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Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES

XX*. NOVEL ANCHIMERIC ASSISTANCE IN THE ADDITION OF ARYL PHOSPHINES TO $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$

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Summary

Kinetic studies in acetone solvent of the addition of triarylphosphines, $(XC_6H_4)_3P$, to the dienyl ring of $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (I) reveal the following rate variation with X: 2-MeO > 4-MeO > 4-Me > H >> 2-Me (relative rates $90/9/4/1/10^{-3}$). The unexpectedly rapid reaction with $(2\text{-}MeOC_6H_4)_3P$ is rationalised in terms of stabilization of the transition state via an anchimeric effect involving overlap between the filled $2p$ orbital of the 2-MeO oxygen and the empty phosphorus $3d$ orbital. This anchimeric effect, quantified by the k(2-MeO)/k(H) ratio of 91, is considerably larger than that previously observed for addition of arylphosphines to benzyl chloride, suggesting a greater degree of phosphorus-carbon bond formation in the transition state for attack on (I).

During the course of a detailed investigation of the mechanisms of attack by tertiary phosphines upon $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (I), we recently examined the influence of aryl substituents upon the nucleophilicity of triarylphosphines. The reactions of I (X = H, 4-Me, 4-MeO, 2-MeO) proceeded to completion in acetone under the kinetic conditions employed ($[Fe] = 2—3 \times 10^{-4}$ mol dm^{-3}, $[PR_3] = 3—50 \times 10^{-4}$ mol dm^{-3}), and obeyed eq. 2. On the other hand, the related addition by $(2\text{-}MeC_6H_4)_3P$ was an equilibrium process, obeying the 2-term expression (eq. 3).

As expected on electronic grounds, the presence of a 4-Me or 4-MeO sub-

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*For part XIX see ref. 5.

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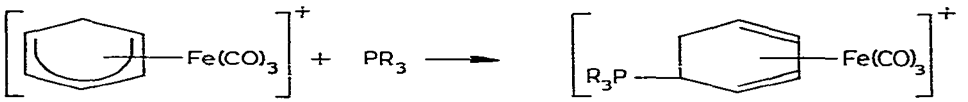


(1)

$$k_{obs} = k_1[PR_3] \qquad (2)$$

$$k_{obs} = k_1[PR_3] + k_{-1} \qquad (3)$$

stituent on the aryl group enhanced the reactivity of arylphosphines relative to triphenylphosphine (by factors of ca. 4 and 9, respectively) (Table 1). In contrast, the presence of a blocking methyl substituent in the 2-position caused a marked retardation in k_1 (k(H)/k(2-Me) = 10^3), emphasising the importance of steric effects. For example, approach of arylphosphines towards the dienyl ring of I is considerably more susceptible to steric constraints than is analogous addition to benzyl chloride, for which a much smaller k(H)/k(2-Me ratio of 23 has been reported [1].

TABLE 1

KINETIC RESULTS FOR ADDITION OF ARYLPHOSPHINES TO $[Fe(CO)_3(1-5\text{-}\eta\text{-}C_6H_7)]^+$ IN ACETONE AT 20°C

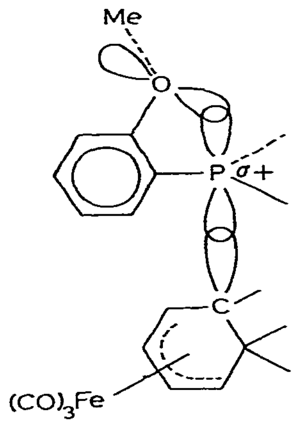
Phosphine	10^{-2} k_1 (mol^{-1} dm^3 s^{-1})	k_{-1} (s^{-1})	rel k_1
Ph_3	74.6	—	1 [a]
$(4\text{-}MeC_6H_4)_3P$	283	—	3.8 [a]
$(2\text{-}MeC_6H_4)_3P$	0.077	0.127	0.001
$(4\text{-}MeOC_6H_4)_3P$	642	—	8.6
$(2\text{-}MeOC_6H_4)_3P$	6800	—	91

[a] Ref. 4.

Classical electronic considerations would predict similar basicities for $(2\text{-}MeOC_6H_4)_3P$ and $(4\text{-}MeOC_6H_4)_3P$. Therefore, in view of the major steric effects apparent in reactions I, it was anticipated that $(2\text{-}MeOC_6H_4)_3P$ would be significantly less reactive than $(4\text{-}MeOC_6H_4)_3P$ towards I. However, it was found to be 11 times more nucleophilic, showing a k(2-MeO)/k(H) ratio of 91 (Table 1).

Interestingly, a similar observation was recently reported by McEwen et al. [1] for the reactions of $(2\text{-}MeOC_6H_4)_3P$ and Ph_3P with benzyl chloride (k(2-MeO)/k(H) = 27). This surprising result was rationalised in terms of an anchimeric effect involving overlap of the filled $2p$ orbital of the 2-MeO oxygen with the empty $3d$ orbital of the phosphorus atom in the transition state. We propose a similar through-space interaction in the transition state (A) for reaction 1 (X = 2-MeO) (only one aryl group is shown for clarity). Movement of electron density from oxygen to phosphorus will help to reduce the positive charge generated on the phosphorus centre in the transition state, thereby lowering its free energy and causing a more rapid reaction.

The magnitude of the anchimeric effect, quantified by the ratio k(2-MeO)/k(may be a sensitive probe for estimating the extent of phosphorus—carbon bond formation and concomitant build-up of positive charge on the phosphorus atom in the transition state. We prefer this ratio to the k(2-MeO)/k(2-M ratio previously suggested by McEwen et al. [1], since we feel that the latter



(A)

is too sensitive to steric effects. In this respect, it is interesting that the k(2-MeO)/k(H) ratio for reaction 1 of 91 is considerably larger than that (27) found [1] for related processes [4]. For these latter reactions with benzyl chloride, McEwen et al. [1] have proposed a relatively early transition state.

$$PhCH_2Cl + (XC_6H_4)_3P \rightarrow (XC_6H_4)_3\overset{+}{P}CH_2PhCl^- \quad (4)$$

On the other hand, the anchimeric effect is considerably smaller than that observed for attack of arylphosphines on α-halobenzylphenylsulphones (k(2-MeO)/k(H) = 142—446) where a large degree of positive charge is believed to be present on the phosphorus atom in the transition state and phosphorus—halogen bond formation is considered almost complete [2]. On the basis of these various k(2-MeO)/k(H) ratios, a transition state is suggested for reaction 1 involving considerable, but far from complete, phosphorus—carbon bond formation in the transition state.

It is also striking that although we have recently observed [3] similar anchimeric assistance in the addition of $(2\text{-}MeOC_6H_4)_3P$ to some other transition metal π-hydrocarbon complexes such as $[Co(\eta\text{-}Cp)(\eta^5\text{-}C_8H_{11})]^+$ (II), it is not found for addition of arylphosphines to $[Cr(CO)_3(\eta\text{-}C_7H_7)]^+$ (III). Thus, the relative rates of attack by $(XC_6H_4)_3P$ upon cation III decrease markedly in the order X = 4-MeO > H >> 2-MeO (relative rates 17/1/4 × 10^{-4}). The significance in terms of intimate mechanism of this dramatic difference compared with reactions (1) is currently being assessed.

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