$ to be reactive species for ring attack based on authors' observations.

ⁱStarting material is either $(C_6H_6)Ru(PPh_3)Cl_2$ or $[(C_6H_6)Ru(PPh_3)_2Cl]^+$, but $[(C_6H_6)Ru(PPh_3)(PMe_3)Cl]^+$ is believed to be reactive species.

^jR-group unspecified.

^kFinal product has also undergone chloride substitution by a second molecule of nucleophile after attack on benzene.

R-M ^d and R-MgX	Stabilized Carbanions	Others	References
MeLi, PhLi MeMgCl, MeMgI	CH(CO ₂ Et) ₂ ⁻	CN ⁻ , N ₃ ⁻ , OH ⁻ , OMe ⁻ LiAlH ₄ , NaBH ₄	51, 52, 53 54, 55 48, 54
n-BuLi, MeMgBr		NaBH ₄ , OH ⁻ , CN ⁻	58
MeLi		NaBH ₄ , OMe ⁻	59
MeLi, PhLi,		NaBH ₄	57, 60
EtLi, PhCH ₂ MgCl			47, 61
PhMgBr		CN ^{- e} , OH ^{- e}	62, 63
			64, 65

Table 3.2. Continued

Compound $[L_n M(C_6H_6)]$	$\nu_{CO}(cm^{-1})$			PR ₃
	$[L_n M(CO)_3]$	$k_{CO}^*{}^b$	$k_{CO}^*{}^c$	
$(C_6H_6)Ru(PMe_3)_2Cl/Br^+{}^1$			17.67/17.59	
$(C_6H_6)OsCp^+$			17.52	R_3P^j
$(C_6H_6)Mn(CO)_2(PPh_3)^+$	2141.8 ⁶⁶ 2063 2052.0	17.43 ⁶⁶	17.76	
$(C_6H_6)Os(PMe_3)_2I^+$			17.38	
$(C_6H_6)Ru(PPh_3)Cl_2$			17.13	
$(C_6H_6)Ru(PEt_3)Cl_2$			17.04	$Ph_3P, n-Bu_3P,$ $Et_3P, Ph_2MeP,$ $PhMe_2P, (MeO)_3P,$ $(PhO)_3P, Ph_3As$
$(C_6H_6)Cr(CO)_3$	1985 ⁸	16.49 ⁸	16.47	

¹Starting complex is $[(C_6H_6)Ru(PMe_3)_2Cl]^+$. PhLi solution contained LiBr and product isolated was $[(C_6H_6 \cdot Ph)Ru(PMe_3)_2Br]$. Authors did not comment on reaction sequence.

^mDisplacement of chloride occurs.

ⁿLithiation of benzene occurs.

^oReaction carried out in 1:5 THF/HMPA, compare result to $LiCH_2COCH_3$ reaction run in THF alone.

R-M ^d and R-MgX	Stabilized Carbanions	Others	References
PhLi			60
		H ⁻ , CN ⁻ , OH ⁻	64
		CN ⁻	52
MeLi, PhLi, EtLi, n-BuLi, t-BuLi, n-PrLi			60
MeLi ^m			67
RLi ^j , RMgX ^j			68
t-BuLi, p-tolLi, n-BuLi ⁿ , t-BuMgCl	LiCHS ⁱ CH ₂ CH ₂ CH ₂ S ⁱ , LiCH ₂ CN, LiCH(SPh) ₂ , LiCH ₂ COCMe ₃ , KCH ₂ COCMe ₃ ^o		3a, d

react with $(C_6H_6)Mn(CO)_3^+$ (18.33), and reaction also fails for $P(OMe)_3$ with $(C_6H_6)RuCp^+$ (17.62) and $(C_6H_6)Ru(PEt_3)Cl_2$ (17.04 \bar{T}). The threshold k_{CO}^* for the $P(OR)_3$ and PPh_3 nucleophiles is thus approximately 18.3. Although the benzene ligand in $CpCo(C_6H_6)^{2+}$ (19.55 \bar{T}) would be expected to add PPh_3 , this reaction gives decomposition products and free benzene presumably by initial displacement of the arene by PPh_3 . The analogous $(C_5Me_4Et)Rh(C_6H_6)^{2+}$ (19.27 \bar{T}) reportedly does not react with PPh_3 ; however, this is likely in error since we have observed that displacement of benzene by PPh_3 in the very similar $Cp^*Rh(C_6H_6)^{2+}$ complex ($Cp^* = C_5Me_5$) is essentially complete in 50 minutes at room temperature.

Tri-*n*-butylphosphine adds to $Cp^*Co(C_6H_6)^{2+}$ (19.42 \bar{T}), $(C_6H_6)Rh(C_5Me_4Et)^{2+}$, and $(C_6H_6)_2M^{2+}$ ($M = Fe, Ru, Os$, with k_{CO}^* values of 18.88 \bar{T} , 18.90 \bar{T} , 18.82 \bar{T} , respectively), and to $(C_6H_6)Mn(CO)_3^+$ (18.33) and $(C_6H_6)Re(CO)_3^+$ (18.09). Dimethylphenylphosphine reacts with $(C_5Me_4Et)Rh(C_6H_6)^{2+}$ and $(C_6H_6)Ru(PPh_3)(PMe_3)Cl^+$ (17.71 \bar{T}); likewise, PMe_3 reacts with $(C_6H_6)Ru(PMe_3)_2(CH_3CN)^{2+}$ (18.12 \bar{T}), $(C_6H_6)Ru(PPh_3)(PMe_3)Cl^+$, and $(C_6H_6)Ru(PMe_3)_2Cl^+$ (17.67 \bar{T}). Tri-alkyl phosphines do not add to benzene in $(C_6H_6)Ru(PMe_2Ph)(bpy)^{2+}$ (17.70 \bar{T}), $CpRu(C_6H_6)^+$ (17.62), and $CpOs(C_6H_6)^+$ (17.52 \bar{T}). Though the non-reacting complex $(C_6H_6)Ru(PMe_2Ph)(bpy)^{2+}$ has a k_{CO}^* value slightly greater than that of the reacting $(C_6H_6)Ru(PMe_3)_2Cl^+$ species, the magnitude of the difference is well within the error margins of the correlation method. Thus, the threshold value for addition of tri-alkylphosphines and PMe_2Ph is in the area of 17.7

Carbanion nucleophiles

Alkyl- and aryl-lithium reagents add to the arene in a variety of π -benzene complexes. $(C_6H_6)_2Ru^{2+}$ (18.90^T) reacts with PhLi, $(C_6H_6)Co(C_4Ph_4)^+$ (17.69^T) with n-BuLi, and $CpFe(C_6H_6)^+$ (17.71) with Me-, Et-, and PhLi. $(C_6H_6)Ru(PMe_3)_2Br^+$ (17.59^T) is attacked by PhLi, $(C_6H_6)Os(PMe_3)_2I^+$ (17.38^T) by Ph-, *t*-Bu-, n-Bu-, n-Pr-, Et- and MeLi, and the neutral $(C_6H_6)Cr(CO)_3$ complex (16.49) by *p*-tolyl- and *t*-BuLi. One complex that does not follow this trend is $(C_6H_6)Ru(PEt_3)Cl_2$ (17.04^T), which was reported not to react with alkyl-lithium reagents, but this report may not be correct since the PPh_3 complex $(C_6H_6)Ru(PPh_3)Cl_2$ (17.48^T) has been shown to undergo displacement of chloride by MeLi. Since no cases of failed reactions have been reported below a k_{CO}^* value of 16.49, the threshold for these very reactive nucleophiles can be assumed to be below this value.

There are few examples of Grignard reagent reactions with π -benzene complexes. The Grignard reagents MeMgX attack benzene in $(C_6H_6)Mn(CO)_3^+$ (18.33), and $PhCH_2MgCl$ adds to $CpFe(C_6H_6)^+$ (17.71), but MeMgBr fails to react with $(C_6H_6)Co(C_4Ph_4)^+$ (17.69^T). Reaction also fails for *t*-BuMgCl with $(C_6H_6)Cr(CO)_3$ (16.49); so, for Grignard reagents the k_{CO}^* threshold can be estimated at 17.7. Though $CpCo(C_6H_6)^{2+}$ has a k_{CO}^* value of 19.55^T, reaction with MeMgI results only in decomposition of the complex.

The stabilized carbanion, $CH_2NO_2^-$, adds to the arene in $Cp^*Ir(C_6H_6)^{2+}$ (19.36^T), $CH(CO_2Et)_2^-$ reacts with $(C_6H_6)Mn(CO)_3^+$ (18.33), and $(C_6H_6)Cr(CO)_3$ (16.49) undergoes attack at benzene by several different reagents, including $LiCH_2CN$, $LiCH(SPh)_2$, and KCH_2COCMe_3 . As in the case

of alkyl- and aryl-lithium reagents, a threshold value is not well defined for these nucleophiles, but should be lower than 16.49.

Other nucleophiles

A number of other common nucleophiles have been successfully added to benzene in transition metal complexes. Methoxide ion reacts to give 6-exo-methoxycyclohexadienyl derivatives with $\text{Cp}^*\text{Ir}(\text{C}_6\text{H}_6)^{2+}$ (19.36^T), $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33), and gives double addition with $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ (19.55^T). There is no reaction with $(\text{C}_6\text{H}_6)\text{Co}(\text{C}_4\text{Ph}_4)^+$ (17.69^T); so, the k_{CO}^* threshold for MeO^- is approximately 17.7.

Cyanide and hydroxide add to $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ and to $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_2\text{Ph})\text{-}(\text{bpy})^{2+}$ (17.74^T), but neither reacts with $\text{CpOs}(\text{C}_6\text{H}_6)^+$ (17.52^T). The threshold value would seem to be 17.52; however, CN^- adds to benzene in $(\text{C}_6\text{H}_6)\text{Mn}(\text{PPh}_3)(\text{CO})_2^+$ (17.43). But in this latter case, there is considerable disagreement between the Timney and IR data force constants with the Timney value equal to 17.76. Uncharacterized products were obtained from the reactions of $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ (19.55^T) and $\text{CpRu}(\text{C}_6\text{H}_6)^+$ (17.52) with both CN^- and OH^- .

Comparison of Threshold k_{CO}^* Values for Different Nucleophiles

Because there are insufficient data to establish threshold k_{CO}^* values for many nucleophiles, one can only draw tentative conclusions from the values in Table 3.3. For nucleophilic addition to the π -benzene ligand, the carbanions (RLi , CH_2NO_2^- , and CH_2CN^-) are the most reactive with threshold k_{CO}^* values below 16.5. Next, comes a group of nucleophiles ($\text{P}(\text{alkyl})_3$, OMe^- , RMgX , and CN^-) with threshold k_{CO}^* values in the

Table 3.3. Threshold k_{CO}^* values for nucleophilic addition to π -ethylene and π -benzene ligands

Nucleophile	k_{CO}^* Threshold ^a	
	π -Ethylene	π -Benzene
PPh_3	16.8	18.3
$\text{P(OR)}_3^{\text{b}}$	-	18.3
NR_3	16.8	-
$\text{CH(COR)}_2^-^{\text{c}}$	(16.6)	(18.3)
PR_3^{b}	(15.5)	17.7
OMe^-	16.6	17.7
RMgX	-	17.7
CN^-	-	17.5
RLi	-	(16.5)
$\text{CH}_2\text{X}^-^{\text{d}}$	-	(16.5)

^aDefined as the highest value for which addition was not observed. Values in parentheses refer to the lowest k_{CO}^* at which addition was observed when no examples of no-reaction were reported.

^bR = alkyl.

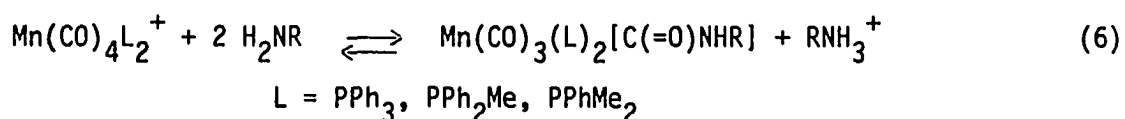
^cR = alkyl, alkoxy.

^dX = NO_2 , CN.

approximate range 17.5-17.7. And finally, the least reactive nucleophiles (PPh_3 and P(OR)_3) have threshold k_{CO}^* values of approximately 18.3. For additions to the π -ethylene ligand there are fewer results available, but P(alkyl)_3 has a lower threshold (< 15.5) than PPh_3 , NR_3 , and OMe^- which all fall in the range 16.6-16.8.

Kinetic or Thermodynamic Control of Nucleophilic Addition

Although k_{CO}^* values are useful guidelines for predicting whether or not π -ethylene and π -benzene ligands are susceptible to nucleophilic attack, there is the question of whether this reactivity is determined by kinetic or thermodynamic factors. Studies^{6a} of organolithium addition to CO ligands (eq. 3) were discussed in terms of the importance of kinetic factors, but thermodynamic factors were not specifically excluded. In a study⁶⁹ of amine attack on CO ligands (2nd order in amine), both the rate and equilibrium constants were affected by the electronic (i.e., k_{CO}) and steric properties of L (eq. 6).



There are a few studies of the reactions in equations 1 and 2 which have some bearing on the question of whether k_{CO}^* is related to equilibrium or rate. Equilibrium studies of amine attack on several Pt(II) ethylene complexes do not show a direct relationship between k_{CO}^* and K_{eq} . For example, at 25°C $n\text{-PrNH}_2$ adds to trans- $\text{PtCl}_2(n\text{-PrNH}_2)(\text{C}_2\text{H}_4)$ (18.25) with $K_{\text{eq}}=20$, yet its reaction with $\text{PtCl}(\text{acac})(\text{C}_2\text{H}_4)$ (17.25) has $K_{\text{eq}} \sim 73$.

Kinetic studies of the reaction of PPh_3 with $(\text{C}_6\text{H}_6)_2\text{M}^{2+}$ complexes of Fe, Ru, and Os show that the Fe complex is more reactive than either the Ru or Os analog,⁵ although their k_{CO}^* values are very similar. The second-order rate constants at 20°C are $3.2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for $(\text{C}_6\text{H}_6)_2\text{Fe}^{2+}$ (18.88^T), 8400 for $(\text{C}_6\text{H}_6)_2\text{Ru}^{2+}$ (18.90^T), and 1500 for $(\text{C}_6\text{H}_6)_2\text{Os}^{2+}$ (18.82^T). The equilibrium constants parallel this trend, with values of 139, 2.0, and 1.1 for Fe, Ru, and Os, respectively, since the reverse rate constants are comparable for all three reactions. Neither the rate nor the equilibrium constants are reflected in the k_{CO}^* values. The problem could be in the estimation of k_{CO}^* using the Timney method, but the method seems to work well for many other Ru(II) complexes of the type $\text{RuX}_2\text{L}(\text{CO})_3$, and comparison of analogous Fe and Ru complexes does not reveal a large difference in CO stretching frequencies. A possible, but incomplete, explanation is that the well-known unusually strong back-bonding abilities of Ru(II) and Os(II) are not, for some reason, reflected in the $\nu(\text{CO})$ values. It appears k_{CO}^* values are not able to predict trends in reactivity where k_{CO}^* differences are small, as in this series of complexes.

The k_{CO}^* parameters are available from IR data for the complexes $(\text{C}_6\text{H}_6)\text{M}(\text{CO})_3^+$ ($\text{M} = \text{Mn}, \text{Re}$), and the kinetics of their reactions with $\text{P}(\text{n-Bu})_3$ have also been studied.⁵³ The second-order rate constant for the Mn complex (18.33) is $2000 \text{ M}^{-1}\text{s}^{-1}$ at 25°C in nitromethane and is 1800 for $(\text{C}_6\text{H}_6)\text{Re}(\text{CO})_3^+$ (18.09) under the same conditions. The equilibrium constants are 400 for $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ and 450 for $(\text{C}_6\text{H}_6)\text{Re}(\text{CO})_3^+$. Thus, the k_{CO}^* values predict the relative rate order, but not the K_{eq} order,

though the differences in both the rate and equilibrium constants may be too small to yield a substantial conclusion. The $(C_6H_6)_2M^{2+}$ complexes ($M = Fe, Ru, Os$), which all have higher k_{CO}^* 's than the Mn and Re compounds, react rapidly to give quantitative yields of the $P(n-Bu)_3$ adducts, and neither $(C_6H_6)Mn(CO)_3^+$ nor $(C_6H_6)Re(CO)_3^+$ forms an adduct with PPh_3 . Therefore, while k_{CO}^* apparently reflects large qualitative differences in reactivity, it appears not to be sensitive to small differences in closely related compounds.

On the basis of the above studies, one must conclude that it is not clear whether k_{CO}^* is related to kinetic or thermodynamic factors and that k_{CO}^* is useful primarily for predictions when fairly large differences in reactivity are involved.

CONCLUSIONS

Results of this paper show that k_{CO}^* is a very useful parameter for predicting the susceptibility of π -ethylene or π -benzene ligands to nucleophilic addition. The k_{CO}^* values of the π -ethylene or π -benzene complexes may be calculated from experimental $\nu(CO)$ values of the analogous metal carbonyl complexes or by Timney's method⁹ using known, additive parameters. This latter method is a particularly useful and simple way to obtain k_{CO}^* values. Threshold k_{CO}^* values establish approximate lower limits for reaction of π -ethylene and π -benzene ligands with different nucleophiles; these threshold values should be of particular value in designing syntheses where nucleophilic addition to the π -ligands is involved. The usefulness of k_{CO}^* values for predicting nucleophilic addition to CO^6 and the π -hydrocarbon ligands reported herein suggests that k_{CO}^* may be helpful for predicting reactions of other ligands and correlating properties of complexes which depend upon the electron density on the metal.

REFERENCES

1. a) Pauson, P. L. J. Organomet. Chem. **1980**, 200, 207.
b) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. Tetrahedron **1978**, 34, 3047.
c) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. Chem. Rev. **1984**, 84, 525.
2. Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. J. Am. Chem. Soc. **1979**, 101, 2411.
3. a) Semmelhack, M. F.; Hall, H. T.; Yoshifuji, M.; Clark, G. J. Am. Chem. Soc. **1975**, 97, 1247.
b) Semmelhack, M. F.; Hall, H. T. Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. J. Am. Chem. Soc. **1979**, 101, 3535.
c) Semmelhack, M. F. J. Organomet. Chem. Lib. **1976**, 1, 361.
d) Kündig, E. P.; Simmons, D. P. J. Chem. Soc., Chem. Commun. **1983**, 1320.
e) Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. J. Am. Chem. Soc. **1977**, 99, 2823.
f) Genco, N.; Marten, D.; Raghu, S.; Rosenblum, M. J. Am. Chem. Soc. **1976**, 98, 848.
g) Salzer, A.; Hafner, A. Helv. Chim. Acta **1983**, 66, 1774.
4. a) Eisenstein, O.; Hoffmann, R. J. Am. Chem. Soc. **1981**, 103, 4308.
b) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J. Inorg. Chem. **1982**, 21, 2723.

- c) Clack, D. W.; Kane-Maguire, L. A. P. J. Organomet. Chem. **1979**, 174, 199.
- d) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. J. Organomet. Chem. **1976**, 107, C40.
- e) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. J. Organomet. Chem. **1976**, 120, C25.
- f) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Seigbahn, P. J. Am. Chem. Soc. **1984**, 106, 4369.
5. Domaille, P. J.; Ittel, S. D.; Jesson, J. P.; Sweigart, D. A. J. Organomet. Chem. **1980**, 202, 191.
6. a) Darensbourg, D. J.; Darensbourg, M. Y. Inorg. Chem. **1970**, 9, 1691.
- b) Angelici, R. J.; Blacik, L. J. Inorg. Chem. **1972**, 11, 1754.
- c) Angelici, R. J. Acc. Chem. Res. **1972**, 5, 335.
- d) Angelici, R. J.; Christian, P. A.; Dombek, B. D.; Pfeffer, G. A. J. Organomet. Chem. **1974**, 67, 287.
7. Hall, M. B.; Fenske, R. F. Inorg. Chem. **1972**, 11, 1619.
8. Cotton, F. A.; Kraihanzel, C. S. J. Am. Chem. Soc. **1962**, 84, 4432.
9. Timney, J. A. Inorg. Chem. **1979**, 18, 2502.
10. a) Kurosawa, H.; Majima, T.; Asada, N. J. Am. Chem. Soc., **1980**, 102, 6996.
- b) Kurosawa, H.; Asada, N. Tetrahedron Lett. **1979**, 255.
- c) Åkermark, B.; Bäckvall, J. E.; Siirala-Hansén, K.; Sjöberg,
11. Olgemöller, B.; Beck, W. Ang. Chem. Int. Ed. Eng. **1980**, 19, 834.

12. Brause, A. R.; Rychek, M.; Orchin, M. J. Am. Chem. Soc. 1967, 89, 6500.
13. Kaplan, P. D.; Schmidt, P.; Orchin, M. J. Am. Chem. Soc. 1968, 90, 4175.
14. Al-Najjar, I. M.; Green, M. J. Chem. Soc., Dalton Trans. 1979, 1651.
15. Al-Najjar, I. M.; Green, M. J. Chem. Soc., Chem. Commun. 1977, 926.
16. Werner, H.; Freser, R.; Werner, R. J. Organomet. Chem. 1979, 181, C7.
17. Ellis, R.; Weil, T. A.; Orchin, M. J. Am. Chem. Soc. 1970, 92, 1078.
18. Majima, T.; Kurosawa, H. J. Organomet. Chem. 1977, 134, C45.
19. Anderson, G. K.; Clark, H. C.; Davies, J. A. Inorg. Chem. 1981, 20, 1636.
20. Panunzi, A.; DeRenzi, A.; Palumbo, R.; Paiaro, G. J. Am. Chem. Soc. 1969, 91, 3879.
21. DeRenzi, A.; Paiaro, G.; Panunzi, A.; Paolillo, L. Gazz. Chim. Italiani 1972, 102, 281.
22. Chatt, J.; Johnson, N. P.; Shaw, B. L. J. Chem. Soc. 1964, 1662.
23. Johnson, B. V.; Ouseph, P. J.; Hsieh, J. S.; Steinmetz, A. L.; Shade, J. E. Inorg. Chem. 1979, 18, 1796.
24. Knoth, W. H. Inorg. Chem. 1975, 14, 1566.
25. Rosan, A.; Rosenblum, M.; Tancrede, J. J. Am. Chem. Soc. 1973, 95, 3062.
26. Lennon, P.; Rosan, A. M.; Rosenblum, M. J. Am. Chem. Soc. 1977, 99, 8426.
27. Bodnar, T.; LaCroce, S. J.; Cutler, A. R. J. Am. Chem. Soc. 1980, 102, 3292.

28. Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. J. Organomet. Chem. **1970**, 25, 207.
29. Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. J. Organomet. Chem. **1976**, 108, 93.
30. Kruse, A. E.; Angelici, R. J. J. Organomet. Chem. **1970**, 24, 231.
31. Behrens, H.; Jungbauer, A. Z. Naturforsch., B **1979**, 34b, 1477.
32. Hulley, G.; Johnson, B. F. G.; Lewis, J. J. Chem. Soc. A **1970**, 1732.
33. Johnson, B. V.; Steinmetz, A. L. J. Organomet. Chem. **1980**, 190, 187.
34. Jetz, W.; Angelici, R. J. J. Am. Chem. Soc. **1972**, 94, 3799.
35. Olgemöller, B.; Beck, W. Chem. Ber. **1981**, 114, 867.
36. Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. J. Chem. Soc., Dalton Trans. **1976**, 953.
37. Stephenson, M.; Mawby, R. J. J. Chem. Soc., Dalton Trans. **1981**, 2112.
38. Reger, D. L.; Culbertson, E. C. J. Organomet. Chem. **1977**, 131, 297.
39. Haas, H.; Sheline, R. K. J. Chem. Phys. **1967**, 47, 2996.
40. Roberts, B. W.; Wong, J. J. Chem. Soc., Chem. Commun. **1977**, 20.
41. Green, M. L. H.; Mahtab, R. J. Chem. Soc., Dalton Trans. **1979**, 262.
42. Green, M. L. H. Pure & Appl. Chem. **1978**, 50, 27.
43. Tolman, C. A. Chem. Rev. **1977**, 77, 313.
44. Lai, Y.-H.; Tam, W.; Vollhardt, K. P. C. J. Organomet. Chem. **1981**, 216, 97.
45. Bailey, N. A.; Blunt, E. H.; Fairhurst, G.; White, C. J. Chem. Soc., Dalton Trans. **1980**, 829.

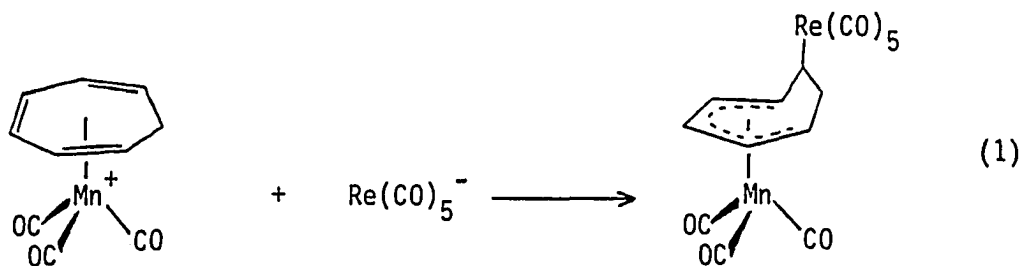
46. Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. J. Chem. Soc., Dalton Trans. 1984, 1747.
47. Jones, D.; Pratt, L.; Wilkinson, G. J. Chem. Soc. 1962, 4458.
48. Chung, Y. K.; Honig, E. D.; Sweigart, D. A. J. Organomet. Chem. 1983, 256, 277.
49. Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. J. Am. Chem. Soc. 1984, 106, 3381.
50. Sarapu, A. C.; Fenske, R. F. Inorg. Chem. 1975, 14, 247.
51. Mawby, A.; Walker, P. J. C.; Mawby, R. J. J. Organomet. Chem. 1973, 55, C39.
52. Walker, P. J. C.; Mawby, R. J. Inorg. Chim. Acta 1973, 7, 621.
53. Evans, D. J.; Kane-Maguire, L. A. P.; Sweigart, D. A. J. Organomet. Chem. 1981, 215, C27.
54. Kane-Maguire, L. A. P.; Sweigart, D. A. Inorg. Chem. 1979, 18, 700.
55. Chung, Y. K.; Williard, P. G.; Sweigart, D. A. Organometallics 1982, 1, 1053.
56. Abel, E. W.; McLean, R. A. N.; Tyfield, S. P.; Braterman, P. S.; Walker, A. P.; Hendra, P. J. J. Mol. Spectrosc. 1969, 30, 29.
57. Werner, H.; Werner, R. Chem. Ber. 1984, 117, 142.
58. Robertson, D. R.; Robertson, I. W.; Stephenson, T. A. J. Organomet. Chem. 1980, 202, 309.
59. Efraty, A.; Maitlis, P. M. J. Am. Chem. Soc. 1967, 89, 3744.
60. Werner, H.; Werner, R. Chem. Ber. 1984, 117, 152.
61. Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrovka, V. A. Bull. Acad. Sciences USSR, Chem. Sciences 1975, 24, 1057.

62. Michaud, P.; Astruc, D.; Ammeter, J. H. J. Am. Chem. Soc. **1982**, 104, 3755.
63. Khand, I. U.; Pauson, P. L.; Watts, W. E. J. Chem. Soc. C. **1969**, 2024.
64. Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. J. Organomet. Chem. **1982**, 228, 171.
65. Gill, T.P.; Mann, K.R. Organometallics **1982**, 1, 485.
66. Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. Inorg. Chem. **1975**, 14, 1579.
67. Bennett, M. A.; Smith, A. K. J. Chem. Soc., Dalton Trans. **1974**, 233.
68. Zelonka, R. A.; Baird, M. C. Can. J. Chem. **1972**, 50, 3063.
69. Angelici, R. J.; Brink, R. W. Inorg. Chem., **1973**, 12, 1067.

SECTION 4. SYNTHESIS AND STRUCTURE OF $[1-5-\eta-6-\text{exo}-\text{Re}(\text{CO})_5-\text{C}_7\text{H}_8]\text{Mn}(\text{CO})_3$.
THE FIRST EXAMPLE OF METAL CARBONYL ANION ADDITION
TO A COORDINATED CYCLIC π -HYDROCARBON

COMMUNICATION

A variety of nucleophiles are known¹ to add to coordinated π -hydrocarbon ligands; however, analogous reactions of transition metal carbonyl anion nucleophiles have received little attention. Additions to ethylene were achieved in the reactions of $\text{CpM}(\text{CO})_3(\eta^2\text{-C}_2\text{H}_4)^+$ ($\text{M} = \text{Mo}, \text{W}$) with $\text{CpM}(\text{CO})_3^-$ ($\text{M} = \text{Mo}, \text{W}$) and $\text{Re}(\text{CO})_5^-$,² $\text{CpW}(\text{CO})_2(\text{PPh}_3)(\eta^2\text{-C}_2\text{H}_4)^+$ with $\text{CpW}(\text{CO})_2(\text{PPh}_3)^-$,² and $\text{M}'(\text{CO})_5(\eta^2\text{-C}_2\text{H}_4)^+$ with $\text{M}'(\text{CO})_5^-$ ($\text{M}' = \text{Mn}, \text{Re}$).³ Attempts to add metal carbonyl anions to π -tropylium and π -benzene complexes have been unsuccessful,³ resulting in reductive coupling of $(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^+$ through the tropylium ligand ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) or in complex salt formation with $(\eta^7\text{-C}_7\text{H}_7)\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})^+$, $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$, and $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\text{PBU}_3)^+$. Extending our interest⁴ in nucleophilic additions to π -hydrocarbon complexes, we now report the reaction (eq. 1) of $\text{Re}(\text{CO})_5^-$ with $(\eta^6\text{-cycloheptatriene})\text{Mn}(\text{CO})_3^+$ to form $[1\text{-}5\text{-}\eta\text{-}6\text{-exo-}\text{Re}(\text{CO})_5\text{-C}_7\text{H}_8]\text{Mn}(\text{CO})_3$ (1), the first example of a complex resulting from nucleophilic addition of a metal carbonyl anion to a coordinated cyclic π -hydrocarbon.



Addition of a slight excess of $\text{NaRe}(\text{CO})_5$ in THF solution to a stirred suspension of $[(\eta^6\text{-C}_7\text{H}_8)\text{Mn}(\text{CO})_3](\text{BF}_4)^5$ (102 mg, 0.321 mmole) in THF at 0° for 5 min under N_2 , resulted in a clear orange solution whose IR spectrum

in the $\nu(\text{CO})$ region showed **1** as the major product. Evaporation of the solvent gave an orange residue which was chromatographed on silica gel; a broad yellow product band was eluted with hexane. The yellow solution was concentrated, and successive crystallizations from hexane at -20°C yielded pale yellow crystals (24.1 mg, 13.5%) of [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃, **1**. An additional 23.0 mg (12.8%) of the product was isolated by evaporation of the mother liquor as a slightly impure powder. The relatively low yield appears to be due to losses during purification; no attempt was made to optimize the yield. The product was characterized by elemental analysis and its IR, ¹H NMR and mass spectra;⁶ all data were consistent with the formulation of the compound as [η -C₇H₈•Re(CO)₅]Mn(CO)₃. A single crystal X-ray diffraction study⁷ of **1** has confirmed the identity of the product and also clearly established the exo-orientation of the Re(CO)₅ fragment at C6 (Fig. 4.1). The Re-C6 bond distance is 2.335(9) Å, which is slightly longer than rhenium-methylene carbon bond lengths in (η -C₅H₅)Re(CO)₂H(CH₂Ph) (2.29(1) Å),⁸ (CO)₅Re-CH₂CH₂-Re(CO)₅ (2.304(8) Å),³ and (-)-(R)-(η -C₅H₅)Re(NO)(PPh₃)(CH₂Ph) (2.203(8) Å),⁹ but is in the range of Re-C(η^1 -C₅H₅) bond lengths in (η^1 -C₅H₅)Re(Me)(CO)(NO)(PMe₃)₂ (2.32(1) Å)¹⁰ and (η^1 -C₅H₅)Re(CO)₃(PMe₃)₂ (2.360(10) Å).¹¹

The Mn is bonded to the η -cycloheptadienyl ligand through the five unsaturated carbons with Mn-C distances of 2.218(10) (C1), 2.090(11) (C2), 2.145(13) (C3), 2.132(11) (C4), and 2.285(9) Å (C5). Carbon-carbon distances in the ring are 1.425(20) (C1-C2), 1.413(20) (C2-C3), 1.437(20) (C3-C4), 1.372(14) (C4-C5), 1.474(12) (C5-C6), 1.549(12) (C6-C7), and

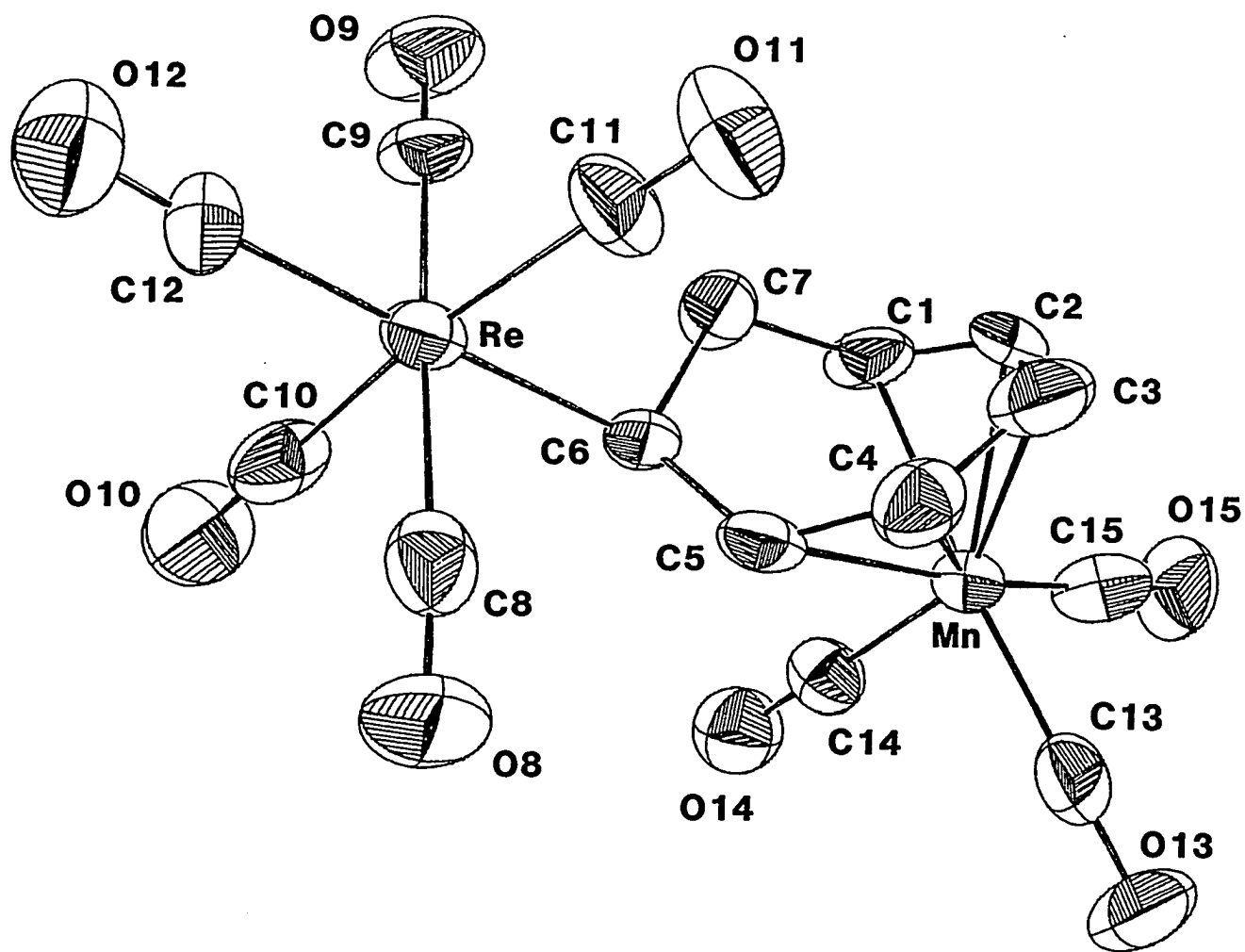


Figure 4.1. ORTEP drawing of [1-5-h-6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃, 1; hydrogen atoms omitted

1.530(14) Å (C1-C7). The C5-C6 distance of 1.474(12) Å is somewhat shorter than C1-C7 (1.530(14) Å), a typical C(sp²)-C(sp³) bond distance. The C5-C6 length is, however, similar to those found for C-C bonds adjacent to the Re-C bonds in η^1 -C₅H₅ compounds, (η^1 -C₅H₅)Re(Me)(CO)(NO)(PMe₃)₂ (1.48 and 1.44 Å)¹⁰ and (η^1 -C₅H₅)Re(CO)₃(PMe₃)₂ (1.475 and 1.448 Å).¹¹ The C-C-C angles at each of the ring carbon atoms are 120.6(11) (C1), 123.5(10) (C2), 120.2(11) (C3), 128.7(10) (C4), 132.5(8) (C5), 116.7(7) (C6), and 112.7(8)° (C7).

The C5-C6-C7-C1 linkage is twisted as depicted in Fig. 4.2. The planes defined by C5, C6, C1 and C5, C7, C1 are bent 37° and 54°, respectively, away from the plane of the pentadienyl carbons, resulting in a twist angle of 17° for the saturated carbon bridge. This distortion is not observed for the related PPh₃ adduct, [(η^5 -6-exo-PPh₃-C₇H₈)Mn(CO)₃](BF₄),¹² which has an essentially planar set of carbon atoms corresponding to C5, C6, C7, and C1 in **1**.

The Mn-C distances to the CO carbons, 1.837(10) (C13), 1.792(10) (C14), and 1.796(12) Å (C15), are within the normal range.¹³ The Re-C carbonyl distances range from 1.97 to 2.01 Å (average of 1.99 Å), again similar to distances observed in other rhenium carbonyl compounds.^{3,14}

Since **1** involves Mn bonded to five cycloheptadienyl carbon atoms and Re to only one, it was of interest to explore the possibility that **1** could be converted to a complex in which both Mn and Re were bonded to three carbon atoms (η^3) while shifting a CO ligand from Re to Mn. In attempts to induce these changes, a hexane solution of **1** was heated at 45°C for 1 h while CO was bubbled through the reaction flask. However, no reaction was

observed, even after heating at 60°C for an additional 30 min. Photolysis of 1 in hexane in the presence of CO for 3 h resulted only in decomposition of the starting material.

In summary, the occurrence of the reaction in eq. 1 demonstrates that despite earlier unsuccessful attempts, metal carbonyl anion additions to cyclic π -hydrocarbons are possible, and other reactions of this type may be anticipated in the future.

REFERENCES

1. a) Davis, S. G.; Green, M. L. H.; Mingos, D. M. P. Tetrahedron **1978**, 34, 3047.
 b) Pauson, P. L. J. Organomet. Chem. **1980**, 200, 207.
 c) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. Chem. Rev. **1984**, 84, 525.
2. Olgemöller, B.; Beck, W. Chem. Ber. **1981**, 114, 867.
3. Raab, K.; Nagel, U.; Beck, W. Z. Naturforsch. **1983**, 38B, 1466.
4. Bush, R. C.; Angelici, R. J. J. Am. Chem. Soc. **1986**, 108, 2735.
5. Haque, F.; Miller, J.; Pauson, P. L.; Tripathi, J. B. P. J. Chem. Soc. C **1971**, 743.
6. IR (hexanes) $\nu(\text{CO})$ 2126(w) 2019(vs), 1993(s), 1949(ms), 1936(ms) cm^{-1} ; $^1\text{H NMR}(\text{CDCl}_3)$: δ 1.45 (m, H7exo), 2.07 (dt, H7endo), 3.36 (td, H6), 3.99 (m, H1), 4.44 (dd, H4), 5.31 (dd, H5), 5.50 (dd, H2), 5.69 (brt, H3); coupling constants: $J_{1-2} = 8.1$ Hz, $J_{2-3} = 5.6$ Hz, $J_{3-4} = 6.3$ Hz, $J_{4-5} = 9.9$ Hz, $J_{5-6} = 3.6$ Hz, $J_{6-7\text{exo}} \approx 9.8$ Hz, $J_{6-7\text{endo}} = 8.6$ Hz, $J_{1-7\text{exo}} = 3$ Hz, $J_{1-7\text{endo}} \approx 8.6$ Hz, $J_{7\text{endo}-7\text{exo}} = 13$ Hz, $J_{1-3} \approx 2$ Hz. Assignments were made on the basis of observed coupling in the spectrum run in CDCl_3 solvent and a 2-D proton-proton coupling experiment carried out on a C_6D_6 solution of 1. Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{O}_8\text{MnRe}$: C, 32.32; H, 1.45. Found: C, 32.15; H, 1.69. MS (16 eV), m/e (intensity): 473.7(0.72) M^+-3CO , 445.8(0.27) M^+-4CO , 417.8(0.89) M^+-5CO , 231.0(100.0) $\text{M}^+-\text{Re}-5\text{CO}$.
7. Crystallographic data for 1: mol wt. 557.36; triclinic; space group $\text{P}\bar{1}$; $a = 11.098(6)$ Å, $b = 12.177(3)$ Å, $c = 6.823(3)$ Å, $\alpha = 106.35(3)^\circ$,

$\beta = 106.45(5)^\circ$, $\gamma = 87.27(5)^\circ$, $V = 848.1 \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 2.182 \text{ g cm}^{-3}$, $\mu = 79.8 \text{ cm}^{-1}$. Diffraction data were collected using an automated diffractometer (Mo K_α radiation, ω scan) and corrected for absorption (3308 measured reflections with $2\theta \leq 50^\circ$, 2745 observed reflections with $I \geq 1.5 \sigma_I$ were used for structural solution and refinement). The structure was solved by analysis of a sharpened Patterson map to locate the metal atoms. Successive electron density maps were used to locate the lighter atoms. The structure was refined by a combination of block and full matrix refinement techniques with all non-hydrogen atoms anisotropic. The hydrogen atoms were fixed at calculated positions. $R = 0.049$ and $R_w = 0.065$ ($w = \sigma_F^{-2}$).

8. Fischer, E. O.; Frank, A. Chem. Ber. **1978**, 111, 3740.
9. Merrifield, J. H.; Strouse, C. E.; Galdysz, J. A. Organometallics **1982**, 1, 1204.
10. Casey, C. P.; Jones, W. D. J. Am. Chem. Soc. **1980**, 102, 6154.
11. Casey, C. P.; O'Conner, J. M.; Jones, W. D.; Haller, K. J. Organometallics **1983**, 2, 535.
12. Honig, E. D.; Quin-jin, M.; Robinson, W. T.; Williard, P. G.; Sweigart, D. A. Organometallics **1985**, 4, 871.
13. a) Fitzpatrick, P. J.; Le Page, Y.; Sedman, J.; Butler, I. S. Inorg. Chem. **1981**, 20, 2852.
b) Bryan, R. F.; Weber, H. P. J. Chem. Soc. A **1969**, 843.
c) Khotsyanova, T. L.; Kuznetsov, S. I.; Bryukhova, E. V.; Makarov, Yu, V. J. Organomet. Chem. **1975**, 88, 351.

- d) Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. A. J. Organomet. Chem. **1969**, 8, 1950.
- e) Churchill, M. R.; Scholer, F. R. Inorg. Chem. **1969**, 8, 1950.
14. Couldwell, M. C.; Simpson, J.; Robinson, W. J. J. Organomet. Chem. **1976**, 107, 323.

SUPPLEMENTARY MATERIAL

Table 4.1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA} \times 10^3$) for [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃

atom	x	y	z	U, \AA^2
Re	3903(0)	2586(0)	659(1)	44(0)
Mn	-1064(1)	2768(1)	-951(2)	46(0)
C6	1748(9)	2536(7)	-1009(13)	42(3)
O9	4130(11)	203(8)	-2486(18)	87(4)
C8	3708(10)	4109(9)	2590(16)	52(3)
O11	3150(11)	1391(9)	3633(16)	87(4)
O8	3602(8)	5007(6)	3682(13)	68(3)
C7	1200(10)	1306(8)	-2207(19)	60(4)
C5	1049(9)	3145(7)	497(15)	46(3)
C13	-1693(11)	3994(10)	686(19)	56(4)
C3	-300(12)	1776(11)	1239(25)	77(6)
O13	-2134(10)	4738(7)	1601(16)	82(4)
C12	5725(11)	2592(9)	2015(16)	53(4)
C4	480(10)	2785(10)	1762(17)	61(4)
O10	4295(11)	3848(9)	-2572(17)	87(4)
C11	3456(11)	1796(9)	2587(19)	59(4)
O12	6763(7)	2529(8)	2718(14)	79(4)
C1	-218(10)	1207(8)	-2542(23)	71(4)
C14	-881(10)	3498(8)	-2798(16)	52(3)
O15	-3705(8)	1991(8)	-3127(17)	88(4)
O14	-717(9)	3941(8)	-4024(14)	74(3)
C15	-2670(12)	2287(10)	-2274(20)	68(4)
C10	4131(11)	3376(10)	-1382(19)	59(4)
C9	4028(11)	1060(9)	-1354(18)	56(3)
C2	-698(12)	1077(10)	-888(29)	84(7)
H2 ^a	-1569	592	-1110	95
H3	-795	1887	2444	95
H1	-524	538	-3977	95
H4	570	3342	3297	95
H5	1738	3807	1007	95
H7 _{exo}	1667	727	-1311	95
H7 _{endo}	1409	1049	-3702	95
H6	1496	3063	-2028	95

^aHydrogen atom positions calculated and not refined.

Table 4.2. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Re	38(0)	46(0)	47(0)	13(0)	13(0)	2(0)
Mn	39(1)	45(1)	57(1)	13(1)	19(1)	4(1)
C6	42(5)	42(4)	36(4)	-2(3)	13(4)	-1(4)
O9	92(7)	64(5)	96(7)	8(5)	30(6)	21(5)
C8	40(5)	65(6)	52(5)	20(5)	9(4)	-7(4)
O11	97(7)	97(7)	82(6)	44(5)	25(6)	-17(6)
O8	68(5)	52(4)	71(5)	-4(4)	23(4)	2(4)
C7	38(5)	45(5)	84(7)	-3(5)	18(5)	-4(4)
C5	42(5)	43(4)	50(5)	7(4)	13(4)	3(4)
C13	49(6)	64(6)	70(7)	30(5)	30(5)	8(5)
C3	60(8)	76(8)	114(11)	43(8)	42(8)	27(6)
O13	90(7)	68(5)	101(7)	21(5)	55(6)	32(5)
C12	60(7)	60(6)	44(5)	15(4)	20(5)	-6(5)
C4	50(6)	82(7)	59(6)	26(5)	26(5)	19(5)
O10	101(8)	95(6)	95(7)	49(5)	58(6)	22(6)
C11	62(7)	56(5)	64(6)	22(5)	19(6)	-9(5)
O12	35(5)	118(7)	79(6)	32(5)	3(4)	-5(4)
C1	37(5)	43(5)	115(10)	-4(5)	169(6)	-1(4)
C14	49(6)	59(5)	52(5)	17(4)	20(5)	6(4)
O15	44(5)	101(7)	107(7)	5(5)	24(5)	-9(4)
O14	75(6)	83(5)	70(5)	24(4)	28(5)	7(4)
C15	52(7)	72(7)	76(7)	9(5)	25(6)	9(5)
C10	52(6)	69(6)	71(7)	29(5)	32(5)	20(5)
C9	54(6)	48(5)	64(6)	11(5)	21(5)	12(4)
C2	54(7)	60(7)	170(15)	61(9)	55(9)	15(5)

^aThe expression used for the anisotropic temperature factor is $\exp(-[2\pi^2(h^2a^2U(1,1)+\dots+2hka^*b^*U(1,2)+\dots)])$.

Table 4.3. Selected bond distances (Å) for [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃

Mn-C1	2.218(10)	C1-C2	1.425(20)
Mn-C2	2.090(11)	C2-C3	1.413(20)
Mn-C3	2.145(13)	C3-C4	1.437(20)
Mn-C4	2.132(11)	C4-C5	1.372(14)
Mn-C5	2.285(9)	C5-C6	1.474(12)
Mn-C13	1.837(10)	C6-C7	1.549(12)
Mn-C14	1.792(10)	C1-C7	1.530(14)
Mn-C15	1.796(12)	C8-08	1.157(12)
Re-C6	2.335(9)	C9-09	1.134(12)
Re-C8	1.993(10)	C10-010	1.175(14)
Re-C9	2.001(9)	C11-011	1.102(14)
Re-C10	1.976(11)	C12-012	1.123(13)
Re-C11	2.010(10)	C13-013	1.121(13)
Re-C12	1.971(10)	C14-014	1.175(12)
		C15-015	1.153(14)

Table 4.4. Selected bond angles ($^{\circ}$) for [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃

C1-C2-C3	123.5(10)	C13-Mn-C14	95.2(4)
C2-C3-C4	120.2(11)	C14-Mn-C15	97.0(5)
C3-C4-C5	128.7(10)	C13-Mn-C15	86.4(5)
C4-C5-C6	132.5(8)	Re-C8-O8	178.5(8)
C5-C6-C7	116.7(7)	Re-C9-O9	178.3(10)
C6-C7-C1	112.7(8)	Re-C10-O10	178.5(10)
C7-C1-C2	120.6(11)	Re-C11-O11	176.1(10)
C6-Re-C12	178.6(3)	Re-C12-O12	175.8(9)
C6-Re-C8	88.4(3)	Mn-C13-O13	176.4(10)
C8-Re-C9	177.7(4)	Mn-C14-O14	176.9(9)
C6-Re-C10	87.1(4)	Mn-C15-O15	179.2(10)
C10-Re-C11	173.4(4)		

SUMMARY

Protonation enthalpies (ΔH_{HP} 's) of tertiary phosphines can be measured readily, using CF_3SO_3H in 1,2-dichloroethane as the protonating medium. The ΔH_{HP} values are excellent measures of phosphine basicity, as evidenced by comparisons with other basicity and electron donor scales. The ΔH_{HP} 's should prove to be valuable in the study of the effects of phosphine substitution on metal complexes.

The reactivities of benzene and ethylene complexes toward nucleophilic addition are correlated quite well by the force constant parameter, k_{CO}^* . In its simplicity, the predictive approach is well suited for use in synthetic organometallic chemistry.

A further application of nucleophilic addition to π -hydrocarbons was realized in the synthesis of the bimetallic complex [1-5- η -6-exo-Re(CO)₅-C₇H₈]Mn(CO)₃. This compound represents the first example of the formation of such a complex from the reaction of a metal-based nucleophile with a cyclic π -hydrocarbon.

ACKNOWLEDGMENTS

I would like to express my extreme gratitude to Professor Angelici for his guidance and support during my graduate work, as well as to the remainder of the Angelici group for their advice and also their great friendship.

Special thanks also go to The Procter and Gamble Company for a graduate research fellowship, and to Nancy Qvale for the preparation of this manuscript.