Chemical Reviews

Nucleophilic Addition to Coordinated Cyclic π-Hydrocarbons: Mechanistic and Synthetic Studies

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I. Introduction

The ability of certain transition-metal centers (ML_n) to activate normally unreactive π-hydrocarbons (R) toward nucleophilic attack has been known for several decades (eq 1; charges omitted for clarity).[1-3] In a

$$R\text{–}ML_n + Nu \rightarrow (NuR)ML_n \qquad (1)$$

complementary fashion, the stabilization of certain highly reactive carbonium ions (e.g., $C_6H_7^+$, $C_7H_7^+$) by
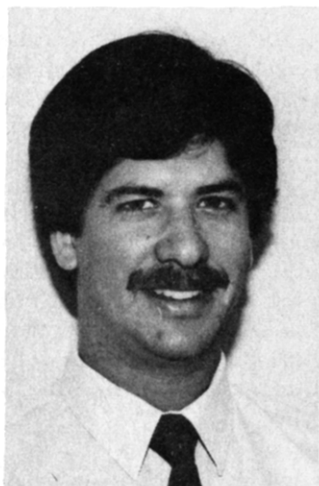
metal coordination has greatly facilitated the investigation of their electrophilic chemistry (eq 1). This area has attracted considerable interest in recent years due to its potential applications in organic synthesis. A wide range of novel routes has been developed to organic molecules often inaccessible by conventional strategies. The most thoroughly investigated stoichiometric reactions of this type involving cyclic π-hydrocarbons have been nucleophilic additions to the tricarbonyl(1-5-η-cyclohexadienyl)iron cation (1) (eq 2; Nu = hydride, amines, phosphines, alkoxides, carbanions, etc.)[4-7] and carbanion attack on the arene ring of tricarbonyl(η-arene)chromium complexes (eq 3).[8] Many of these
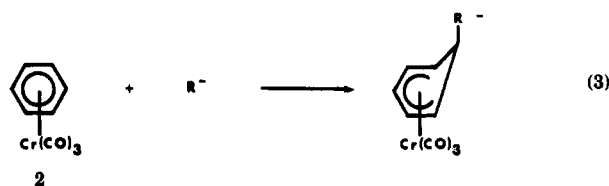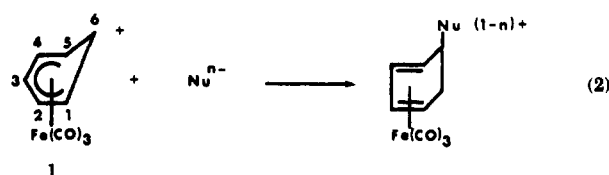
processes are characterized by high regio- and stereoselectivity. For example, in reactions 2 and 3 exo products are almost invariably obtained, as shown. The functionalized diene or dienyl ligands may be removed by a variety of oxidizing methods, in the latter case being converted with iodine to the corresponding substituted arene.

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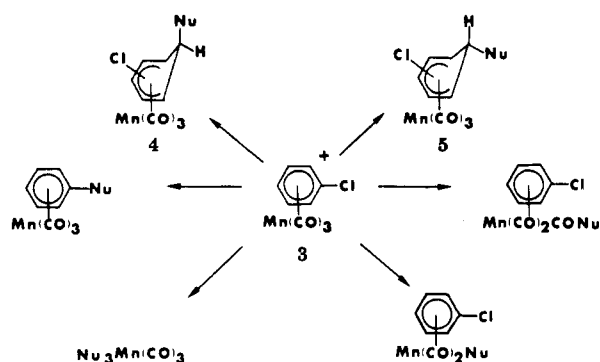
generalizations that address the mechanistic aspects of these reactions and point the way to rational synthetic applications. Herein we present a summary of present knowledge in this area. The emphasis is placed on reactions of cyclic π-hydrocarbons. First we discuss mechanistic features such as the factors controlling π-hydrocarbon reactivity (e.g., the role of the metal, other ligands, nucleophile, etc.), the relationship to organic electrophile–nucleophile combination reactions, and the correlation of π-hydrocarbon electrophilicity with results of MO calculations. This is followed by a discussion of synthetic applications, with emphasis on aromatic nucleophiles, single and double nucleophile addition to coordinated arenes, and the observation and utilization of chiral discrimination in nucleophile addition reactions.

II. Mechanistic Aspects

Nucleophiles can react with organometallic electrophiles ($R–ML_n$) by several alternative pathways which depend on the nature of the nucleophile, solvent, temperature, etc. For example, complex 3 can undergo attack at the metal with arene or CO displacement, at the ring with chloride displacement, at a carbonyl carbon, or at the ring.[13,14] All these observations can be rationalized by the general Scheme I (charges omitted for clarity). With studies that have centered on the ring addition processes, an important concern in all cases has been the possible involvement of other pathways in either intermediate or "dead-end" equilibria. Except in two instances (vide infra), exo products such as 4 are obtained rather than the endo species 5, suggesting that attack at the metal or a carbonyl does not normally occur prior to ring addition.

In the first kinetic investigation of stoichiometric nucleophile addition to a coordinated cyclic π-hydrocarbon, we examined[15] the attack of β-diketones (BH) such as acetylacetone and dimedone on complex 1 and related dienyl cations. The postulated mechanism in-

The electrophilic activation of *acyclic* π-hydrocarbons has also permitted a variety of important stoichiometric and catalytic transformations. Best known are reactions promoted by Pd(II) that have as the crucial step nucleophilic attack on an alkene or allyl ligand.[9,10] Similarly, nucleophilic additions to olefins coordinated to $Fe(CO)_2(Cp)^+$ (Fp^+) have been elegantly exploited,[11] and it appears that carbanion additions to the olefin in $Fe(CO)_4$(alkene) may prove useful.[12] Generally, nucleophilic addition to simple acyclic olefins occurs trans via an intermolecular mechanism. However, cis addition is sometimes possible via initial nucleophilic attack at the metal followed by migration to the olefin; usually this mechanism leads to overall ligand displacement as well as addition to the olefin.

Nucleophilic addition to coordinated π-hydrocarbons is a conceptually simple and very fundamental reaction in organometallic chemistry. Only recently has sufficient information become available to allow useful

SCHEME I

volves rapid preequilibrium dissociation of the β-diketone to give a reactive carbanion, which then reacts with 1 in a rate-determining fashion (eq 2, Nu = B⁻). The observation[16] of general base catalysis and the absence of a primary kinetic isotope effect using deuterated acetylacetone further supports this mechanism. Direct addition of acac⁻ to the dienyl ring of the Fe-$(CO)_3(1-5-\eta$-dienyl)⁺ cations is indicated by the dienyl reactivity sequence C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9. A more recent kinetic study has appeared[17] which examines in detail the influence of dienyl ring substituents on acac⁻ addition (vide infra).

A. Phosphorus Nucleophiles

Tertiary phosphines and phosphites have proved to be particularly convenient nucleophiles for mechanistic investigations because they generally undergo clean addition to the π-hydrocarbon ligands to yield stable phosphonium adducts.

The first system studied in detail was the reaction between $Mn(CO)_3(\eta$-arene)⁺ complexes and tri-n-butylphosphine (PBu₃).[14,18] Although other workers reported[13] $Mn(CO)_2(PBu_3)(\eta$-arene)⁺ as the product, we found that the initial reaction is rapid addition to the arene ring and that CO substitution occurs by a slower photochemical process that is quenched completely by oxygen (Scheme II). Rate law 4 (Nu = PBu₃) was obtained for the ring addition process. We also pre-

$$\text{rate} = k_1[\text{complex}][\text{Nu}] + k_{-1}[\text{complex}] \quad (4)$$

pared a series of new $Re(CO)_3(arene)$⁺ complexes and found that they undergo an analogous ring addition with PBu₃, but not the photochemical CO substitution.[14,19] The k_1 values for Re are almost the same as those found for the Mn cations.

Interestingly, addition of tertiary phosphines to the cycloheptatriene ring of the related $Mn(CO)_3(1-6-\eta$-$C_7H_8)$⁺ cation is ca. 10^4 times faster than to the benzene ring in $Mn(CO)_3(C_6H_6)$⁺.[20] This difference is primarily due, no doubt, to the resonance energy of the arene ring which is lost upon adduct formation. An X-ray structure of the triphenylphosphine adduct $Mn(CO)_3(6-PPh_3C_7H_8)$⁺ was determined[21] and shows that the cycloheptadienyl ring is not twisted as previously suggested,[22] but is quite symmetrical (Figure 1).

Detailed kinetic studies have also been carried out for the additions of a range of phosphorus nucleophiles to the following π-hydrocarbon complexes: $Fe(CO)_3$-$(1-5-\eta$-dienyl)⁺ [dienyl = C_6H_7, 2-$MeOC_6H_6$, C_7H_9, $(MeO)_xMe_yC_6H_{7-x-y}$ (x = 0, 1; y = 0-2)];[23,24] $Fe(CO)_2$-
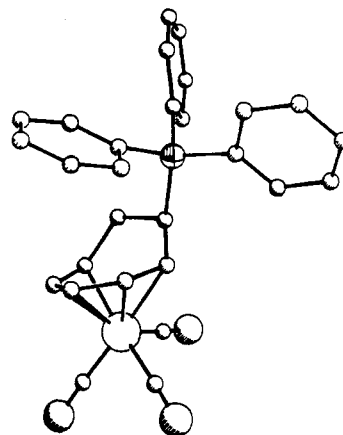
Figure 1. Structure of $[Mn(CO)_3(6-PPh_3-C_7H_8)]BF_4$.

SCHEME II
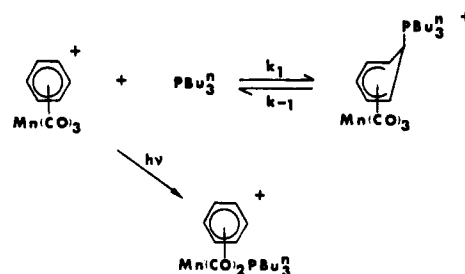
(L)(1-5-η-dienyl)$^{n+}$ (L = PPh₃, I; dienyl = C_6H_7, C_7H_9; n = 1, 0);[25] $M(Cp)(1-5-\eta$-dienyl)⁺ (M = Co, Rh; dienyl = C_6H_7, C_7H_9);[26] $Mn(CO)(NO)(L)(1-5-\eta$-6-RC_6H_6)⁺ (L = CO, PPh₃; R = Me, Ph, CN);[27] $Mn(CO)_2(NO)(1-5-\eta$-6-RC_7H_8)⁺ (R = H, Ph);[28] $M(CO)_3(\eta$-C_7H_7)⁺ (6; M = Cr, Mo, W);[29,30] $Fe(CO)(NO)(L)(\eta$-C_4H_4)⁺ (7; L = CO, $P(p$-$C_6H_4X)_3$, $P(C_2H_4CN)_3$, $AsPh_3$, $SbPh_3$);[31] $M(\eta$-$C_6H_6)_2^{2+}$ (8; M = Fe, Ru, Os);[19,32] $Fe(Cp)(CO)_2(1-2-\eta$-CH_2CHR)⁺ (R = H, Me);[33] $Co(Cp)(1-2,4-6-\eta$-$C_8H_{11})^+$,[34] $Fe(Cp)(1-6-\eta$-$C_7H_8)^{+}$.[35] Equations 5–7 illustrate typical reactions. In all cases the general rate law 4 was followed. Some typical rate and activation parameters are summarized in Table I.

$$(5)$$

$$(6)$$

$$(7)$$
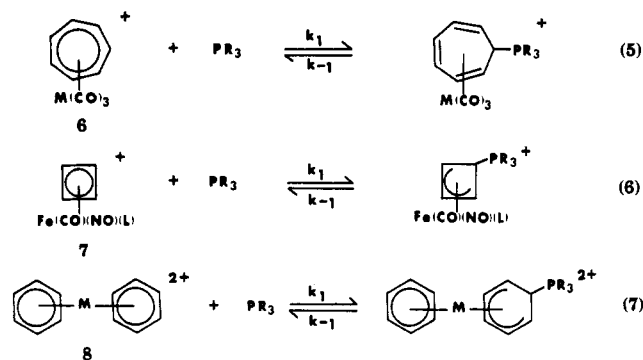
The rapid forward addition processes (k_1) are characterized by relatively low enthalpies of activation (14–50 kJ mol⁻¹) and large negative ΔS_1^* values (−30 to −130 J K⁻¹ mol⁻¹), consistent with bimolecular processes. In no instance was spectroscopic or kinetic evidence found for the presence of intermediate species, supporting the direct bimolecular mechanism for addition to the π-hydrocarbon ligands. This conclusion is further supported by (i) the small sensitivity of k_1 to the nature of the metal in the additions of PBu₃ to

TABLE I. Rate and Activation Parameters for Selected Phosphorus Donor Nucleophile Additions

complex	PR₃	solvent	k_1,[c] M⁻¹ s⁻¹	k_{-1},[c] s⁻¹	$\Delta H_1^\ddagger$, kJ mol⁻¹	$\Delta S_1^\ddagger$, J K⁻¹ mol⁻¹	$\Delta H_{-1}^\ddagger$, kJ mol⁻¹	$\Delta S_{-1}^\ddagger$, J K⁻¹ mol⁻¹	ref
Fe(CO)₃(C₆H₇)⁺	PBu₃	acetone	340000						24
	P(4-MeC₆H₄)₃	CH₃NO₂	41000		21	−84			23
	PPh₃	CH₃NO₂	16000		34	−50			23
	P(OBu)₃	CH₃NO₂	135		50	−33			23
	P(OPh)₃	CH₃NO₂	0.035						23
Fe(CO)₂(PPh₃)(C₆H₇)⁺	PPh₃	CH₃CN	120		40	−68			56
Fe(CO)₃(2-MeOC₆H₆)⁺	P(4-MeC₆H₄)₃	CH₃NO₂	8000		24	−89			23
	PPh₃	CH₃NO₂	1900		26	−91			23
	P(OBu)₃	CH₃NO₂	24						23
	P(OPh)₃	CH₃NO₂	0.0036						23
Fe(CO)₂I(C₆H₇)	PBu₃	acetone	1.8		32	−130			39
Co(Cp)(C₆H₇)⁺	PBu₃	acetone	310		29				26
Mn(CO)₂(NO)(6-PhC₆H₆)⁺	PBu₃	CH₃NO₂	1000[a]						27
	PPh₃	CH₃CN	0.56[a]						27
	P(OBu)₃	CH₃NO₂	0.30[a]						27
Mn(CO)₂(NO)(6-CNC₆H₆)⁺	PPh₃	CH₃CN	330[a]						27
Mn(CO)₂(NO)(6-MeC₆H₆)⁺	PBu₃	CH₃CN	400[a]						27
	P(2-MeOC₆H₄)₃	CH₃CN	200[a]						27
	P(4-MeOC₆H₄)₃	CH₃CN	13[a]						27
	P(4-MeC₆H₄)₃	CH₃CN	6.9[a]						27
	PPh₃	CH₃CN	2.0[a]						27
	P(OBu)₃	CH₃NO₂	0.20[a]						27
Mn(CO)(NO)(PPh₃)(6-MeC₆H₆)⁺	PBu₃	CH₃CN	2.1[a]						27
Mn(CO)(NO)(PPh₃)(C₆H₇)⁺	PBu₃	CH₃CN	4500[a]						27
	PPh₃	CH₃CN	88[a]						27
	P(OBu)₃	CH₃CN	0.85[a]						27
Fe(CO)₃(C₇H₉)⁺	PPh₃	CH₃CN	215		41	−60			23
	P(4-MeC₆H₄)₃	acetone	420						25
Fe(CO)₂I(C₇H₉)	PBu₃	acetone	0.020						39
Co(Cp)(C₇H₉)⁺	PBu₃	acetone	1.5						26
Mn(CO)₂(NO)(C₇H₉)⁺	P(2-MeOC₆H₄)₃	CH₃NO₂	27000[a]						28
	P(4-MeOC₆H₄)₃	CH₃NO₂	1100[a]						28
	P(4-MeC₆H₄)₃	CH₃NO₂	590[a]						28
	PPh₃	CH₃NO₂	210[a]						28
	P(OBu)₃	CH₃NO₂	3.5[a]						28
	P(C₂H₄CN)₃	CH₃NO₂	2.7[a]						28
Mn(CO)₃(C₆H₆)⁺	PBu₃	acetone	770	1.8	31	−84	80	34	14
	PBu₃	CH₃NO₂	2000[a]	5.0[a]					19
Mn(CO)₃(MeC₆H₅)⁺	PBu₃	CH₃NO₂	1500[a]	7.0[a]					19
Re(CO)₃(C₆H₆)⁺	PBu₃	CH₃NO₂	1800[a]	4.0[a]					19
Re(CO)₃(MeC₆H₅)⁺	PBu₃	CH₃NO₂	750[a]	5.2[a]					19
Fe(C₆H₆)₂²⁺	PPh₃	CD₃CN	320000	2300	18	−80	52	−4	32
	P(OBu)₃	CH₃CN	1550[a]						19
Ru(C₆H₆)₂²⁺	PPh₃	CD₃CN	8400	4100	30	−67	51	0	32
	P(OBu)₃	CH₃CN	70[a]	0.08[a]					19
Os(C₆H₆)₂²⁺	PPh₃	CD₃CN	1500	1400	37	−59	58	13	32
	P(OBu)₃	CH₃CN	24[a]	0.06[a]					19
Mn(CO)₃(C₇H₈)⁺	P(4-ClC₆H₄)₃	CH₃NO₂	53000		21	−84			20
	P(C₂H₄CN)₃	CH₃NO₂	8300[a]						28
	P(OBu)₃	CH₃NO₂	7000[a]						28
	P(2-MeC₆H₄)₃	CH₃NO₂	310	0.15	24	−110	81	13	20
	P(OPh)₃	CH₃NO₂	3.1[a]						28
Mn(CO)₂(PPh₃)(C₇H₈)⁺	PPh₃	CH₃NO₂	21000[a]						28
	P(OBu)₃	CH₃NO₂	120[a]						28
	P(C₂H₄CN)₃	CH₃NO₂	94[a]						28
Fe(Cp)(C₇H₈)⁺	PBu₃	acetone	2200[a]						35
	P(OBu)₃	acetone	0.50[a]						35
Cr(CO)₃(C₇H₇)⁺	PBu₃	acetone	41000		25	−71			29, 30
	P(4-MeC₆H₄)₃	acetone	8600	22	29	−71	49	−54	30
	PPh₃	acetone	890	21					30
	P(OBu)₃	acetone	8.5		41	−88			30
Mo(CO)₃(C₇H₇)⁺	PBu₃	acetone	7500[b]		19	−100			29
W(CO)₃(C₇H₇)⁺	PBu₃	acetone	3900[b]		40	−31			30
Fe(CO)₂(NO)(C₄H₄)⁺	PPh₃	acetone	44000		24	−73			20, 31
	P(4-ClC₆H₄)₃	acetone	4000	2.0	25	−92	70	0	20
	P(OBu)₃	CH₃NO₂	510[a]						31
Fe(CO)(NO)(PPh₃)(C₄H₄)⁺	PBu₃	CH₃NO₂	120000[a]						31
	PPh₃	CH₃NO₂	1700[a]	44[a]					31
	P(OBu)₃	CH₃NO₂	9.8[a]	0.03[a]					31
Fe(Cp)(CO)₂(C₂H₄)⁺	PPh₃	acetone	120		42	−63			33
	P(OEt)₃	acetone	0.99						33
	P(OPh)₃	acetone	0.0006						33
Fe(Cp)(CO)₂(CH₂CHMe)⁺	PBu₃	acetone	140						33
	PPh₃	acetone	3.8						33
Co(Cp)(C₈H₁₁)⁺	PBu₃	acetone	48000		14				34
	PPh₃	acetone	1200	3.8	21	−110	86	60	34

[a]Temperature 25 °C. [b]Temperature 0 °C. [c]Temperature at 20 °C unless otherwise indicated.

TABLE II. LFERs between log k_1 and log K_{eq} for Nucleophilic Addition Reactions

complex	variable nucleophile	slope, m	ref
$Fe(CO)(NO)(PPh_3)(C_4H_4)^+$	PR_3	0.38	31
$Cr(CO)_3(C_7H_7)^+$	PR_3	0.66	30
$Fe(CO)_3(C_6H_7)^+$	XC_5H_4N	0.38	30

TABLE III. Hammett σ Plots for Nucleophilic Addition Reactions

complex	nucleophile	solvent	slope, ρ	ref
EtI	$PEt_2(C_6H_4X)$	acetone	−1.1	38
	XC_5H_4N	CH_3CN	−2.3	52, 53
$Fe(CO)_3(C_6H_7)^+$	$P(C_6H_4X)_3$	acetone	−1.3[a]	24
	XC_5H_4N	CH_3CN	−2.4	30
$Fe(CO)_3(2\text{-MeOC}_6H_6)^+$	$XC_6H_4NH_2$	CH_3CN	−2.7	46, 49b
$Fe(CO)(NO)\-(PPh_3)(C_4H_4)^+$	$P(C_6H_4X)_3$	CH_3NO_2	−1.0[a]	31
$Cr(CO)_3(C_7H_7)^+$	$P(C_6H_4X)_3$	acetone	−1.6[a]	30
$Mn(CO)_2(NO)\-(6\text{-MeC}_6H_6)^+$	XC_5H_4N	CH_3CN	−2.4	27
	$P(C_6H_4X)_3$	CH_3CN	−1.0[a]	27

[a] This value is the total slope divided by 3 (the number of X groups).

**TABLE IV. Anchimeric Effect in the Reactions of $P(C_6H_4X)_3$ with Various Substrates**

substrate	$k_{2\text{-MeO}}/k_{4\text{-MeO}}$	$k_{2\text{-MeO}}/k_H$	$k_{2\text{-MeO}}/k_{2\text{-Me}}$	ref
$PhCH_2Cl^a$	4	27	610	38b
$Fe(CO)_3(C_6H_7)^{+\,b}$	11	91	89000	24
$Mn(CO)_2(NO)(6\text{-MeC}_6H_6)^{+\,c}$	16	100		27
$Mn(CO)_2(NO)(C_7H_9)^{+\,d}$	24	130		28

[a] Solvent benzene/methanol (3:2) at 31 °C. [b] Solvent acetone at 0 °C. [c] Solvent acetonitrile at 25 °C. [d] Solvent nitromethane at 25 °C.

cations $M(CO)_3(\eta\text{-arene})^+$ (M = Mn, Re), 6 (M = Cr, Mo, W), and $M(Cp)(1\text{-}5\text{-}\eta\text{-}C_6H_7)^+$ (M = Co, Rh) (vide infra, Table IX), (ii) the general marked decrease in k_1 down the series $C_6H_7 > 2\text{-MeOC}_6H_6 > C_7H_9$ for addition to dienyl ligands (vide infra), and (iii) our X-ray structural studies[21] of the phosphonium adducts [Mn(CO)$_3$(6-PPh$_3$C$_7$H$_8$)][BF$_4$] and [Mn(CO)$_2$(NO)(5-PBu$_3$-6-PhC$_6$H$_6$)][PF$_6$], which confirm an exo configuration for the phosphine substituents. Similar exo addition of tertiary phosphines to coordinated cyclohexadienyl and cyclobutadiene rings has been established by others[36,37] from X-ray studies of the adducts [Fe(CO)$_3$(6-PPh$_3$C$_6$H$_7$)][BF$_4$] and [Fe(CO)$_2$(NO)(4-PMe$_3$C$_4$H$_4$)][PF$_6$].

As expected, considerably higher $\Delta H_{-1}^{\ddagger}$ values and less negative or even positive $\Delta S_{-1}^{\ddagger}$ values were generally found for the reverse dissociation (k_{-1}) of the phosphonium adducts (Table I). In certain cases the position of the transition state for adduct formation could be estimated from the slopes of linear free energy relationships (LFERs) between log k_1 and log K_{eq} as PR_3 varied (Table II). The relatively small slope of 0.38 found for reaction 6 suggests that P–C bond formation and sp^2 to sp^3 rehybridization is approximately one-third complete in the transition state.[31] In contrast, a fairly "late" transition state with considerable bond formation is indicated for reaction 5 (M = Cr) from its slope of 0.66.[30] These conclusions are further supported by the relative magnitudes of the Hammett slopes given
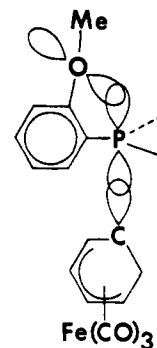
Figure 2. Anchimeric assistance with $P(2\text{-MeOC}_6H_4)_3$ as the nucleophile.

SCHEME III
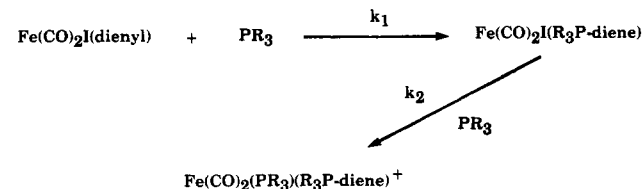
in Table III. An "early" transition state has previously been established for the related reactions of triarylphosphines with EtI and PhCH$_2$Cl for which $\rho = -1.1$ and −1.2, respectively.[38]

An unusual feature of the triarylphosphine additions to $Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)^+$ (1) is the remarkable reactivity of $P(2\text{-MeOC}_6H_4)_3$.[24] On classical electronic and steric grounds one would expect it to be less nucleophilic than $P(4\text{-MeOC}_6H_4)_3$. However, as shown in Table IV, the reactivity sequence $P(2\text{-MeOC}_6H_4)_3 > P(4\text{-MeOC}_6H_4)_3 > PPh_3$ (91:8:1) was observed towards cation 1. Following McEwen et al.,[38b] who made similar observations for the reactions of $P(C_6H_4X)_3$ nucleophiles with benzyl chloride, we explain the unexpected reactivity of $P(2\text{-MeOC}_6H_4)_3$ in terms of anchimeric assistance in which a pair of 2p electrons on the methoxy oxygen overlap with a vacant 3d orbital on the phosphorus.[24] This interaction helps to delocalize the positive charge buildup on the phosphorus center in the transition state (Figure 2). A similar anchimeric effect was observed with the cation $Mn(CO)_2(NO)(1\text{-}5\text{-}\eta\text{-}6\text{-MeC}_6H_6)^+$ (Table IV).[27]

From our experience with the wide range of organometallic substrates in Table I it appears that addition of tertiary phosphines to the π-hydrocarbon ligand (C_3H_5, C_4H_4, C_6H_6, C_6H_7, C_7H_7, C_7H_8, C_7H_9, and C_8H_{11}) will in general be kinetically favored over attack at the metal unless a particularly labile ligand such as acetone is present. This is due to the relatively low $\Delta H_1^{\ddagger}$ values for the forward rate constant k_1 (Table I). A demonstration of this general feature is given by the reactions of PBu_3 and $P(i\text{-Pr})_3$ with $Fe(CO)_2I(1\text{-}5\text{-}\eta\text{-dienyl})$ (dienyl = C_6H_7, C_7H_9) where, unusually, nucleophilic attack occurs at both the hydrocarbon ligand and the metal center. These processes have been shown to occur via two distinct steps (Scheme III).[39] The kinetically favored addition (k_1) to the C_6H_7 ligand has a much lower $\Delta H_1^{\ddagger}$ value (32 kJ mol^{-1}) than the subsequent iodide substitution process $(\Delta H_2^{\ddagger} = 91$ kJ mol^{-1}). In certain cases, such as the reactions of trialkylphosphines with cations $Mn(CO)_3(\eta\text{-}C_6H_6)^+$ and $Mo(CO)_3(\eta\text{-}C_7H_7)^+$, where only carbonyl or π-hydrocarbon displaced products were isolated by others,[13,40]
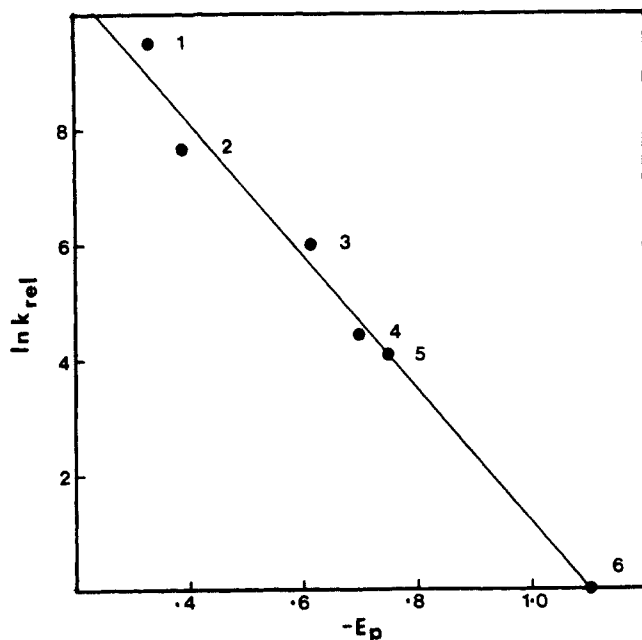
Figure 3. Correlation of rate constants for phosphorus nucleophile addition with reduction potentials for planar cyclic π-hydrocarbon complexes. (1) $[Fe(C_6H_6)_2](PF_6)_2$; (2) $[Fe(CO)_2(NO)(C_4H_4)]PF_6$; (3) $[Ru(C_6H_6)_2](PF_6)_2$; (4) $[Cr(CO)_3(C_7H_7)]BF_4$; (5) $[Fe(CO)(NO)(PPh_3)(C_4H_4)]PF_6$; (6) $[Mn(CO)_3(C_6H_6)]PF_6$.

we have shown that reversible and rapid ring addition is the initial reaction.[14,18,41] Examination of other apparent contradictions in the synthetic literature may well reveal similar conflict between kinetic and thermodynamic products.

Arbusov rearrangement to give the corresponding phosphonates was observed for some of the phosphonium adducts with tertiary phosphites. For example, the salts $[Fe(CO)_3(5\text{-}P(OBu)_3\text{diene})][BF_4]$ (diene = C_6H_7 or 2-MeOC_6H_6), although stable for long periods at room temperature as solids, eliminate a butyl group in a FD mass spectrometer.[23] More significantly, the highly electrophilic $M(\eta\text{-arene})_2{}^{2+}$ cations (M = Fe, Ru, Os) rapidly catalyze the hydrolysis of trialkyl phosphites to dialkyl phosphites (eq 8).[42] The mechanism of this reaction involves addition of $P(OR)_3$ to the coordinated arene, water-induced conversion to the phosphonate adduct with liberation of alcohol and H^+ ions, and finally cleavage to the dialkyl phosphite and regeneration of $M(\eta\text{-arene})_2{}^{2+}$.

$$P(OR)_3 + H_2O \xrightarrow[\text{CH}_3\text{CN}]{M(\text{arene})_2{}^{2+}} HP(O)(OR)_2 + ROH \quad (8)$$
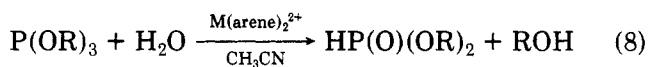
An alternative to the classical acid–base (two-electron donation) type mechanism discussed above for tertiary phosphine additions is an electron-transfer mechanism involving rate-determining electron transfer to the electrophile, followed by rapid reaction of the radicals. For example, recent studies have shown that hydride addition to $Fe(Cp)(arene)^+$ cations proceeds via initial electron transfer under some conditions.[43] With phosphine nucleophiles, we found an excellent correlation between relative reactivity and the reduction potentials for a series of complexes containing planar π-hydrocarbon rings, Figure 3 and eq 9.[19] E_p and k_{rel}

$$\ln k_{rel} = 11.7E_p + 12.9 \quad (9)$$

span a range of more than 0.7 V and 10^4, respectively.

SCHEME IV

9

10
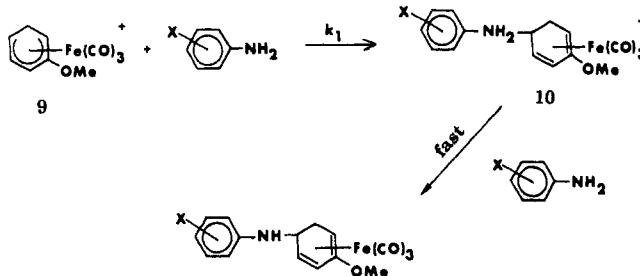
However, eq 9 is *not* evidence for an electron-transfer mechanism because the slope of 11.7 is considerably smaller than would be expected for the rate-determining step in a highly endoergic electron transfer process.[44,45] Nevertheless, the correlation shown in Figure 3 is useful since it suggests that reduction potential data can be used to predict reactivities.

B. Amine Nucleophiles

Synthetic and mechanistic studies with amines have utilized substituted pyridines, imidazoles, and anilines to examine the effect of variation in the steric and electronic properties of the nucleophile. Pyridines generally react cleanly to give stable pyridinium salts, e.g., eq 2 (Nu = XC_5H_4N, $X_2C_5H_3N$, $X_3C_5H_2N$) and obey rate law 4.[27,30,46,47] The reactions with the related imidazole nucleophiles[35,48] and with primary and secondary amines (anilines,[27,46,49] amino acid esters,[50] morpholine[51]) occur in two steps as illustrated in Scheme IV. Except for the less basic anilines, which gave more complex equilibrium behavior,[49b] the reactions with amine nucleophiles proceed to completion and obey rate law 4 with k_{-1} = 0. These observations can be rationalized in terms of rate-determining formation of cationic intermediates such as 10, followed by rapid base-catalyzed deprotonation to yield the neutral product. Typical rate and activation parameters for amine additions (k_1) to $Fe(CO)_3(1\text{-5-}\eta\text{-dienyl})^+$ and $Mn(CO)_2(NO)(1\text{-5-}\eta\text{-dienyl})^+$ cations are summarized in Table V.

As with the phosphorus nucleophiles discussed above, the amine additions generally show low enthalpies of activation (8–45 kJ mol^{-1}) and large negative $\Delta S_1{}^‡$ values (–32 to –150 J K^{-1} mol^{-1}), consistent with simple bimolecular processes. Again no spectroscopic or kinetic evidence was found for intermediates. With the iron dienyl substrates the order $C_6H_7 > 2\text{-MeOC}_6H_6 > C_7H_9$ was again observed. Both amine and phosphine nucleophiles react more rapidly with a C_6H_7 ring compared to a C_7H_9 ring; the $k_1(C_6H_7)/k_1(C_7H_9)$ ratio is in the range 16–47 for amines and in the range 60–200 with the bulkier tertiary phosphines (vide infra).

For reaction 2 with substituted pyridine nucleophiles a LFER was found between log k_1 and log K_{eq} (Table II).[30] The slope of 0.38 suggests a relatively early transition state with N–C bond formation about one-third complete. This conclusion is also supported by the Hammett slope ρ of –2.4, which is very similar to that reported[52] for the related quaternization of ethyl iodide in the same solvent (ρ = –2.3; Table III). For the latter reaction a wide variety of experimental evidence has clearly established an "early" transition state.[53] Similarly, the large negative Hammett slope of

TABLE V. Rate and Activation Parameters for Typical Reactions with Amine Nucleophiles in Acetonitrile

complex	amine	k_1,[d] M⁻¹ s⁻¹	ΔH_1^*, kJ mol⁻¹	$\Delta S_1^*/$ J K⁻¹ mol⁻¹	ref
Fe(CO)₃(C₆H₇)⁺	morpholine	265000			51
	2-methylimidazole	14000			48
	N-methylimidazole	10000			48
	imidazole	4400			48
	H₂NCH(Me)CO₂Et	5000	15	−120	50
	H₂NCH(Ph)CO₂Et	3500	19	−110	50
	H₂NCH(CH₂Ph)CO₂Me	2950	16	−120	50
	C₅H₅N	2200	37	−45	46, 47
	2-MeC₅H₄N	770	31	−74	47
	2,6-Me₂C₅H₃N	6.7	46	−61	47
	C₆H₅NH₂	2000			49b
	4-MeC₆H₄NH₂	6500	24	−82	49a
	2-MeC₆H₄NH₂	690	35	−60	49b
Fe(CO)₃(2-MeOC₆H₇)⁺	morpholine	55000			51
	imidazole	380	33	−72	48
	H₂NCH(Me)CO₂Et	700	23	−105	50
	H₂NCH(Ph)CO₂Et	500	26	−100	50
	H₂NCH(CH₂Ph)CO₂Me	610	24	−110	50
	C₅H₅N	425	36	−63	47
	2-MeC₅H₄N	96	40	−60	47
	C₆H₅NH₂	370	17	−130	46, 49b
	4-MeC₆H₄NH₂	1000	42	−32	49a
	2-MeC₆H₄NH₂	56	45	−45	49b
Fe(CO)₃(C₇H₉)⁺	imidazole	93			48
	C₅H₅N	140	26	−110	47
	2-MeC₅H₄N	22	31	−100	47
	2,6-Me₂C₅H₃N	0.42	45	−88	47
	4-MeC₆H₄NH₂	390	28	−93	49a
	2-MeC₆H₄NH₂	43	30	−100	49b
Fe(CO)₂(PPh₃)(C₇H₉)⁺	morpholine	40			51
Fe(Cp)(C₇H₈)⁺	imidazole	67[a,b]			35
Mn(CO)₂(PPh₃)(C₇H₈)⁺	3-MeC₅H₄N	40000[a,c]			28
Mn(CO)₂(NO)(C₇H₉)⁺	imidazole	370[a,c]			28
	C₅H₅N	350[a,c]			28
	3-MeC₅H₄N	550[a,c]			28
Mn(CO)₂(NO)(6-MeC₆H₆)⁺	imidazole	74[a]			27
	C₅H₅N	13[a]			27
	4-MeC₅H₄N	33[a]			27
	C₆H₅NH₂	1.2[a]			27
Mn(CO)₂(NO)(6-PhC₆H₆)⁺	C₅H₅N	6.8[a]			27
	4-MeC₅H₄N	25[a]			27
	C₆H₅NH₂	1.6[a]			27
Mn(CO)₂(NO)(6-CNC₆H₆)⁺	4-MeC₆H₄NH₂	350[a]			27
Mn(CO)₂(NO)(2-MeO-6-PhC₆H₆)⁺	C₆H₅NH₂	0.15[a]			27
PdCl₂(1,5-COD)	PhCH₂NH₂	7200[b]			56
	t-BuNH₂	520[b]			56

[a] Temperature 25 °C. [b] Acetone solvent. [c] Nitromethane solvent. [d] Temperature at 0 °C unless otherwise specified.

−2.7 found for the additions of substituted anilines to cation 9 (Scheme IV) suggests significant N–C bond formation and buildup of positive charge on the aniline nitrogen in the transition state.[49b] A very similar ρ value has been reported for the reaction of substituted anilines with benzoyl chloride.[54]

Not included in Table V are data for the addition of cyclohexylamine to the π-hydrocarbon ligands of W-(CO)₃(η-C₇H₇)⁺,[55] PdCl₂(η⁴-1,5-COD), and MBr₂(η⁴-1,5-COD) (M = Pd(II), Pt(II)),[56] for which a second-order dependence of k_{obsd} on [RNH₂] was observed. This behavior can be explained in terms of steady-state formation of amine adducts followed by base-catalyzed deprotonation, e.g., Scheme V. Assuming the steady-state formation of zwitterion 11, and the condition $k_2[C_6H_{11}NH_2] \ll k_{-1}$, this mechanism leads to expression 10. For the MBr₂(η⁴-1,5-COD) complexes,

$$k_{obsd} = K_1 k_2 [C_6H_5NH_2]^2 \qquad (10)$$

$K_1 k_2$ values of 1.9×10^6 and 2.6×10^4 M⁻² s⁻¹ were calculated at 0 °C in acetone for the Pd(II) and Pt(II) substrates, respectively. These results provide the first

SCHEME V
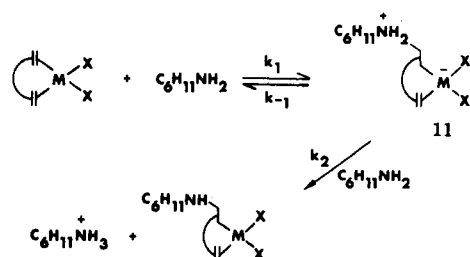
quantitative demonstration of the greater effectiveness of Pd(II) compared to Pt(II) in activating olefins towards nucleophilic attack (factor of 70).

C. Anionic Nucleophiles

Very few quantitative studies exist describing the addition of anions to coordinated π-hydrocarbons (Table VI). For the first system studied, namely attack on the arene cation Mn(CO)₃(η-C₆H₆)⁺, reaction with N₃⁻ was too rapid to follow by stopped-flow techniques,

TABLE VI. Kinetic Data for the Addition of Anions to M(CO)₃(π-hydrocarbon)⁺ in Water

substrate[a]	nucleo-phile	k_1, $M^{-1} s^{-1}$	rel k_1	ref
$Mn(CO)_3(C_6H_6)^+$	N_3^-	$>10^5$	$>10^5$	57
	OH^-	290	360	57
	CN^-	0.8	1	57
$Fe(CO)_3(C_6H_7)^+$	N_3^-	2050	1	30, 58
	OH^-	8800	4.3	58
$Fe(CO)_3(C_7H_9)^+$	OH^-	4000		30

[a] Mn results at 20 °C and ionic strength 0.25 M; Fe results at 0 °C and 0 ionic strength.

SCHEME VI
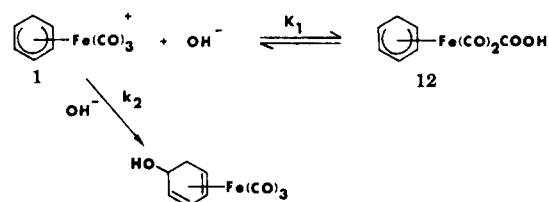
indicating the unusual reactivity order $N_3^- \gg OH^- \gg CN^-$ (vide infra).[57] Analogous studies of hydroxide ion attack on dienyl cation **1** revealed more complex behavior.[58] The observed kinetics fit the mechanism shown in Scheme VI, in which rapid formation of a carboxylic acid complex **12** in a "dead-end" preequilibrium (K_1) is followed by slower but irreversible hydroxide addition (k_2) to the cyclohexadienyl ring. K_1 and k_2 values of 70 M^{-1} and 8800 $M^{-1} s^{-1}$ were calculated at 0 °C. The formato species **12** could be isolated as an air-sensitive solid (admixed with **1**), showing an IR $\nu(CO)$ band at 1658 cm⁻¹ attributable to the coordinated COOH group. Similar alkoxycarbonyl complexes of the type $Fe(CO)_2(COOR)(1,5-\eta-C_7H_9)$ (R = Me, Et) have recently been prepared via attack of RO^- on $Fe(CO)_3$-$(1-5-\eta-C_7H_9)^+$.[59]

D. Aromatic Nucleophiles

We have shown that organometallic cations such as **1** can act as rather exotic electrophiles towards a variety of activated aromatic substrates, providing novel routes to substituted arenes and heterocyclic molecules, e.g., eq 11 (ArX = pyrrole, indole, furan, thiophene, N,N-dimethylaniline, di- and trimethoxybenzenes, and $RC_6H_4M'Me_3$ (M' = Si, Sn, Ge, Pb)).[60-70]
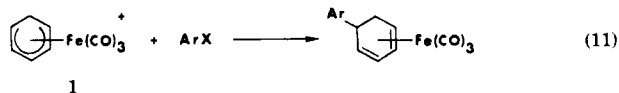
Representative kinetic data are summarized in Table VII for the most common situation in which the simple rate law 4 (Nu = ArX; k_{-1} = 0) was obeyed. These results together with those for all other aromatic substrates may be accommodated by the general mechanism outlined in Scheme VII (M = Fe, Ru, Os; X = H or M'Me₃ (M' = Si, Sn, Ge, Pb)) for activated arenes. An analogous mechanism can be envisaged for heterocyclic substrates. Proton loss (k_3) can be assisted by either excess nucleophile, e.g., N,N-dimethylaniline, or the solvent, and is possibly further facilitated by the known[71] electron-withdrawing character of the (diene)Fe(CO)₃ moiety. Rapid proton loss was confirmed for the reactions of **1** with pyrrole and indole and of

SCHEME VII
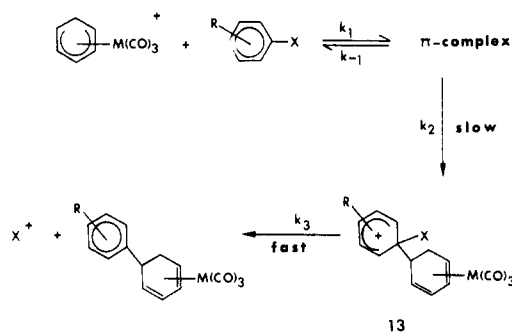
$Ru(CO)_3(1-5-\eta-C_6H_7)^+$ with pyrrole by the absence of primary kinetic isotope effects using deuterated pyrrole and indole.[62,63] In only one instance, namely the reaction of $Cr(CO)_3(\eta-C_7H_7)^+$ with N,N-dimethylaniline, is slow proton loss implicated.[66] This latter system follows a complex two-term rate law, including a second-order term in $[Me_2NC_6H_5]$.

No spectroscopic or kinetic evidence was found for a π-complex intermediate in any of the reactions listed in Table VII. Assuming that formation of the Wheland type σ-intermediate **13** is rate determining, and that the K_1 value for preequilibrium formation of the π-complex is small, the results are given by eq 12. The activation

$$k_{obsd} = (k_1 k_2 / k_{-1})[ArX] \qquad (12)$$

parameters in Table VII are consistent with such a mechanism. The $\Delta H_{obsd}^{\ddagger}$ values for the composite constants $k_1 k_2 / k_{-1}$ are in general considerably higher than those found for the simple bimolecular addition of phosphorus and nitrogen donor nucleophiles (Tables I and V). The large negative $\Delta S_{obsd}^{\ddagger}$ values are equal to $\Delta S_1° + \Delta S_2^{\ddagger}$, where $\Delta S_1°$ is the standard entropy change for preequilibrium formation of the π-complex and $\Delta S_2^{\ddagger}$ is the entropy of activation for the $\pi \rightarrow \sigma$ conversion.

Support for the involvement of π-complexes, rather than simple rate-determining formation of the σ-complex from separated reactants, comes from the marked dependence of the complex electrophilicity order on the nature of the aromatic reactant. For example, k_{Fe}/k_{Ru} quotients of 4500, 45, 18, and 2 have been found for the reactions of $M(CO)_3(1-5-\eta-C_6H_7)^+$ (M = Fe, Ru) with pyrrole, N,N-dimethylaniline, 2-methylfuran, and 4-$Me_2NC_6H_4SnMe_3$, respectively.[63,65,69] These variations may be explained in terms of changes in the π-complex equilibrium constant $(K_1 = k_1/k_{-1})$. In contrast, for reactions with phosphine, phosphite, and nitrogen donor nucleophiles, where π-complexes of the type in Scheme VII seem unlikely, the organometallic cation electrophilicity order is virtually nucleophile independent (Tables I, V, and VIII below).

For the reactions of various di- and trimethoxybenzenes with **1**, of indole with $Ru(CO)_3(1-5-\eta-C_6H_7)^+$, and of N,N-dimethylaniline with $Mn(CO)_3(1-6-\eta-C_7H_8)^+$ there is strong kinetic evidence for π-complex intermediates.[62,67,70] Unlike the systems in Table VII, plots of k_{obsd} vs. [ArX] for these reactions are curved and are consistent with expression 13, which is predicted by Scheme VII. Despite the significant con-

$$k_{obsd} = \frac{k_2 K_1 [ArX]}{1 + K_1 [ArX]} \qquad (13)$$

TABLE VII. Rate and Activation Parameters for Selected Reactions with Aromatic Nucleophiles in Nitromethane

complex	aromatic nucleophile	$10^6 k,$[f] $M^{-1}\ s^{-1}$	rel k	$\Delta H^{\ddagger}_{obsd},$ kJ mol^{-1}	$\Delta S^{\ddagger}_{obsd},$ J K^{-1} mol^{-1}	ref
$Fe(CO)_3(C_6H_7)^+$	pyrrole	890000	3.2×10^6	47	−96	63
	indole	560000	2.0×10^6	43.5	−110	62
	$4\text{-Me}_2NC_6H_4SnMe_3$	100000	3.6×10^5	71	−43	69
	$Me_2NC_6H_5$	61000	2.2×10^5	53	−100	65
	$Me_2NC_6H_5$	28000[a]		56[a]	−99[a]	64
	$4\text{-Me}_2NC_6H_4SiMe_3$	34000	1.2×10^5	72	−46	69
	2-methylfuran	390	1.4×10^3			63
	$4\text{-MeOC}_6H_4SnMe_3$	170	6.2×10^2			69
	2-Me_3Si-furan	100	3.6×10^2			69
	2-methylthiophene	9.2	33			63
	furan	6.4	23			63
	$4\text{-MeOC}_6H_4SiMe_3$	4.2	15			69
	2-Me_3Si-thiophene	2.0	7.2			69
	$4\text{-CF}_3C_6H_4SnMe_3$	1.0	3.6			69
	thiophene	0.28	1			63
$Fe(CO)_3(2\text{-MeOC}_6H_6)^+$	indole	16000[b]		46	−120	62
	2-methylindole	120000[b]				62
	N-methylindole	97000[b]				62
	$Me_2NC_6H_5$	12000				64
	$4\text{-Me}_2NC_6H_4SnMe_3$	6100				69
	$4\text{-Me}_2NC_6H_4SiMe_3$	1900				69
$Ru(CO)_3(C_6H_7)^+$	pyrrole	198		41	−190	63
	indole	c		60.5	−100	62
	$Me_2NC_6H_5$	1400		63	−100	64, 65
	2-methylfuran	22				63
$Os(CO)_3(C_6H_7)^+$	$Me_2NC_6H_5$	4500				64
$Fe(CO)_2(NO)(C_4H_4)^+$	$Me_2NC_6H_5$	14000[d]		47[a]	−130[a]	68
$Mn(CO)_3(C_7H_8)^+$	pyrrole	680000[d,e]				70
	N-methylpyrrole	12000000[d,e]				70

[a] CH_3CN solvent. [b] Temperature 20 °C. [c] k_{obsd} has the form $x[\text{indole}]/(y + z[\text{indole}])$. [d] Temperature 25 °C. [e] k_{obsd} becomes independent of [Nu] at high nucleophile concentrations. [f] Temperature at 45 °C unless otherwise specified.

TABLE VIII. Relative Electrophilicies of π-Hydrocarbon Complexes Toward Phosphorus Nucleophiles at 20 °C

complex	relative k_1[a]	ref
$Mn(CO)_3(C_7H_8)^+$	$2.0 \times 10^9 (2.0 \times 10^9)$	20, 27, 28
$Fe(C_6H_6)_2^{2+}$	$8.3 \times 10^8 (3.0 \times 10^8)$	19, 32
$Fe(CO)_2(NO)(C_4H_4)^+$	$1.4 \times 10^8 (7.0 \times 10^7)$	31
$Mn(CO)_2(PPh_3)(C_7H_8)^+$	$3.0 \times 10^7 (3.0 \times 10^7)$	28
$Fe(CO)_3(C_6H_7)^+$	$2.8 \times 10^7 (2.8 \times 10^7)$	23, 24
$Ru(C_6H_6)_2^{2+}$	$2.7 \times 10^7 (9.0 \times 10^6)$	19, 32
$Os(C_6H_6)_2^{2+}$	$6.9 \times 10^6 (2.3 \times 10^6)$	19, 32
$Fe(CO)_3(2\text{-MeOC}_6H_6)^+$	$5.3 \times 10^6 (1.1 \times 10^7)$	23
$Fe(CO)(NO)(PPh_3)(C_4H_4)^+$	$3.0 \times 10^6 (1.5 \times 10^6)$	31
$Cr(CO)_3(C_7H_7)^+$	$3.0 \times 10^6 (8.6 \times 10^5)$	29, 30
$Co(Cp)(C_8H_{11})^+$	$2.7 \times 10^6 (5.4 \times 10^6)$	34
$Mn(CO)_2(NO)(6\text{-PhC}_7H_8)^+$	$1.3 \times 10^6 (2.6 \times 10^6)$	28
$Mn(CO)_2(NO)(6\text{-CNC}_6H_6)^+$	$1.2 \times 10^6 (1.2 \times 10^6)$	27
$Mo(CO)_3(C_7H_7)^+$	$1.0 \times 10^6 (3.2 \times 10^5)$	29
$Mn(CO)_2(NO)(C_7H_9)^+$	$6.2 \times 10^5 (6.2 \times 10^5)$	28
$W(CO)_3(C_7H_7)^+$	$5.9 \times 10^5 (1.7 \times 10^5)$	30
$Fe(CO)_3(C_7H_9)^+$	$4.7 \times 10^5 (4.7 \times 10^5)$	23, 25
$Fe(CO)_2(PPh_3)(C_6H_7)^+$	$4.2 \times 10^5 (4.2 \times 10^5)$	56
$Fe(Cp)(CO)(C_2H_4)^+$	$4.1 \times 10^5 (4.1 \times 10^5)$	33
$Mn(CO)(NO)(PPh_3)(C_6H_7)^+$	$3.0 \times 10^5 (3.0 \times 10^5)$	27
$Fe(Cp)(C_7H_8)^+$	$1.8 \times 10^5 (1.8 \times 10^5)$	35
$Mn(CO)_2(NO)(6\text{-PhC}_6H_6)^+$	$6 \times 10^4 (6 \times 10^4)$[b]	27
$Mn(CO)_3(C_6H_6)^+$	$5.0 \times 10^4 (1.7 \times 10^4)$	14
$Re(CO)_3(C_6H_6)^+$	$4.5 \times 10^4 (1.5 \times 10^4)$	14, 19
$Mn(CO)_2(NO)(6\text{-MeC}_6H_6)^+$	$4 \times 10^4 (4 \times 10^4)$[b]	27
$Co(Cp)(C_6H_7)^+$	$1.5 \times 10^4 (1.5 \times 10^4)$	26
$Fe(Cp)(CO)_2(CH_2CHMe)^+$	$1.3 \times 10^4 (2.6 \times 10^4)$	33
$Mn(CO)(NO)(PPh_3)\text{-}$ $(6\text{-MeC}_6H_6)^+$	$1 \times 10^2 (1 \times 10^2)$[b]	27
$Fe(CO)_2I(C_6H_7)$	$9.0 \times 10^1 (9.0 \times 10^1)$	39
$Co(Cp)(C_7H_9)^+$	$7.5 \times 10^1 (7.5 \times 10^1)$	26
$Fe(CO)_2I(C_7H_9)$	1 (1)	39

[a] Values in parentheses are adjusted for statistical factors. [b] Value is sensitive to steric bulk of the nucleophile.

centrations of the intermediates calculated to be present at the start of these reactions (K_1 = 1.4–12), the only

$\nu(CO)$ bands observed are assignable to the original cations and the products. This is not surprising for a loose π-complex, but is inconsistent with an intermediate involving attachment of ArX to the metal or a carbonyl ligand. Similar kinetic behavior to eq 12 has been reported by Powell et al.,[72] for the faster analogous reactions of $Fe(CO)_3(1\text{-}5\text{-}\eta\text{-acyclic dienyl})^+$ cations with methoxybenzenes. They proposed preequilibrium rearrangement to trans geometry intermediates, a route not feasible for cyclic dienyl cations.

One system where direct rate-determining formation of the σ-complex from the reactants may be involved is the reactions of $M(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)^+$ (M = Fe, Ru) cations with aryltrimethylstannanes, $RC_6H_4SnMe_3$. Excellent LFERs are obtained between the log k values for these demetalation reactions (X = $SnMe_3$) and log k for the related protiodemetalations of $RC_6H_4Sn\text{-}(C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol (R = H, 4-Me, 4-MeO, 4-F, 4-Cl, 4-Br).[69] For the protiodemetalations no π-complexes are possible. Relatively early transition states with only a moderate amount of C–C bond formation is suggested for the Fe and Ru reactions by the low slopes (ρ) of Yukawa–Tsuno plots. As with protiodemetalation, the rates of the reactions between cation 1 and $RC_6H_4M'Me_3$ varies markedly with the metal M' in the order Pb >> Sn >> Ge >> Si. As expected, the substrates $RC_6H_4M'Me_3$ are generally more reactive toward 1 than are corresponding compounds RC_6H_5. The only exceptions are the more basic $4\text{-Me}_2NC_6H_4M'Me_3$ (M' = Si, Sn), which may employ π-complex intermediates.

We have confirmed exo attack of N,N-dimethylaniline on the coordinated cyclobutadiene ligand in $Fe(CO)_2(NO)(\eta\text{-}C_4H_4)^+$ from an X-ray structure of the adduct (Figure 4).[68] The electron-impact mass spectra
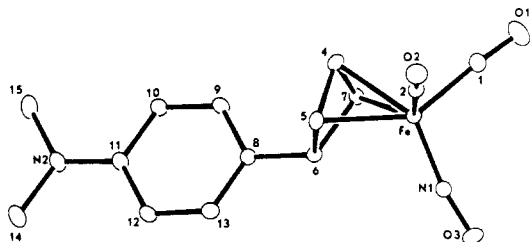
Figure 4. Structure of $Fe(CO)_2(NO)(Me_2NC_6H_4C_4H_4)$.

of various $Fe(CO)_3(ArC_6H_7)$ products are also characteristic of exo species.[64,67,69]

III. Factors Governing Reactivity

A consideration of the above kinetic studies leads to surprisingly consistent structure–reactivity relationships. The most important feature to emerge from the mechanistic work with P- and N-donor nucleophiles is the observation that *relative nucleophilic reactivities are independent of the organometallic electrophile.* Even more surprisingly, *the same relative nucleophilic reactivities are found for addition to free carbonium ions.*[73] Thus, a quantitative understanding of the factors important in controlling the reactivity of coordinated π-hydrocarbons is now emerging, and this will be of substantial help in planning synthetic procedures. We have established an electrophilicity order for π-hydrocarbon metal complexes (Table VIII). This order, covering a reactivity range of 10^9, is based on data with tertiary phosphines, usually with PPh_3 or PBu_3 as the reference nucleophile. The electrophilicity order is, however, independent of the particular nucleophiles chosen (P- or N-donor), except when steric factors are present (vide infra). Rate constants vary with solvent only slightly (factor of 2) along the series MeCN, $MeNO_2$, Me_2CO. The reactivities in Table VIII have been normalized to acetone as solvent. The values in brackets take into account a statistical effect associated with the number of sites for nucleophilic addition present in each substrate. The cations at the higher end of the range are quite active electrophiles. For example, $Mn(CO)_3(1-6-\eta-C_7H_8)^+$ and $Fe(\eta\text{-arene})_2^{2+}$ are ca. 10^4 times as effective alkylating agents as magic methyl, $MeSO_3F$.

A. Nature of the Metal

The dependence of the electrophilicity of coordinated π-hydrocarbons on the metal in a given triad follows an interesting pattern, which is summarized in Table IX. For the chromium[29,74,75] and manganese[14,19] triads very little variation in rate occurs with change of metal. Preliminary results for addition of PBu_3 to the cyclohexadienyl rings of $Co(Cp)(1-5-\eta-C_6H_7)^+$ (M = Co, Rh) similarly indicate a weak metal dependence with the cobalt triad.[26] In contrast, for attack on π-hydrocarbons coordinated to the iron triad metals electrophilicity decreases markedly in the order Fe >> Ru, Os.[19,32,64] Similarly, large differences Pd >> Pt are seen for attack on 1,5-cyclooctadiene attached to Pd(II) and Pt(II).[56] In general it appears that first-row transition metals are as effective, and in the case of the iron triad far more effective, than their second- and third-row counterparts in activating π-hydrocarbons towards nucleophilic at-

TABLE IX. Metal Dependence of Coordinated π-Hydrocarbon Electrophilicities

electrophile	nucleophile	rel k_1 values			ref
$M(CO)_3(C_7H_7)^+$	PBu_3	Cr > 4.4	Mo > 1.9	W 1	29
	Hacac	W > 2.3	Mo > 1.9	Cr 1	74
	$MG(OMe)^a$	Mo > 10	W > 6	Cr 1	
$M(CO)_3(C_6H_6)^+$	PBu_3		Mn ≈ 1.1	Re 1	14
$M(CO)_3(MeC_6H_5)^+$	PBu_3		Mn > 2.0	Re 1	19
$M(C_6H_6)_2^{2+}$	PPh_3	Fe > 390	Ru > 6.9	Os 1	32
	$P(OBu)_3$	Fe > 65	Ru > 2.9	Os 1	19
$M(CO)_3(C_6H_7)^+$	$C_6H_5NMe_2$	Fe > 41	Os > 3.6	Ru 1	64
$M(Cp)(C_6H_7)^+$	PBu_3		Co > 4	Rh 1	26
$MBr_2(1,5\text{-COD})$	$C_6H_{11}NH_2$		Pd > 70	Pt 1	56

^{a} MG is Malachite Green.

tack. The rate order Fe >> Ru, Os for ring addition is explicable in terms of the well-documented[76] π-back-bonding ability order Fe(II) << Ru(II), Os(II). The higher ionization potential of Pd^{2+} compared to Pt^{2+} likewise suggests that Pd(II) is a less effective π-back-bonder, thus facilitating nucleophilic attack at a coordinated olefin.[77] In the chromium and manganese triads there is probably little variation in π-back-bonding ability with the metal. Also in general agreement with the reactivity orders in Table VIII are observations that the redox potentials of iron triad organometallics generally follow the order Fe(II) >> Ru(II), Os(II),[78] while the chromium triad shows little metal dependence.[79]

In contrast to these ring addition processes where little metal dependence is observed in the chromium, manganese, and cobalt triads, reactions involving associative attack at the metal with ring displacement show marked variations in rate in the order Mo > W >> Cr,[80] Re(I) >> Mn(I),[14] and Ru >> Fe.[81] These differences provide further support for the direct bimolecular addition mechanism to the π-hydrocarbon ligand in reactions like eq 1.

B. Nature of the Nucleophile

Table X summarizes rate constants for the addition of a wide range of nucleophiles to cation 1 at 20 °C. This nucleophilicity range of ca. 10^7 is extended to 10^{12} if aromatic nucleophiles, which appear to react by a different mechanism, are included. Similar, but less extensive, nucleophilicity data are available for other organometallic electrophiles. As stated above, an examination of the available data with P- and N-donors reveals that relative nucleophilic reactivities are electrophile independent. Whenever an exception to this empirical rule is found, there is a clear and convincing steric explanation. This means that one need know the rate with only one nucleophile to know the rates for all other nucleophiles, and that the relative reactivities of the coordinated π-hydrocarbons are invariant.

Nucleophilic addition to the π-hydrocarbon ring in $(ring)ML_n^+$ is obviously closely related to additions *to*

TABLE X. Relative Nucleophile Reactivities for Addition to Coordinated π-Hydrocarbons[a]

nucleophile	N_{Fe}	N_M[b]
P(2-MeOC$_6$H$_4$)$_3$	3.9	3.9
PBu$_3$	3.6	3.8
morpholine	3.5[c]	(3.5)[c]
PEt$_2$Ph	3.3	(3.3)
P(4-MeOC$_6$H$_4$)$_3$	2.9	3.0
P(4-MeC$_6$H$_4$)$_3$	2.5	2.6$_5$
4-MeOC$_6$H$_4$NH$_2$		2.6
4-MeC$_6$H$_4$NH$_2$	2.4	2.4
3-MeC$_5$H$_4$N	2.4	2.4
imidazole	2.2	2.1
PPh$_3$	1.9$_5$	2.1
OH$^-$	2.0[d]	(2.0)[d]
C$_5$H$_5$N	1.9	2.0
H$_2$NCH(Me)CO$_2$Et	2.0	(2.0)
C$_6$H$_5$NH$_2$	1.9	1.9
H$_2$NCH(Ph)CO$_2$Et	1.9	(1.9)
H$_2$NCH(CH$_2$Ph)CO$_2$Et	1.8	(1.8)
2-MeC$_5$H$_4$N	1.4	1.4
N$_3^-$	1.4[d]	(1.4)[d]
2-MeC$_6$H$_4$NH$_2$	1.4	1.3
P(4-FC$_6$H$_4$)$_3$	1.3	(1.3)
P(4-ClC$_6$H$_4$)$_3$	1.0	1.0
P(CH$_2$CH$_2$CN)$_3$	0.2	0.1
P(OBu)$_3$	0.0	0.0
P(OEt)$_3$	-0.3	(-0.3)
P(OMe)$_3$	-0.5	(-0.5)
2,6-Me$_2$C$_5$H$_3$N	-0.5	(-0.5)
pyrrole	-2.7	(-2.7)
indole	-2.8	(-2.8)
P(OPh)$_3$	-3.3	-3.3
4-Me$_2$NC$_6$H$_4$SnMe$_3$	-3.7	(-3.7)
4-Me$_2$NC$_6$H$_4$SiMe$_3$	-5.0	(-5.0)

[a] Calculated from data at 20 °C in acetone, acetonitrile, or nitromethane as solvent. [b] This is an average N value calculated from data for a variety of organometallic electrophiles. Values in parentheses indicate that data is available only for the substrate Fe(CO)$_3$(C$_6$H$_7$)$^+$. [c] Refers to data collected at 0 °C. [d] Refers to data collected at 0 °C in water solvent.

free carbonium ions. The latter reaction involves simple electrophile–nucleophile (E–N) combination, whereas the organometallic reactions also involve cleavage of a metal–metal bond, i.e., are really S$_N$2 reactions in which the leaving group (ML$_n$) remains bonded to the periphery of the molecule. Ritchie[82] has found that oxygen and nitrogen donor nucleophiles add to free carbonium ions (trityl, tropylium, pyronin, etc.) such that the relative nucleophilic reactivity is electrophile independent. Furthermore, this may also be true for attack on esters and activated arenes, providing the leaving group departure is not rate determining. This surprising result is highly significant, both in a theoretical and practical sense.

Mathematically, invariant reactivity orders can be expressed according to the Ritchie relationship,[82] eq 14, in which N depends only on the nucleophile and k_0 only on the electrophile. For the organometallic electro-

$$\log (k_1/k_0) = N \qquad (14)$$

philes, N values (labeled N_{Fe}) were calculated using 1 as the reference substrate. The rate constant k_0 is for P(OBu)$_3$ as the reference nucleophile. If the reactivities are indeed nucleophile independent, a plot of log (k_1/k_0) or log k_1 vs. N_{Fe} should be linear with unit slope for *all* electrophiles. Indeed, plots of log k_1 vs. these N_{Fe} values for additions to a range of other organometallic electrophiles, e.g., Fe(CO)$_3$(1,5-η-2-MeOC$_6$H$_6$)$^+$, Fe(CO)$_3$(1-5-η-C$_7$H$_9$)$^+$, Fe(Cp)(1-6-η-C$_7$H$_8$)$^+$, Mn(CO)$_3$(1-6-η-
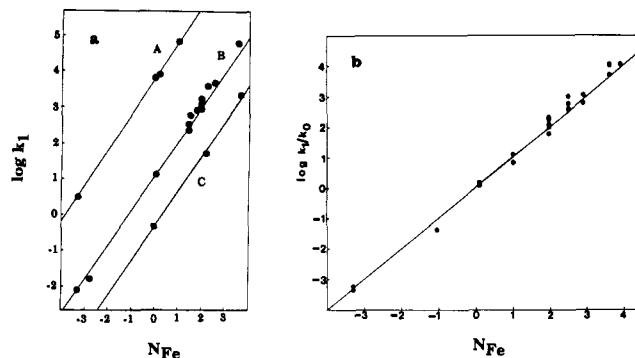
Figure 5. (a) Plot of reactivity vs. N_{Fe} for three electrophiles: (A) Mn(CO)$_3$(C$_7$H$_8$)$^+$; (B) Fe(CO)$_3$(2-MeOC$_6$H$_6$)$^+$; (C) Fe-(Cp)(C$_7$H$_8$)$^+$. (b) Plot of relative reactivity vs. N_{Fe} for P- and N-donor nucleophile addition to a variety of electrophiles other than Fe(CO)$_3$(C$_6$H$_7$)$^+$. The standard nucleophile (k_0) is P(OBu)$_3$.

TABLE XI. Electrophilic Transferability Numbers (T_E's) for Organometallic Fragments

fragment	T_E for dienyls
Fe(CO)$_3^+$	1800
Mn(CO)$_2$(NO)$^+$	1800
Fe(CO)$_2$(PPh$_3$)$^+$	28
Mn(CO)(NO)(PPh$_3$)$^+$	20
Co(Cp)$^+$	(1)

fragment	T_E for trienes
Fe(C$_6$H$_6$)$^{2+}$	200000000
Ru(C$_6$H$_6$)$^{2+}$	6000000
Os(C$_6$H$_6$)$^{2+}$	1500000
Mn(CO)$_3^+$	11000
Re(CO)$_3^+$	10000
Mn(CO)$_2$(PPh$_3$)$^+$	160
Fe(Cp)$^+$	(1)
Cr(CO)$_3$	very small

C$_7$H$_8$)$^+$, Mn(CO)(NO)(PPh$_3$)(1-5-η-C$_6$H$_7$)$^+$, Fe(CO)-(NO)(L)(1-4-η-C$_4$H$_4$)$^+$, and Fe(Cp)(CO)$_2$(η-C$_2$H$_4$)$^+$, are linear with slopes near unity in all cases (see Figure 5). This confirms a constant selectivity along this electrophile series despite a change in intrinsic reactivity of ca. 10^6. Figure 5b illustrates the adherence to eq 14 for 25 reactions with a variety of P- and N-donor nucleophiles and electrophiles other than 1. A full list of N_{Fe} values are given in Table X. Included in Table X are N_M parameters, which are N values averaged over a variety of electrophiles. It seems, therefore, that with P- and N-donors relative nucleophilic (electrophilic) reactivities are electrophile (nucleophile) independent regardless of the nature of the metal, nonreacting ligands, or the π-hydrocarbon (unless there are steric effects, vide infra). Whether or not this statement is true of carbon donor nucleophiles is an unknown but very important question. Certainly, eq 14 is not obeyed by aromatic nucleophiles (pyrrole, N,N-dimethylaniline, etc.), but, as discussed above, this is due to the formation of precursor π-complexes between the nucleophile π system and the electrophile. Our expectation, however, is that simple carbanions will be found to react according to eq 14.

A related and quite useful way to look at these effects is via what we call electrophilic transferability numbers (T_E's), which measure the ability of a given organometallic fragment (ML$_n$) to activate π-hydrocarbons. In the absence of steric effects, the T_E's are *independent of the nature of the π-hydrocarbon*. Table XI gives some results. The T_E parameters provide a convenient way to predict the degree of activation of a given π-

TABLE XII. Brønsted Slopes for Reactions Represented by Equation 1

substrate	nucleophile	solvent	slope α	ref
EtI	XC_5H_4N	CH_3CN	0.33	52
	$P(C_6H_4X)_3$	acetone	0.49	38a
$Fe(CO)_3(C_6H_7)^+$	XC_5H_4N	CH_3CN	0.41	30
	$P(C_6H_4X)_3$	acetone	0.50	24
$Fe(CO)_3(2\text{-MeOC}_6H_6)^+$	$XC_6H_4NH_2$	CH_3CN	1.0	49b
$Cr(CO)_3(C_7H_7)^+$	$P(C_6H_4X)_3$	acetone	0.70	30
$Fe(CO)(NO)(PPh_3)(C_4H_4)^+$	$P(C_6H_4X)_3$	CH_3NO_2	0.47	31
$Mn(CO)_2(NO)(6\text{-MeC}_6H_6)^+$	$P(C_6H_4X)_3$	CH_3CN	0.47	27

hydrocarbon. For example, a cyclohexadienyl ring is $1800/20 = 90$ times more reactive when coordinated to $Fe(CO)_3^+$ compared to $Mn(CO)(NO)PPh_3^+$. Similarly, an arene or cycloheptatriene attached to $Fe(C_6H_6)^{2+}$ is 200 000 000 times more reactive than when coordinated to $Fe(Cp)^+$. If a given metal fragment, ML_n, fails to induce the activation required for a synthetic procedure, the T_E numbers show how the metal moiety should be changed.

As noted above, electrophile–nucleophile combination reactions involving free carbonium ions and N- and O-donor nucleophiles obey eq 14.[82] Very recent results from our laboratory with cations 14 and 15 show that phosphines and phosphites seem to obey eq 14 as well.[73]

14   15
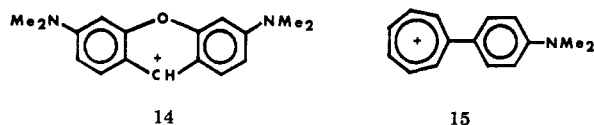
More significantly, the relative reactivities of P- and N-donors toward 14 and 15 are the same as that observed with organometallic electrophiles (Table X). This is a surprising result because (1) the nucleophiles include both "hard" and "soft" donors and (2) the organometallic reactions are in reality substitutions in which a metal–carbon bond is broken. As discussed above, the transition state for most of the organometallic reactions is probably an early one, and the cleavage of the M–C bond does not play a major energetic role. This important point, which may be responsible for the similar behavior of organometallic electrophiles and free carbonium ions, follows from the observation that some nucleophiles react with very small activation energies, yet also involve M–C bond cleavage. In any case, the result is that *nucleophilic attack on both free and complexed π-hydrocarbons follows a simple unified reactivity law* (eq 14). Just why eq 14 holds for either type of reaction is not really understood, especially in view of the substantial Brønsted slopes observed (Table XII and ref 82). Nevertheless, it is a very significant and useful fact. Deviations from eq 14 do exist for attack on some free carbonium ions[73,82] and some organometallics (vide infra), but usually the deviations are due to steric factors.

The importance of nucleophile basicity and polarizability in determining nucleophilicities in reactions like eq 1 has also been examined. Excellent plots of log k_1 vs. pK_a (H_2O) have been obtained for the additions of substituted pyridines,[30] anilines,[49b] and triarylphosphines[24] to the dienyl cation 1, i.e., the Brønsted eq 15 is obeyed (see Figure 6). The Brønsted slopes,
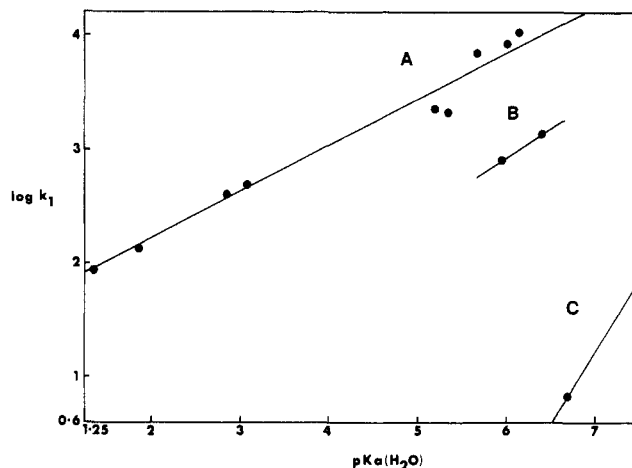
α, of between 0.4 and 1.0 (Table XII) confirm the im-

Figure 6. Brønsted plot for addition of substituted pyridines to $Fe(CO)_3(C_6H_7)^+$ in CH_3CN at 0 °C. (A) Nonsterically crowded pyridines; (B) pyridines with 2-Me groups; (C) pyridines with 2,6-Me_2 groups.

portance of nucleophile basicity with both nitrogen and phosphorus donors. For pyridine nucleophiles an excellent correlation is also obtained between log k_1 and the recently reported[83] gas-phase basicities of the pyridines.

These Brønsted slopes contrast with the very low α values of ca. 0 for attack by amines and phosphines on the very "soft" Pt(II) center in complexes such as trans-$Pt(py)_2Cl_2$,[84] but are similar to the α values for attack on moderately "soft" substrates such as EtI.[52] This suggests that the dienyl ring in cations like 1 is not a "soft" center, but is either "intermediate" or "hard" in character. This observation is in keeping with the partial positive charges calculated by us[85] and others[86] to reside on the ring carbons.

Phosphine basicity is also seen to be important for the additions to the cations 6 (M = Cr), $Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_9)^+$, $Fe(CO)(NO)(PPh_3)(1\text{-}4\text{-}\eta\text{-}C_4H_4)^+$, $Co(Cp)(\eta\text{-}C_8H_{11})^+$, and $Mn(CO)_2(PPh_3)(1\text{-}6\text{-}\eta\text{-}C_7H_8)^+$ (Table XII). Particularly informative is the reaction of $Mn(CO)_2(PPh_3)(1\text{-}6\text{-}\eta\text{-}C_7H_8)^+$ with $P(OBu)_3$ and the caged phosphite $P(OCH_2)_3CH_3$, for which the relative rate constants are 250:1.[87] It was thought that the smaller cone angle of $P(OCH_2)_3CH_3$ might lead to greater than "normal" reactivity. However, clearly what is most important is the greater Lewis basicity of $P(OBu)_3$.[88] On the other hand, nucleophile polarizability seems to be less important. No reactions were noted for cation 1 and 6 (M = Cr) with $AsPh_3$ and $SbPh_3$ despite the rapid additions of PPh_3. Nucleophile polarizability is of considerably less importance for cation 1 than for trans-$Pt(py)_2Cl_2$ or even MeI as the substrate, as shown by the enhanced reactivity of N-donor nucleophiles compared with P-donor and As-donor nucleophiles (Table XIII).

Deviations from Brønsted and Tolman plots (log k_1 versus $\sum\chi$, where χ is a measure of the overall σ- and π-electron-donating or -accepting ability of the phosphorus centers) have allowed us to quantify steric effects in eq 1 type reactions. For example, from Figure 6 the successive introduction of blocking methyl substituents in the 2- and 6-positions of pyridine nucleophiles is seen to decrease log k_1 by about 1 and 3 units, respectively. Steric effects for pyridine addition to the cyclohexadienyl ring are thus larger than for analogous

TABLE XIII. Relative Reactivities of Nitrogen and Phosphorus Nucleophiles toward Various Substrates at 0 °C

| | log (k_1/k_{aniline}) | | |
| | trans- | | $Fe(CO)_3$· |
nucleophile	$Pt(py)_2Cl_2{}^a$	MeI	$(C_6H_7)^{+b}$
PBu_3	5.8	3.0	2.0
PPh_3	5.8	1.3	0.4
imidazole	0.3	0.7	0.3^c
pyridine	0.03	−0.5	0^c
aniline	0	0	0^c
$AsPh_3$	3.8	−0.9	no reaction
$SbPh_3$	3.7	<3.7	<−7.0

^{a} Solvent methanol, ref 84. ^{b} Solvent CH_3NO_2. ^{c} Solvent CH_3CN.

attack on tetrahedral MeI.[89] Similarly, the very large deviation (4.3 log units) of the sterically demanding $P(C_6H_{11})_3$ from the excellent correlation between log k_1 and $\sum\chi$ for phosphine and phosphite additions to 1 contrasts with a deviation of only 0.75 log units in an analogous plot with EtI. Surprisingly, our data with $P(C_6H_{11})_3$ shows that even the flat tropylium ring in substrate 6 (M = Cr) possesses a larger steric demand for phosphine additions than does the tetrahedral EtI.

C. Nature of the π-Hydrocarbon

The main systematic variations in π-hydrocarbon ligands that have been studied involve dienyls and trienes. With trienes, the anticipated result was found that cycloheptatriene is much more reactive than benzene when coordinated to a given metal fragment, ML_n.

With dienyls, some striking steric effects were found. In general, complexed cycloheptadienyl rings are much less reactive than cyclohexadienyl rings. The rates with P- and N-donor nucleophiles are 16–200 times larger for attack on the six-membered ring (Tables I and V). This is readily explained[90] by reference to Figure 7, which shows that with C_7H_9 the methylene hydrogens eclipse the carbon atoms to which the nucleophile adds. With C_6H_7, however, this steric interference is minimal. It seems likely that the tendency of $Fe(CO)_2(L)(1-5-\eta-C_7H_9)^+$ (L = CO, PPh_3) cations to add nucleophiles at the C-2 carbon to give σ,π-allyl complexes may be partly attributable to steric blocking of the C-1 and C-5 positions.

The influence of ring substituents on the rates of PPh_3 additions to dienyl rings has been explored with the cations 16 (L = CO) and 17 (L = CO). With the
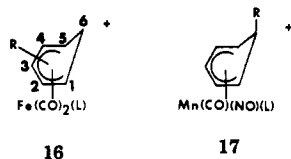
iron complexes k_1 for attack at C-5 decreases in the order R = 3-Me > H > 2-MeO > 2-MeO-3-Me > 2,5-Me_2 > 2-MeO-5-Me (1.03:1.00:0.21:0.07:0.015:0.002).[25] The electronic influence of methyl substituents is thus small, but, as expected, the presence of a methyl group at C-5 causes a marked steric retardation (factor of 33–110). Ring substituent effects have recently been reported by Birch et al. for attack on type 16 cations with acetylacetone.[17] They found the rate order R = 1-CO_2Me > 1-CO_2-Me-2-Me > 1-CO_2Me-2-OMe > 3-
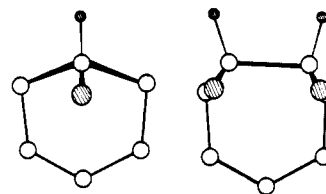

Figure 7. View of coordinated C_6H_7 and C_7H_9 rings from above the dienyl plane. Only hydrogen atoms bonded to methylene carbons are shown.

OMe > H > 3-Me > 2,3-Me_2 1-Me-2-Me > 2-OMe. Fewer data are available for 17 type cations, but it is known that a 2-OMe substituent reduces the reactivity of 16 and 17 by about the same amount.[27]

Very large steric effects occur when the C-6 carbon in 17 contains an exo substituent other than hydrogen.[27] When R is Me or Ph in 17, the rate reduction with PBu_3 as the nucleophile is ca. 10^3. The effect of the R group is further reflected in the relative rate of PPh_3 and $P(OBu)_3$ addition. With R = H, the normal 100:1 ratio was found, whereas a R = Me or Ph group reduces this to 17:1 and 3:1, respectively. The larger cone angle of PPh_3 nicely accords with these changes. Similar steric discrimination occurs with N-donor nucleophiles (Table V). For example, in the absence of steric hindrance pyridine and aniline usually react at similar rates. However, with 17 (R = Me) pyridine is ca. 10 times more reactive than aniline. This is probably due to the different steric environment of the donor orbitals in the nucleophiles. Thus in pyridine the donor orbital is sp^2 and in the molecular plane, whereas in aniline it is a p type perpendicular to the molecular plane. Models suggest that pyridine (or imidazole) should experience considerably less hindrance than aniline when approaching the C-1 (or C-5) carbon.

The presence of significant steric effects means that reactivities no longer obey eq 14. Fortunately, such deviations are often rather small and are limited to a minority of the systems investigated to date, namely, cycloheptadienyls and 6-substituted cyclohexadienyls. The former show small deviations and the latter moderate deviations from eq 14.

D. Nature of the Nonreacting Ligands

Replacing a CO ligand in $M(CO)_3(\pi$-hydrocarbon$)^{n+}$ complexes by other ligands can have a dramatic effect on the hydrocarbon reactivity. Thus, k_1 for addition of $P(OBu)_3$ to the cyclobutadiene ring in $Fe(CO)$-$(NO)(L)(1-4-\eta-C_4H_4)^+$ decreases down the series L = CO > $P(CH_2CH_2CN)_3$ ≈ $P(4-ClC_6H_4)_3$ > $P(4-FC_6H_4)_3$ > $AsPh_3$ ≈ PPh_3 > $SbPh_3$ ≈ $P(4-MeC_6H_4)_3$ > $P(4-MeOC_6H_4)_3$ (overall reactivity range of 100).[31] Similarly, replacing a CO ligand by PPh_3 in 1, 17, and Mn-$(CO)_3(1-6-\eta-C_7H_8)^+$ decreases k_1 by a factor of ca. 100.[27,56,87] It seems, therefore, that substitution of a CO by PPh_3 leads to a fairly invariant reduction in electrophilicity. This, of course, has obvious predictive value. (It should be noted that the regiochemistry of ring addition can also be influenced by CO substitution.[91]) The most dramatic nonreacting ligand effect apparent in Table I is the 2 × 10^5 smaller reactivity of $Fe(CO)_2I(1-5-\eta-C_6H_7)$ compared to the parent cation, 1. However, here not only has a CO ligand been replaced but the overall charge on the complex has been reduced as well.
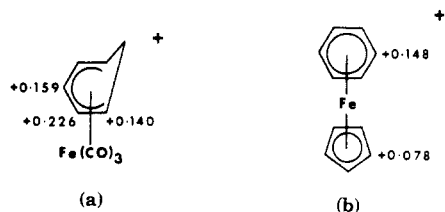
Figure 8. Calculated charges on carbon atoms.

E. Molecular Orbital Calculations

Several attempts have been made at molecular orbital analysis of nucleophilic addition to coordinated π-hydrocarbons. The question of orbital vs. charge control and the factors influencing the observed regiochemistry are the major points that need clarification. Based on first-order perturbation theory applied to Huckel MO's, a set of rules has been proposed[3] that enable predictions to be made concerning the regiochemistry of nucleophilic attack on a π-hydrocarbon. The rules also rationalize which π-hydrocarbon is preferentially attacked when more than one is available within a given complex. Although these rules usually hold reasonably well, there are a number of important reactions for which they fail.[92,93]

The site of nucleophilic attack in the substituted arene complexes $Cr(CO)_3(C_6H_5X)$ is a function of the nature of X and the nucleophile, and also depends on the conformation of the $Cr(CO)_3$ moiety.[92-96] It appears that the reaction can be either charge or orbital controlled, with a good electrophile LUMO and nucleophile HOMO energy match favoring orbital control.

We have carried out INDO MO calculations on a variety of π-hydrocarbon metal complexes to determine whether the patterns of nucleophilic attack can be rationalized in terms of electronic parameters. Calculations on 1 revealed the charge distribution shown in Figure 8a for the cyclohexadienyl ring carbon atoms.[85] This charge pattern correlates well with the variations in ^{13}C chemical shift reported[97] for the dienyl carbon atoms. Others[86] independently calculated a qualitatively similar order for the ring carbon charges. Significantly, no correlation is seen between the magnitude of the dienyl carbon positive charges and the site of nucleophilic attack on 1. The charge variation in Figure 8a would predict the site preference C-2 > C-3 > C-1, whereas nucleophiles add exclusively at C-1. There is also no correlation between the π-electron density at each carbon atom and the site of attack. However, the bond (or free valence) index values at each dienyl carbon correctly predict the site of nucleophilic addition.

Similar INDO calculations[98] on the substituted tropylium complexes $Cr(CO)_3(\eta\text{-}XC_7H_6)^+$ (6; X = H, OMe, COOMe) did not reveal a general correlation between the site of nucleophilic attack and any particular electronic parameter. Coordination of $C_7H_6X^+$ to the $Cr(CO)_3$ unit causes an increase in the positive charge at each ring carbon atom. The overall electron withdrawal by the $Cr(CO)_3$ group occurs from the ring σ-orbitals, but is balanced to some extent by back-donation by the metal into the ring π-orbitals. This explains the decreased susceptibility of $C_7H_6X^+$ to nucleophilic attack upon coordination to $Cr(CO)_3$. Stabilization of the benzyl cation in the isoelectronic complex $Cr(CO)_3$-(benzyl)$^+$ was similarly shown[99] to arise via back-

bonding from a chromium d orbital into the nonbonding π-orbital of the benzyl ligand. For this complex, the back-bonding donation (0.64 e) into the ring π-system dominates over electron withdrawal (0.59 e) from the ring σ-orbitals.

In keeping with our earlier observations with cations 1 and 6, the regiospecificity of nucleophilic addition to the arene ring in the cations $Fe(Cp)(\eta\text{-}XC_6H_5)^+$ (X = H, Me, OMe, COOMe) could not be correlated with calculated ring charges nor with frontier orbital parameters.[100] However, charge arguments do readily explain the chemospecific addition of nucleophiles to the arene ring rather than the cyclopentadienyl ligand (Figure 8b). The charges on the Cp carbon atoms are considerably lower than on the arene ligands.

F. Mechanistic Conclusions

Our mechanistic studies of P- and N-donor nucleophile addition to coordinated π-hydrocarbons suggest that (1) the mechanism is bimolecular with no initial interaction at the metal; (2) the transition state is usually an early one; (3) nucleophile basicity is important; (4) single electron transfer is not important mechanistically; (5) in the absence of steric effects relative nucleophilic reactivities are electrophile independent and are the same as for addition to free carbonium ions. There may be isolated exceptions to these conclusions, but we believe that such exceptions will prove to be rare.

IV. Synthetic Applications

Nucleophilic addition to coordinated π-hydrocarbons has been applied in a variety of useful synthetic procedures. A number of pertinent reviews has been published (see Introduction section). The authors listed in ref 1-12 have made many useful contributions dealing with nucleophilic addition. Also beneficial to those working in this area are the elegant works of Pauson[101] and Lewis.[102]

Our goal has been to establish structure-reactivity relationships that can be used for predictive purposes in synthesis. Substantial progress has been made, although still missing is mechanistic information for the most important nucleophiles—carbon donors. If C-donors mimic the trends observed with P- and N-donors, the synthetic chemist will have a very powerful predictive tool at his disposal. In this section a summary is given of the synthetic applications arising from our mechanistic studies described above.

A. Aromatic Nucleophiles

Our first major synthetic extension of type 1 reactions was the demonstration that cations such as 1 can act as electrophiles towards heterocyclic aromatic molecules, providing novel routes to diene-substituted heterocycles (eq 11).[60,62,63] Attack on pyrrole and indole was shown to occur only at the 2- and 3-positions of the ring, respectively (structures 18 and 19), indicating high regiospecificity. Similar reactions were observed with other organometallic electrophiles such as 6 (M = Cr),[103] $Ru(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)^+$[62,63] and $Mn(CO)_3(1\text{-}6\text{-}\eta\text{-}C_7H_8)^+$,[70] indicating the wide potential of such reactions.

18

19

20

21
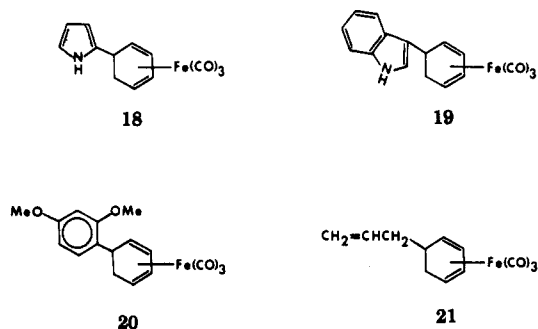
Activated arenes such as N,N-dimethylaniline and a range of di- and trimethoxybenzenes were also shown to undergo electrophilic aromatic substitution with organometallic electrophiles such as 1, 6 (M = Cr), 9, and $Fe(CO)_2(NO)(1-4-\eta-C_4H_4)^+$.[64-68,103] With N,N-dimethylaniline, attack occurs exclusively at the C atom para to the Me_2N substituent and in one case (Figure 4) an X-ray structural study confirmed[68] exo addition of the electrophile. Only one product was also isolated from each of the di- and trimethoxybenzene reactions with 1, again indicating high regioselectivity.[67] The products were generally those expected on electronic grounds, e.g., with 1,3-dimethoxybenzene product 20 was obtained.

However, cation 1 is not sufficiently electrophilic to attack anisole, alkylbenzenes, or benzene. More recently, we have been able to synthesize the diene-substituted derivatives of these less activated arenes using the reaction between 1 and the substrates $RC_6H_4M'Me_3$ (eq 11, M' = Si or Sn).[61,69] These aryltrimethylsilanes and -stannanes are known to be much more reactive towards electrophiles than the corresponding aryl–H compounds. Synthetically useful reactions occur even when strongly deactivating substituents (e.g., R = 4-Cl, 3-F, 4-F, or 3-CF_3) are present on the arene ring of $RC_6H_4SnMe_3$ substrates. Related processes occur between cation 1 and 2-(trimethylsilyl)furan, 2-(trimethylsilyl)thiophene, and the allylic substrate $CH_2CHCH_2SnMe_3$ (giving 21 as product). Other organometallic cations such as $Ru(CO)_3(1-5-\eta-C_6H_7)^+$, 6 (M = Cr), and the acyclic dienyl complex $Fe(CO)_3(1-5-\eta-1-Me-5-PhC_5H_5)^+$ undergo similar reactions.

Another synthetic application using 1 and related cations are the reactions with trialkylalkynylborates, $R^1_3BC\equiv CR^2$, providing novel and stereospecific routes to substituted olefins and ketones (Scheme VIII).[104]

B. Single Addition to Coordinated Arenes

Complexed arenes are particularly important molecules and significant advances have been made towards arene functionalization via nucleophile addition reactions. Nucleophilic aromatic substitution is not commonly used in organic synthesis because of the necessity of introducing and then removing an activating group. With organometallic arene complexes, however, the activating group (the metal moiety) can be easily attached and removed, making (formal) substitution for hydride not only possible but often facile. The most celebrated arene complex so far utilized for synthetic purposes is $Cr(CO)_3(arene)$.[8] However, this complex is only weakly electrophilic and very powerful nucleophiles are required to effect addition to the ring. Synthetically useful nucleophiles such as Grignard
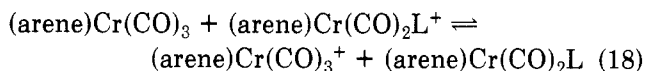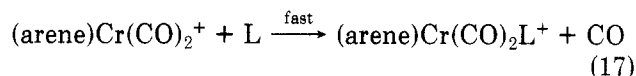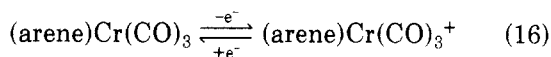
SCHEME VIII
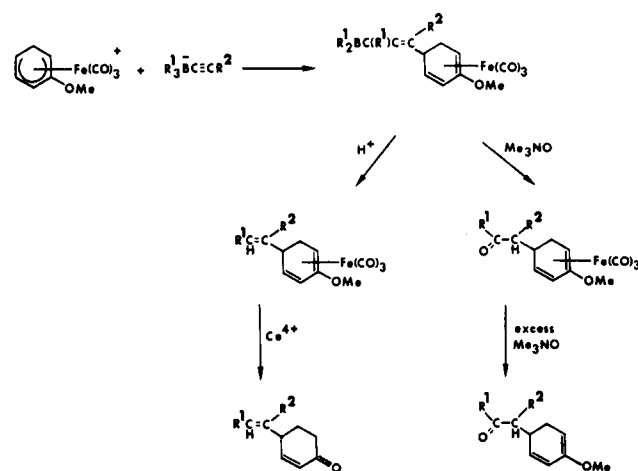
SCHEME IX
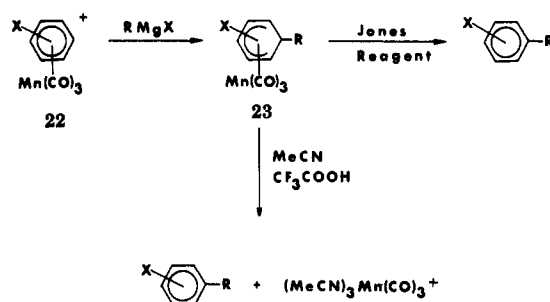
reagents and ketone enolates do not react successfully. A potentially more useful system is $Mn(CO)_3(arene)^+$, which is far more electrophilic than the neutral chromium analogues (Table XI). The manganese complexes are easily synthesized and we found that they react cleanly and rapidly with a variety of nucleophiles, including Grignard reagents and ketone enolates, to give cyclohexadienyl complexes 23 (Scheme IX).[105] The free arene can be removed from the metal moiety in 23 by oxidation with Jones reagent, so that the overall reaction corresponds to substitution of hydride by a carbanion in 22. Ketone enolates add in a similar manner. The functionalization of arenes by such useful nucleophiles should prove to be a valuable procedure, particularly since strong directive effects are seen. For example, Grignard reagents are directed exclusively meta to the OMe^- in $Mn(CO)_3(anisole)^+$.[105] Somewhat weaker directive effects are found with addition of hydride or an organolithium reagent.[106] Another interesting aspect of our work is the observation that refluxing 23 in acidified CH_3CN frees the functionalized arene without destroying the $Mn(CO)_3^+$ moiety, which can be isolated as $[(CH_3CN)_3Mn(CO)_3]PF_6$ and recycled to give starting material 22. The mechanism of this reaction in CH_3CN probably involves endo hydride migration to the metal, reaction with H^+ to give H_2, and then known[14] solvolysis to give the products.

We are also exploring the feasibility of inducing nucleophilic addition by activating unreactive π-hydrocarbon complexes via electrochemical oxidation. The idea is that mild nucleophiles may add to the coordinated ring when the complex is oxidized. The first system studied was $Cr(CO)_3(arene)$ in the presence of phosphines and phosphites.[107] So far, ring attack has not been demonstrated, but such reactions may be possible if proper conditions can be elaborated. Instead

of ring attack, CO substitution occurs very rapidly in $Cr(CO)_3(arene)^+$ (the neutral complexes are inert). Rybinskaya et al.[108] recently reported similar observations. Our studies also produced the surprising result

$$(arene)Cr(CO)_3 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} (arene)Cr(CO)_3^+ \qquad (16)$$

$$(arene)Cr(CO)_2^+ + L \xrightarrow{fast} (arene)Cr(CO)_2L^+ + CO \qquad (17)$$

$$(arene)Cr(CO)_3 + (arene)Cr(CO)_2L^+ \rightleftharpoons$$
$$(arene)Cr(CO)_3^+ + (arene)Cr(CO)_2L \qquad (18)$$

that the production of $Cr(CO)_2(L)(arene)$ occurs catalytically by a SET mechanism. The homogeneous electron-transfer reaction 18 has $\Delta G \gg 0$, yet occurs rapidly because reaction 17 is irreversible. Such catalyzed ligand substitutions induced by oxidation are rare, although the synthetically less useful case when the SET reaction is thermodynamically favored is well documented.[109]

C. Double Addition to Coordinated π-Hydrocarbons

The addition of two nucleophiles to the arene in 22 represents a route to difunctionalized cyclohexadienes. There are several known examples of such double additions. Vollhardt et al.[110] found that two methoxide or cyclopentadienide ions add to the benzene in Co-(Cp)(benzene)$^{2+}$. Unfortunately, most other nucleophiles react in more complex ways to give uncharacterizable organometallic products and free benzene. Brookhart et al.[111] found that strong hydride donors $(Et_3BH^-, (i-PrO)_3BH^-)$ react with 22 to give Mn-$(CO)_3(cyclohexadiene)^-$ anions which react with electrophiles (H^+, MeI) to give cyclohexenyl complexes containing a three-center Mn–H–C bond. We recently reported[112,113] the first general procedure for the double addition of a variety of nucleophiles to a coordinated arene. The procedure is a very simple one, and is shown in Scheme X. First, the desired nucleophile is added to 22 to give 23. With the exception of strong hydride donors,[111] double addition directly to 22 by using excess nucleophile (carbanion, phosphine, borohydride, etc.) is not possible because 23 is too weakly electrophilic. To effect the second addition, complex 23 is reactivated by substitution of CO by NO^+ to give 24, which was found to be even more electrophilic than the starting complex 22. So far complexes 24 and 25 have been made with X = H, Me, OMe; R = H, Me, Ph, CN, CH_2COCMe_3; Nu = PBu_3, PPh_3, $P(OMe)_3$, $PhNH_2$, pyridine, imidazole, H, Me, and $CH(CO_2Me)_2$. Similar chemistry has been developed with one CO replaced by PPh_3 and PBu_3.[27]

There are substantial reasons for desiring a good synthesis of complex 25, from which the diene can be liberated by well-established procedures. For example, starting with anisole as the arene in 22, the ultimate
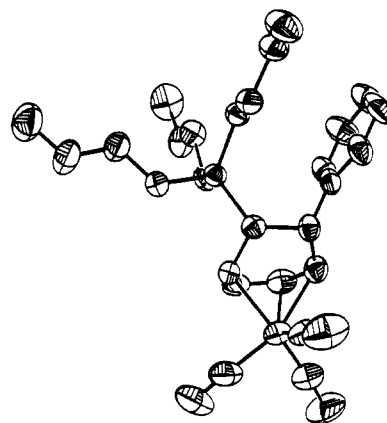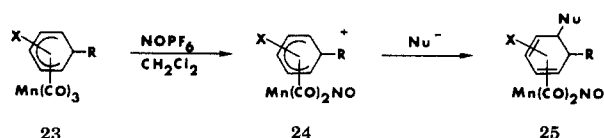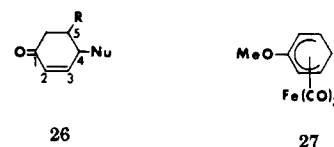
SCHEME X

Mn(CO)₃   NOPF₆/CH₂Cl₂   Mn(CO)₂NO   Nu⁻   Mn(CO)₂NO
   23   24   25

Figure 9. Structure of $[Mn(CO)_2NO(5-PBu_3-6-PhC_6H_6)]PF_6$.

26   27

product obtained (after hydrolysis) would be the 4,5-disubstituted cyclohex-2-enone 26. Substituted cyclohex-2-enones are important in natural products synthesis due to their widespread occurrence in nature. Positions 4 and 5 (especially 5) are difficult to functionalize by standard procedures, and the only currently available method is nucleophilic attack on 27. This, however, gives only monofunctionalization.[114] The very useful $Fe(CO)_3(1,5-\eta-cyclohexadienyl)^+$ complexes are difficult to synthesize with a substituent at C-6.[115] The manganese analogues, 24, are difficult, though not impossible, to synthesize without a substituent at C-6. Thus, these two classes of compounds complement each other nicely. When fully developed, the manganese complexes may prove to be exceptionally versatile reagents for the functionalization of arenes and cyclohexadienes. It is interesting that the $Mn(CO)_2NO^+$ and $Fe(CO)_3^+$ moieties are almost identical in their ability to activate dienyl rings (Table XI).

Carbanions can react with 24 in a variety of ways, including attack at a CO, the metal, and electron transfer as well as ring addition. We have recently found[27] what may be the first example of initial attack at CO followed by migration to a ring with no CO reduction or loss, reaction 19. It is not yet known if the methyl is endo as would be expected.

$$\text{(19)}$$

Mn(CO)₃NO   MeMgBr   CH₂Cl₂   Mn(CO)(NO)COMe   Mn(CO)₂NO
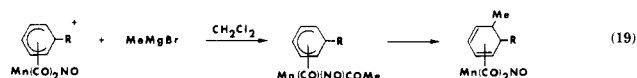
Our addition–reactivation–addition procedure was tested briefly with the synthetically useful seven-membered ring systems $Mn(CO)_3(1-6-\eta-C_7H_8)^+$ and 6 (M = Cr). In both cases, hydride or carbanion addition followed by treatment with $NOPF_6$ gives the expected products.[27,28] Nucleophile addition then converts these to the diene and dienyl complexes, respectively.

^1H NMR data suggested that phosphines add exo to the metal in 24, and a recent structure of 25 (R = Ph; Nu = PBu_3; X = H) confirms this expected result (Figure 9).[21] However, a very unexpected result was suggested by NMR data for 25 obtained by hydride and deuteride addition to 24. An analysis of coupling con-

SCHEME XI

Figure 10. Structure of $Mn(CO)_2NO(2\text{-}MeO\text{-}5\text{-}Me\text{-}6\text{-}PhC_6H_5)$.
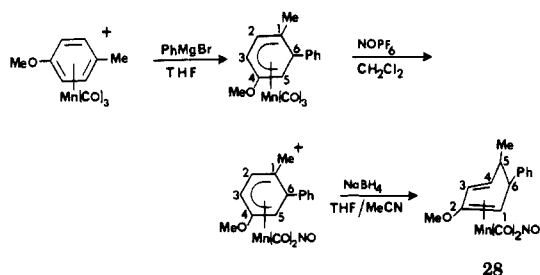
stants implied that hydride (BH_4^-, BH_3CN^-, etc.) adds endo stereospecifically to **24** (R = Me, Ph, CN; X = H, OMe, Me). Replacement of a CO by PBu_3 in **24** also led to endo hydride addition. To verify this conclusion, which represented the first example of stereospecific kinetic endo hydride addition to a coordinated ring, we designed Scheme XI and obtained the structure of the product, **28** (Figure 10).[113] The exo position of the C-5 methyl confirms endo hydride addition. That the endo product is the *kinetic* one was shown by adding boro-deuteride to **24** (R = Me, Ph; X = H) and observing that only the endo deuterium species is formed. Preliminary results with $Mn(CO)_2(NO)(1\text{-}5\text{-}\eta\text{-}C_7H_8R)^+$ suggests that hydride addition is also endo for these complexes.[28]

Why the $Mn(CO)_2(NO)(cyclohexadienyl)^+$ complexes react in this unique manner is not known. Hydride addition to a variety of other ring systems was examined and found to be exo: $Mn(CO)_3(C_6H_6)^+$, $Mn(CO)_3(C_6H_7)$, $Re(CO)_3(C_6Me_6)^+$, $Fe(CO)_3(C_6H_7)^+$, $Cr(CO)_2$-$(NO)(C_6H_6)^+$.[27,28,111,116,117] These results and our X-ray structures show that endo addition to **24** is not due to steric congestion around the carbon being attacked. Brookhart et al.[111] have proposed that apparent endo hydride addition at a carbon bonded to a methyl in tricarbonyl(1,3,5-trimethylcyclohexadienyl)manganese may in fact occur via exo addition at an unsubstituted carbon to give a σ, π-allyl intermediate that undergoes endo hydride migration via the metal to give product. Such a mechanism in our reactions can be ruled out because of the results with borodeuteride, and because the reaction conditions were too mild to allow ring isomerizations. The endo stereochemistry found in reactions of **24** and hydride suggests an initial interaction at the metal or CO, followed by migration to the ring (e.g., similar to eq 19). The presence of a nitrosyl ligand may be important since it can act as an electron sink if the metal is attacked. It is also quite possible that the initial interaction of borohydride and **24** involves single electron transfer to generate a reactive radical that can be a 19- or 17-electron species depending on the nitrosyl bonding mode. However, electron transfer does not necessarily lead to an endo product since $Fe(Cp)(arene)^+$ cations give exo hydride addition products[28] that are thought to be formed following initial electron transfer.[43]

There is one other very recent report of endo hydride addition to a coordinated cyclic π-hydrocarbon.[118] This is shown in eq 20 (R = Me, Ph, t-Bu), in which hydride attacks a thiabenzene 1-oxide ligand to give a σ,π-allyl complex.

There are also several reports[111,119-121] of hydride addition yielding a mixture of exo and endo products, with the amount of endo being at most 50%. However, due
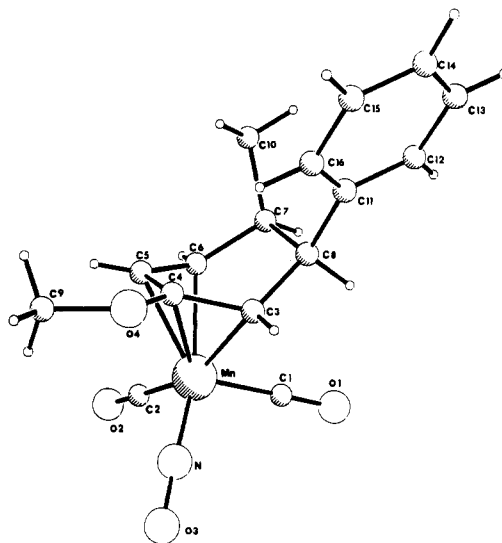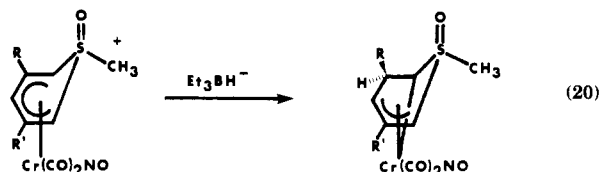

(20)

to reaction conditions used, some of these reactions may simply reflect thermodynamic exo/endo equilibration.

## D. Chiral Discrimination in Nucleophilic Additions

There has been considerable recent interest in the synthesis of optically active $Fe(CO)_3(\pi\text{-hydrocarbon})^{n+}$ (hydrocarbon = diene or dienyl; n = 0 or 1) complexes and their potential use in asymmetric synthesis. A few partially or fully resolved complexes have been obtained by classical diastereomer separation,[122] the reaction of 1,3-dienes with chiral transfer agents,[123] and diastereotopic discrimination in the reactions of chiral dienyl cations with optically active nucleophiles.[124] We have concentrated on the last mentioned approach. Thus, treatment of racemic $(2R,2S)\text{-}Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)^+$ (**9**) with $(S,S)\text{-}(-)_{589}\text{-}o\text{-}phenylenebis(methylphenylphosphine)$ (**29**) in a 2:1 ratio in acetone or acetonitrile gave a 57/43 mixture of diastereomers **30** and **31** (eq 21).[125] Recovery of unreacted dienyl salt

(21)
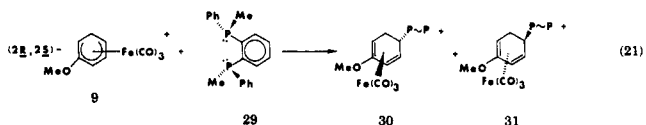
from this reaction provided a convenient and rapid method for preparing **9** (11% enantiomeric excess), whose CD spectrum was recorded for the first time. Quantitatively similar chiral discrimination occurs in the analogous reaction with $(-)_{589}\text{-neomenthyldiphenylphosphine}$.[126] However, discrimination is considerably less with the other optically active tertiary phosphines $(S,S)\text{-}(-)_{589}\text{-chiraphos}$ and $(+)_{589}\text{-diop}$.

Clues as to the steric source of the chiral discrimination in type 21 reactions has come from related ^1NMR and CD spectral studies of the reactions between phosphine **29** and a variety of ring-substituted dienyl

cations.[125] The out-of-plane methylene group was found to play a role, but the most dramatic effect was achieved by placing a methyl substituent in the C-5 position of the dienyl ring. Thus, phosphine 29 prefers the opposite hand of cation 32 to that preferred with cation 9 (diastereomer ratio 41/59). The diastereotopic dis-

32
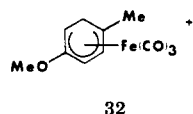
crimination was also shown[125] to be kinetic in origin from the increase in selectivity observed in reaction 21 on increasing the electrophile:nucleophile ratio. For example, with an initial 9:29 ratio of 14:1 the diastereomer ratio increased substantially to ca. 70:30. These studies have also provided simple synthetic routes to a range of novel optically active Fe(CO)$_3$(dienyl)$^+$ complexes. Related chiral discrimination studies have been made with cation 9 using (R)-(+)$_{589}$-1-phenylethylamine (33)[127] and a range of amino acid esters, (-)-H$_2$NCH-(R)COOR (R = Me, CH$_2$OH, CH$_2$Ph, Ph; R = Me or Et). In the case of amine 33, the diastereomers obtained from a 1:1 reaction could be readily separated by HPLC, providing a clean route to optically pure 9.

In both phosphine and amine reactions, treatment of the diastereomeric products with acid (neat CF$_3$COOH for the phosphines) rapidly regenerates the original dienyl salt with retention of configuration. Addition of achiral nucleophiles (e.g., PPh$_3$, CN$^-$, C$_5$H$_5$N, etc.) to these optically active dienyl salts produces new optically active (substituted-diene)iron tricarbonyl complexes. Studies with a range of diene and dienyl compounds suggest that the sign of the highest wavelength CD band may be used to assign absolute configurations, obviating the previous need for tedious chemical transformations to terpenes of known configuration. Further studies are planned with a range of π-hydrocarbon complexes and optically active nucleophiles in order to further elucidate the extent, mechanism, and synthetic potential of chiral discrimination in reactions shown in eq 1.

V. Conclusions

This review shows that significant progress has been made toward the goals of understanding the mechanism(s) of organometallic electrophile–nucleophile combination reactions, and of applying this knowledge to the prediction and realization of new synthetically useful reactions. We are especially gratified that our most successful synthetic work grew out of earlier quantitative kinetic studies that made informed guesses possible. We are continuing our investigations of these interesting but complex reactions so that they can be better understood, and utilized in new and useful ways.

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