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A MECHANISTIC STUDY OF TERTIARY PHOSPHINE AND PHOSPHITE ADDITION TO CHROMIUM TRIAD CARBENES

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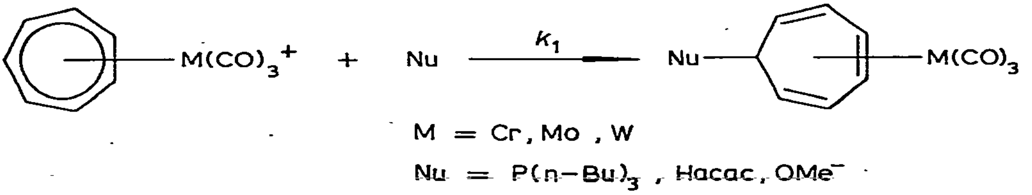
Summary

A stopped-flow kinetic study of tertiary phosphine and phosphite addition to the carbene carbon in chromium triad carbenes, $[(OC)_5MCR'(OEt)]$ (M = Cr, Mo, W; R' = Ph, Me), shows that steric effects markedly influence the equilibrium constant and the reverse rate constant, k_{-1}. The forward rate constant, k_1, measures intrinsic reactivity and is not influenced by steric effects originating in either the size of the nucleophile or the metal. The transition state for the addition step involves little bond formation, and the metal dependence is Mo > W > Cr (8.5 : 5.7 : 1). Comparison is made to previous work on additions to coordinated cyclic π-hydrocarbons.

Introduction

The addition of nucleophiles to organic molecules activated via coordination to a transition metal moiety is an important reaction. Quantitative kinetic studies have appeared [1] concerning the reaction mechanism and the extent of activation or electrophilicity of coordinated cyclic π-hydrocarbons. The application of this information to synthetic procedures is potentially quite significant [2].

The addition of nucleophiles to tricarbonyl(tropylium) cations of the chromium triad, reaction 1, shows almost no metal dependence [3]; the rate constants k_1 for a given nucleophile span at most a factor of two as the metal is varied.



(1)

Interestingly, this behavior is in sharp contrast to that seen in the iron triad [4],

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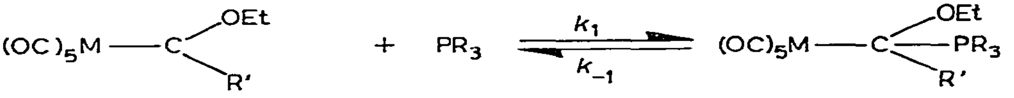
a fact that is likely due to large differences in π-bonding within the iron triad. In this paper we report a kinetic study of phosphine and phosphite addition to chromium triad carbenes, reaction 2. This is a well known reaction [5], and the present study was undertaken in order to compare the carbene-carbon electrophilicity to that in cyclic π-hydrocarbon complexes, and to establish the metal dependence of the electrophilicity. A fairly detailed picture of the transition state structure for phosphine addition to cyclic π-hydrocarbon complexes is emerging [6], and the present study extends this to the primarily σ-bonded carbene systems.



(2)

M = Cr, Mo, W ; R' = Me, Ph ; PR$_3$ = P(n−Bu)$_3$, P (n−OBu)$_3$

Nucleophilic addition to chromium triad carbonyls, $M(CO)_6$, is obviously related to reaction 2. Addition to $M(CO)_6$ is restricted to very strong nucleophiles or to cases in which a second reaction occurs that drives the addition step to completion. The reaction with $PhCH_2MgCl$ shows a slight metal dependence, W ≈ Mo > Cr (2 : 2 : 1) which was attributed to the smaller size of chromium [7]. Rate studies have also appeared for the addition of methyllithium [8] and azide ion [9] to $M(CO)_6$. In the present study of reaction 2, steric effects are shown to markedly influence the equilibrium constant, but not the forward rate constant k_1.

Ritchie and coworkers [10] have shown that the relative rate of nucleophile addition to sp^2 carbon in organic electrophiles is electrophile independent for a substantial range of nucleophiles. The present study shows that this empirical observation does not hold for phosphine addition to $[(C_7H_7)M(CO)_3]^+$ and $[(OC)_5MCR'(OEt)]$ (M = Cr, Mo, W).

Experimental section

The solvent acetone was dried and distilled prior to use. The nucleophiles $P(n\text{-}Bu)_3$ and $P(n\text{-}OBu)_3$ were distilled under N_2 at low pressure. The six carbene complexes $[(OC)_5MCR'(OEt)]$ were prepared by a method essentially identical to that previously described [11]. Purity was established by comparison to published [11] ν(CO) IR frequencies and melting points.

The kinetics of reaction 2 were followed in acetone at 25°C with a Dionex stopped-flow apparatus. The wavelength was either 450 nm or 470 nm. The nucleophile concentration was kept in pseudo first order excess, and plots of the observed rate constant, k_{obs}, as a function of six or more nucleophile concentrations gave excellent fits (correlation coefficients at least 0.99) to eq. 3, the standard expression for a simple approach to equilibrium.

$$k_{obs} = k_1[PR_3] + k_{-1} \tag{3}$$

The equilibrium constants for reaction 2 were determined by three independent methods: from kinetic analysis (k_1/k_{-1}), from IR spectroscopy, and from visible spectroscopy. Agreement among the three methods was excellent.

Results and discussion

A typical plot of eq. 3 is given in Fig. 1 and a complete list of the results is given in Table 1. The phosphine addition reactions are rapid reactions, and are followed by much slower reactions involving carbene and/or CO substitution. These slow substitution steps have been fully characterized elsewhere [5].

Reaction 2 with the sterically demanding nucleophiles $P(t\text{-}Bu)_3$ and $P(t\text{-}OBu)_3$ was studied briefly. The results suggested that addition to the carbene did occur, but separation of this step from the substitution steps was not clean enough for the results to be considered reliable.

The equilibrium and kinetic data in Table 1 clearly show that steric effects are important in reaction 2. In the absence of steric effects one expects the equilibrium constants to follow the order $R' = Ph > R' = Me$ and $P(n\text{-}Bu)_3 > P(n\text{-}OBu)_3$. The order found is Ph > Me for $P(n\text{-}OBu)_3$ and Me > Ph for $P(n\text{-}Bu)_3$. It is also found that for $R' = Me$, $P(n\text{-}Bu)_3$ is greater than $P(n\text{-}OBu)_3$ in stability and that the opposite order holds for $R' = Ph$. These results demonstrate the existence of fairly large steric effects. The cone angle for $P(n\text{-}Bu)_3$, is approximately 20 degrees larger than for $P(n\text{-}OBu)_3$. This increased steric bulk for $P(n\text{-}Bu)_3$ is clearly shown by molecular models to be significant for $R' = Ph$ carbenes, but much less so for the $R' = Me$ carbenes.

It is interesting to see how the individual rate constants, k_1 and k_{-1}, are influenced by steric effects. Table 1 shows a rather striking effect on k_{-1}: for $P(n\text{-}Bu)_3$, k_{-1} $(R' = Ph) > k_{-1}$ $(R' = Me)$ while for $P(n\text{-}OBu)_3$, k_{-1} $(R' = Ph) < k_{-1}$ $(R' = Me)$. Surprisingly, steric effects do not seem to influence k_1. This can be inferred from two observations. First, the relative reactivity of the two nucleophiles is virtually independent of the carbene. Second, the metal dependence of k_1 is almost independent of nucleophile. The first observation in particular is strong evidence for the lack of substantial steric influence on k_1,

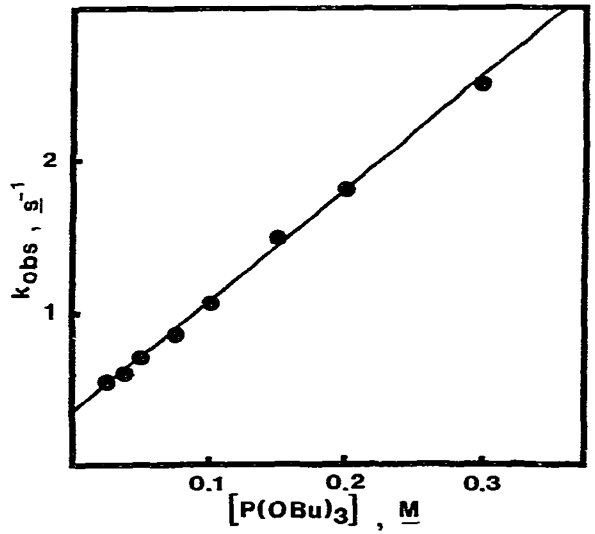


Fig. 1. Plot of eq. 3 for the reaction of $(OC)_5WCMe(OEt)$ and $P(n\text{-}OBu)_3$ in acetone at 25°C.

TABLE 1

RATE DATA [a] FOR REACTION 2 IN ACETONE AT 25°C

M	R'	PR_3	$k_1 (M^{-1} s^{-1})$	$k_{-1} (s^{-1})$	$K^b (M^{-1})$
Cr	Me	$P(n\text{-}Bu)_3$	34.7 ± 1.7	0.70 ± 0.06	50 ± 10
Mo	Me	$P(n\text{-}Bu)_3$	263 ± 15	0.0 ± 1.0	>250
W	Me	$P(n\text{-}Bu)_3$	225 ± 15	1.1 ± 0.6	200 ± 120
Cr	Me	$P(n\text{-}OBu)_3$	1.15 ± 0.05	0.24 ± 0.01	4.8 ± 0.5
Mo	Me	$P(n\text{-}OBu)_3$	10.4 ± 0.5	0.26 ± 0.05	40 ± 9
W	Me	$P(n\text{-}OBu)_3$	7.27 ± 0.35	0.35 ± 0.03	21 ± 3
Cr	Ph	$P(n\text{-}Bu)_3$	111 ± 6	20.9 ± 1.0	5.3 ± 1.0
Mo	Ph	$P(n\text{-}Bu)_3$	830 ± 40	8.0 ± 2.0	100 ± 30
W	Ph	$P(n\text{-}Bu)_3$	560 ± 25	10.5 ± 1.5	53 ± 10
Cr	Ph	$P(n\text{-}OBu)_3$	3.00 ± 0.05	0.095 ± 0.015	32 ± 6
Mo	Ph	$P(n\text{-}OBu)_3$	28.5 ± 1.4	0.0 ± 0.2	>140
W	Ph	$P(n\text{-}OBu)_3$	13.4 ± 0.7	0.32 ± 0.03	42 ± 7

[a] Errors listed are at least one standard deviation. [b] Calculated as k_1/k_{-1}.

and this in turn suggests that the transition state for the k_1 step involves little P—C bond formation. These results also mean that initial attack at the metal and subsequent migration to the carbene can be ruled out. Similar conclusions concerning the transition state for phosphine addition to coordinated cyclic π-hydrocarbons have recently been presented [6].

The dependence of k_1 on the metal is Mo > W > Cr (8.5 : 5.7 : 1). As discussed above, this order is not determined by steric effects originating either in the size of the nucleophile or the metal, and therefore represents intrinsic reactivity. This order differs somewhat from that for addition to $[(C_7H_7)M(CO)_3]^+$, reaction 1, for which Cr > Mo ≈ W (2 : 1 : 1). The two orders are not greatly different in terms of $\Delta G^{\neq}$ requirements, but one can speculate that the different bonding modes of the coordinated ligands being attacked, pi for C_7H_7 and essentially sigma for the carbenes, is responsible.

For all of the reactions in Table 1, the nucleophilicity of $P(n\text{-}Bu)_3$ exceeds that of $P(n\text{-}OBu)_3$ by about 30 : 1. This contrasts with the ratio of 5000 : 1 for reaction 1. In other words, the relative nucleophilic reactivities are electrophile-dependent. This observation does not conform to Ritchie's equation [10] for electrophile-nucleophile combination reactions. Neither does it agree with the reactivity-selectivity principle, for the more reactive $[(C_7H_7)M(CO)_3]^+$ is also more selective.

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