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DEPENDENCE OF THE ELECTROPHILICITY OF COORDINATED CYCLIC π-HYDROCARBONS ON THE METAL IN THE CHROMIUM, MANGANESE, AND IRON TRIADS

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Summary

Phosphorus nucleophiles rapidly add to the coordinated arene in $[(\text{arene})M(CO)_3]^+$ (M = Mn, Re) and $[(\text{arene})_2M]^{2+}$ (M = Fe, Ru, Os). Kinetic data for these reactions are reported. It is suggested that π-bonding is important in determining the dependence of the coordinated ring electrophilicity on the metal within a given triad. The relationship between ring activation and reduction potential of the organometallic electrophile is discussed. It is shown that phosphites as compared to phosphines are much more reactive towards a metal centered electrophile than towards a carbon electrophile.

Introduction

Nucleophilic addition to coordinated cyclic π-hydrocarbons is a reaction of significant mechanistic interest and synthetic utility. Enough results are available to reveal a curious dependence of the ring electrophilicity on the metal within a given triad. In this paper we present kinetic data for phosphorus nucleophile addition to arenes coordinated to manganese, rhenium, iron, ruthenium, and osmium. The relationship between ring reactivity and reduction potential of the organometallic electrophile is discussed. We also show that phosphites are relatively unreactive compared to phosphines for attack at a carbon center while a fundamentally different reactivity pattern holds for attack at a metal center.

Experimental

The solvents CH_3NO_2 and CH_3CN were purified by fractional distillation under N_2. Nucleophiles $P(n\text{-}Bu)_3$ and $P(n\text{-}OBu)_3$ were distilled under N_2 at low pressure. ^1H NMR spectra were obtained on a Bruker WM 250. The complexes $[(C_6H_6)_2M](PF_6)_2$ (M = Fe, Ru, Os) and $[(\text{arene})M(CO)_3]PF_6$ (M = Mn, Re; arene = C_6H_6, C_6H_5Me) were prepared as previously described [1,2].

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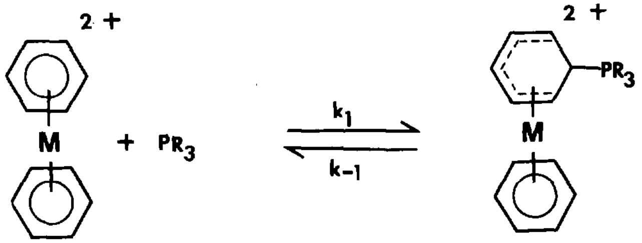
The kinetic studies were done on Dionex 110 stopped-flow spectrometer at 25°C. Pseudo first order conditions were used with the nucleophile in at least a tenfold excess over the electrophile concentration. At least five pseudo first order rate constants were obtained for each reaction, and the results were fit (with a correlation coefficient of at least 0.99) to the linear equation $k_{obs} = k_1[\text{Nucleophile}] + k_{-1}$.

Cyclic voltammetric measurements were made in CH_3NO_2 at room temperature with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Solutions were deoxygenated with argon presaturated with CH_3NO_2 and blanketed with argon during the experiment. A BAS CV-1B-120 instrument was used with a standard three-electrode system. The counterelectrode was a Pt wire, and the working electrode was a Pt disk. The reference electrode was aqueous Ag/AgCl, which was supplied by BAS; its stability was checked by measuring the halfwave potential of ferrocene, which was taken to be +0.400 V.

Results

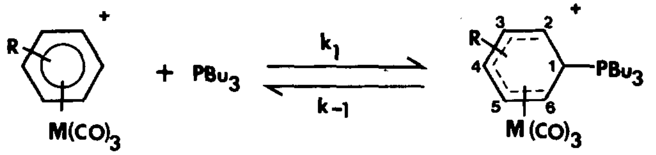
Previous IR and NMR studies [2,3] showed that $[(C_6H_6)_2M](PF_6)_2$ (M = Fe, Ru, Os) react rapidly and cleanly according to reaction 1. With $P(OMe)_3$ as the nucleophile, the product (2) undergoes an Arbuzov rearrangement to yield the corresponding phosphonate [3], but this is slow compared to the very rapid ring addition. In this paper we report that the rate constants for reaction 1 with $P(n\text{-}OBu)_3$ in CH_3CN at 25°C are: k_1 (M^{-1} s^{-1}) 1550 (Fe), 70 (Ru), 24 (Os); k_{-1} (s^{-1}) 0.08 (Ru), 0.06 (Os).



(1)

(1)   (2)

We previously reported [1] a kinetic study of reaction 2 with M = Mn.



(2)

(3)   (4)

Herein we report that **3** (M = Re) undergoes the same reaction to give **4** which was characterized by IR and NMR. Table 1 gives pertinent spectral and kinetic data for the benzene and toluene complexes. ^1H NMR data in CD_2Cl_2 for complexes **4** (R = H) are: M = Mn, δ 6.11 (H(4)), δ 5.15 (H(3,5)), δ 3.97 (H(1)), δ 3.00 (H(2,6)); M = Re, δ 6.09 (H(4)), δ 5.45 (H(3,5)), δ 4.34 (H(1)), δ 3.44 (H(2,6)).

TABLE 1

RATE AND SPECTRAL DATA [a] FOR REACTION 2

M	arene	ν(CO) [b] (cm^{-1})	k_1 (M^{-1} s^{-1}) [c]	k_{-1} (s^{-1})
Mn	C_6H_6	2023, 1948	2000	5.0 ± 1.3
Re	C_6H_6	2027, 1940	1800	4.0 ± 2.0
Mn	C_6H_5Me	2021, 1947	1500	7.0 ± 2.0
Re	C_6H_5Me	2026, 1941	750	5.2 ± 1.0

[a] All data obtained in CH_3NO_2 at 25°C. [b] Refers to complex 4. [c] Estimated error ±15%.

The reduction potentials of six organometallic electrophiles, all containing planar cyclic π-hydrocarbon rings, were measured in CH_3NO_2. All gave completely irreversible waves, indicating rapid decomposition of the reduced complexes on the cyclic voltammetry time scale (scan rate = 0.25–0.75 V s^{-1}). The complex $[(C_6H_6)Re(CO)_3]^+$ was not reduced up to the solvent limit. The corresponding manganese complex could be reduced, but only very near the solvent limit and it is possible, therefore, that these two complexes do not differ by much in reduction potential. The reduction potentials (E_p) obtained are: $[(C_6H_6)Mn(CO)_3]PF_6$, −1.10 V; $[(C_4H_4)Fe(CO)(NO)(PPh_3)]PF_6$, −0.74 V; $[(C_7H_7)Cr(CO)_3]BF_4$, −0.69 V; $[(C_6H_6)_2Ru](PF_6)_2$, −0.61 V; $[(C_4H_4)Fe(CO)_2(NO)]PF_6$, −0.39 V; $[(C_6H_6)_2Fe](PF_6)_2$, −0.33 V.

Discussion

The kinetic studies of reactions 1 and 2 gave no evidence for reaction intermediates. This fact and the *exo* stereochemistry invariably found for phosphine addition products [4,5] strongly suggest that the mechanism consists of a simple bimolecular step. The plots of k_{obs} versus nucleophile concentration gave nonzero intercepts, which are due to the reverse step in reactions 1 and 2. This implies that the reactions did not go to completion at low nucleophile concentrations, and this was verified by independent static IR and NMR measurements.

The dependence of the electrophilicity of the coordinated ring on the metal in a given triad follows an interesting pattern, which is summarized in Table 2. Nucleophilic attack within the chromium and manganese triads show no metal dependence within a factor of about two. In sharp contrast, electrophilicity in the iron triad is strongly metal dependent with Fe ≫ Ru, Os. Available evidence suggests that these kinetic reactivity patterns also apply to the equilibrium constants. Nucleophilic attack at the metal with ring displacement, as opposed to attack at the ring, shows very different reactivities: Mo > W ≫ Cr [9]; Re ≫ Mn [1]; Ru ≫ Fe [10]. These observations provide additional support for the simple direct attack mechanism for ring addition.

The rate order Fe ≫ Ru, Os seen in Table 2 can be understood as due to the well documented π-backbonding ability order Ru^{II}, $Os^{II} \gg Fe^{II}$ [11]. More π-backbonding would reduce the reactivity of the complexed rings towards nucleophiles. With the chromium and manganese triads there is probably little variation of π-backbonding ability with the metal [12]. This explanation of the relative reactivities is supported by published electrochemical data. The reduction potentials of

TABLE 2

RELATIVE REACTIVITIES FOR NUCLEOPHILIC ADDITION TO COORDINATED CYCLIC π-HYDROCARBONS

Electrophile	Nucleophile	Relative reactivity			Reference
$[(C_7H_7)M(CO)_3]^+$	PBu_3	Cr >	W >	Mo	6
		2.3	1.1	1	
$[(C_7H_7)M(CO)_3]^+$	Hacac	W >	Mo >	Cr	7
		2.3	1.9	1	
$[(C_6H_6)M(CO)_3]^+$	PBu_3	Mn >	Re		This work
		1.1	1		
$[(C_6H_5Me)M(CO)_3]^+$	PBu_3	Mn >	Re		This work
		2.0	1		
$[(C_6H_6)_2M]^{2+}$	PPh_3	Fe >	Ru >	Os	2
		390	6.9	1	
$[(C_6H_6)_2M]^{2+}$	$P(OBu)_3$	Fe >	Ru >	Os	This work
		65	2.9	1	
$[(C_6H_7)M(CO)_3]^+$	$C_6H_5NMe_2$	Fe >	Os >	Ru	8
		41	3.6	1	

organometallic complexes should reflect their electrophilicities. In agreement with our kinetic results, the reduction potential of iron triad organometallics generally follow the order $Fe^{II} \gg Ru^{II}$, Os^{II} [13] while the chromium triad shows little metal dependence [14]. The manganese triad gives a less clear cut pattern, although the $E_{1/2}$ values for $[(C_6H_5)M(CO)_5]$ and $(CH_3COM(CO)_5]$ are very similar for Mn and Re [15].

The reduction potentials of a variety of complexes containing planar cyclic π-hydrocarbon ligands have been measured by cyclic voltammetry. The reductions are chemically irreversible, and therefore the peak potentials (E_p) instead of $E_{1/2}$ values were obtained. A plot of relative reactivity for phosphorus nucleophile ring addition [1,2,16] versus E_p gives the interesting result in Fig. 1, and obeys eq. 3 with a correlation coefficient of 0.991. In eq. 3, k_{rel} is defined as the second order rate constant for addition to a complexed ring relative to that for addition to $[(C_6H_6)Mn(CO)_3]^+$. This remarkable correlation suggests that reduction potential

$$\ln(k_{rel}) = 11.7\,E_p + 12.9 \tag{3}$$

data can be used to predict reactivities. It must be noted, of course, that E_p values are unrelated to the thermodynamic $E°$ ones, but the discrepancy is probably no more than a few tenths of a volt [17]. Complexes containing nonplanar hydrocarbon rings were found to deviate from eq. 3; this will be the subject of a future communication.

The slope of 11.7 in eq. 3 corresponds to a slope of 0.30 on a free energy scale. This relatively low value suggests that electron transfer is not occurring in the rate determining step in reactions such as 1 and 2, i.e., the phosphine and phosphite addition reactions are mechanistically of the Lewis acid-base type. Dessy et al. [18] found a slope of 0.39 for organometallic nucleophiles reacting with alkyl halides. However, Kochi et al. [19] reported a slope of 1.0 for the oxidation of olefins with iron(III) phenanthroline complexes and for the electrophilic bromination of olefins;

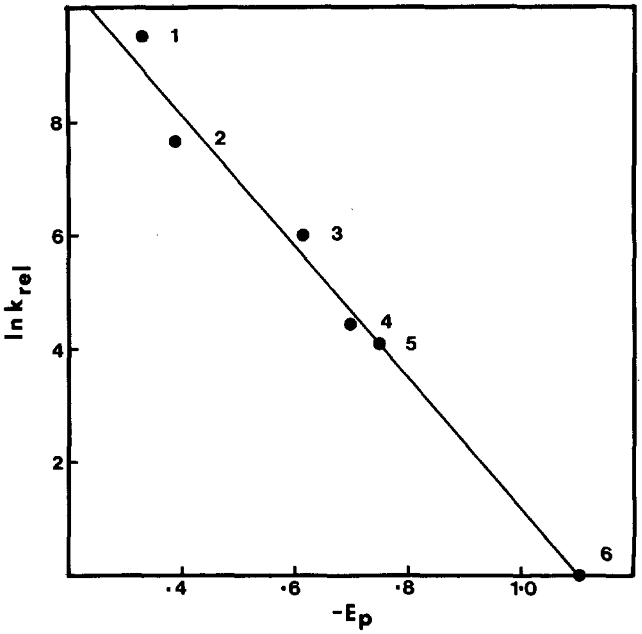


Fig. 1. Correlation of relative rate constants for phosphorus nucleophile addition with reduction potentials for planar cyclic π-hydrocarbon complexes. The key is: (1), $[(C_6H_6)_2Fe](PF_6)_2$; (2), $[(C_4H_4)Fe(CO)_2NO]PF_6$; (3), $[(C_6H_6)_2Ru](PF_6)_2$; (4), $[(C_7H_7)Cr(CO)_3]BF_4$; (5), $[(C_4H_4)Fe(CO)(NO)PPh_3]PF_6$; (6), $[(C_6H_6)Mn(CO)_3]PF_6$.

both reactions probably have single electron transfer as the major contributor to the activation energy.

For attack on the arene ring in $[(\text{arene})_2M]^{2+}$ (M = Fe, Ru, Os) the nucleophilic reactivity order is $PPh_3 > P(OBu)_3$. An examination of available data [1,2,16,20] shows that this order holds for attack at all coordinated rings so far reported, with PPh_3 always about 100 times more reactive than $P(OBu)_3$. For attack at saturated

$$C_2H_5I + PR_3 \rightarrow C_2H_5PR_3^+ I^- \tag{4}$$

carbon as shown in reaction 4 the reactivity order is $PPh_3 > P(OEt)_3$ (26/1) [21]. Interestingly, when the nucleophilic attack is at a transition metal, in contrast to carbon, the order inverts to $P(OBu)_3 > PPh_3$. Reactions 5–8 all follow associative pathways for ligand displacement with the following reactivity ratios ($P(OBu)_3/PPh_3$), reaction 5, 1.2/1; reaction 6, 6.6/1; reaction 7, 1.3/1; reaction 8, >4/1 [22–25]. Although steric factors may contribute in some cases, we suggest that the major reason for the enhanced reactivity of alkyl phosphites towards a metal center

$$Co(NO)(CO)_3 + PR_3 \rightarrow Co(NO)(CO)_2PR_3 + CO \tag{5}$$

$$Fe(NO)_2(CO)_2 + PR_3 \rightarrow Fe(NO)_2(CO)PR_3 + CO \tag{6}$$

$$(C_5H_5)Rh(CO)_2 + PR_3 \rightarrow (C_5H_5)Rh(CO)PR_3 + CO \tag{7}$$

$$(Ph_2C_2S_2)_2M(PPh_3) + PR_3 \rightarrow (Ph_2C_2S_2)_2M(PR_3) + PPh_3 \tag{8}$$

(M = Fe, Co)

is due to π-bonding from the metal to the nucleophile in the activated complex. Alkyl phosphites are better than triphenylphosphine in accepting π-electrons, and therefore the phosphites are more reactive when attacking a metal center compared to a carbon center, where π-bonding probably plays no role in the energy of the activated complex.

If this explanation of phosphite and phosphine reactivity is correct, one would expect a reasonable correlation of reactivity and nucleophile basicity for attack at carbon, but not at a metal center. In fact, just the opposite is claimed to hold. For reactions 5–7 a good Brönsted plot is reported [22–24] for a series of phosphorus nucleophiles. The data points for PPh_3 and $P(OR)_3$ fit the plot quite well. This implies that a good reactivity/basicity correlation does not hold for reactions of carbon-centered electrophiles. However, the quoted basicities of alkyl phosphites [22–24] are surprisingly high compared to estimates made from extrapolations based on ^{31}P NMR data [26], Tolman's χ parameters [27], and Kabachnik's σ^{ϕ} parameters [28]. The basicities reported were obtained by titrating the phosphite with perchloric acid in nitromethane. However, strong acid is known to catalyze Arbuzov rearrangement to the dialkyl phosphite, and it seems possible that the titrations involved more than simple protonation of the trialkyl phosphite, and that the basicities obtained may be in error.

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