

## Preliminary communication

### KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES

#### XI\*. ADDITION OF TERTIARY PHOSPHINES TO $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$

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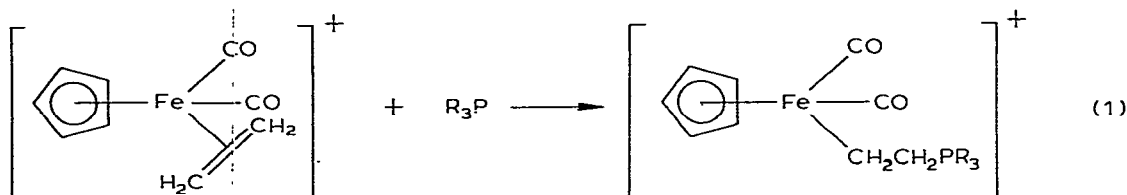
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#### Summary

A stopped-flow investigation of the additions of  $n\text{-Bu}_3\text{P}$  and  $\text{Ph}_3\text{P}$  to the ethylene ligand in  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]^+$  (I) reveals the general rate law,  $k_{\text{obs}} = k[\text{R}_3\text{P}]$ . This is consistent with direct addition, as is the negative  $\Delta S^\ddagger$  of  $-63 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  found for the  $\text{Ph}_3\text{P}$  reaction. The relatively low reactivity of I towards  $\text{Ph}_3\text{P}$  compared with other  $\pi$ -hydrocarbon complexes is seen to arise from its relatively high  $\Delta H^\ddagger$  value of  $42.4 \pm 1.4 \text{ kJ mol}^{-1}$ .

Coordination of olefins to transition metals frequently enhances their susceptibility towards nucleophilic attack. However, apart from the well-documented industrial Wacker process, there are few kinetic studies of nucleophilic addition to coordinated mono-olefins. Cations of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-olefin})]^+$  (I) provide convenient substrates for systematic investigation. The ethylene complex has been reported [1] to react with a very wide range of nucleophiles. In addition, simple synthetic routes have recently been described [2] for analogous cations with a large variety of mono-olefins, as well as for the related carbonyl-displaced cations  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{Ph}_3\text{P})(\eta^2\text{-olefin})]^+$ .

As part of detailed kinetic study of such systems we report here preliminary results for reactions 1 ( $\text{R} = \text{Ph}, n\text{-Bu}$ ).



\*For part X see ref. 8.

Under the conditions employed ( $[\text{Fe}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{R}_3\text{P}] = 5.0 \times 10^{-3}$ – $25.0 \times 10^{-2} \text{ mol dm}^{-3}$ ) both reactions proceed to completion in acetone, as evidenced by the disappearance of the initial carbonyl bands at 2080 and 2045  $\text{cm}^{-1}$  and the growth of product peaks at ca. 2015 and 1960  $\text{cm}^{-1}$ . The reactions were conveniently followed by stopped-flow spectrophotometry at 390 nm, at which wavelength a large increase in absorbance occurred.

From Table 1 the rate law (2) is seen to be obeyed for both phosphine nucleophiles, as expected for direct addition to the ethylene ligand. At 0°C,

$$k_{\text{obs}} = k [\text{R}_3\text{P}] \quad (2)$$

second-order rate constants,  $k$ , of 667 and 30  $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  are calculated for addition of  $n\text{-Bu}_3\text{P}$  and  $\text{Ph}_3\text{P}$ , respectively. Interestingly, the  $k_{\text{Bu}_3\text{P}}/k_{\text{Ph}_3\text{P}}$  ratio of 22 is similar to those previously observed [3–6] for addition of these phosphines at other  $\pi$ -hydrocarbon ligands in complexes such as  $[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+$  (II),  $[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+$  (III), and  $[(\eta^3\text{-C}_8\text{H}_{11})\text{Co}(\eta\text{-C}_5\text{H}_5)]^+$  (IV). With cations II and III the small  $k_{\text{Bu}_3\text{P}}/k_{\text{Ph}_3\text{P}}$  ratios of 17 and 21 (at 20 and 0°C, respectively) were shown to arise from anomalously rapid addition by  $\text{Ph}_3\text{P}$ . It has been suggested [3] that this may be due to specific "stacking" interactions between the aromatic rings of the  $\text{Ph}_3\text{P}$  and the  $\pi$ -hydrocarbon ligands. Since such "stacking" might be expected to be much less significant in mono-olefin complexes, the similar  $k_{\text{Bu}_3\text{P}}/k_{\text{Ph}_3\text{P}}$  ratio found here for cation I suggests that another explanation must be sought for the high reactivity of  $\text{Ph}_3\text{P}$ .

Table 2 compares the reactivity of cation I towards  $n\text{-Bu}_3\text{P}$  with that previously observed with other  $\pi$ -hydrocarbon complexes. The ethylene complex is seen to be one of the least electrophilic species investigated to date. A similar reactivity order is also observed for the analogous reactions with  $\text{Ph}_3\text{P}$  (Table 3). The relatively low reactivity of cation I towards  $\text{Ph}_3\text{P}$  is seen to arise from its comparatively high enthalpy of activation ( $44 \pm 1.4 \text{ kJ mol}^{-1}$ ). Similarly the high

TABLE 1

RATE CONSTANTS FOR ADDITION OF TERTIARY PHOSPHINES TO  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)]\text{BF}_4$  IN ACETONE.  $[\text{Fe}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temperature (°C)	$10[\text{R}_3\text{P}]$ ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )
<i>Triphenylphosphine</i>		
0.0	0.50	1.50
8.1	0.50	2.54
15.5	0.050	0.390
15.5	0.10	0.774
15.5	0.30	2.46
15.5	0.50	4.07
15.5	1.00	9.12
15.5	2.50	22.2
20.0	0.50	5.76
24.1	0.50	6.74
33.1	0.50	13.2
<i>Tri-n-butylphosphine</i>		
0.0	0.090	6.00
0.0	0.22	15.2
0.0	0.36	25.0
0.0	0.45	34.1
0.0	0.89	56.9

TABLE 2  
RELATIVE REACTIVITY OF  $\pi$ -HYDROCARBON COMPLEXES TOWARDS  $n\text{-Bu}_3\text{P}$  IN ACETONE

Complex	$k_0^{\circ\text{C}}$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$k_{\text{rel}}$	Ref.
$[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+$	47 000	160	3
$[(\eta^3\text{-C}_8\text{H}_{11})\text{Co}(\eta\text{-C}_5\text{H}_5)]^+$	40 800	140	6
$[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+$	17 400	59	4
$[(\eta^5\text{-2-MeOC}_6\text{H}_5)\text{Fe}(\text{CO})_3]^+$	10 900	37	3
$[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]^+$	667	2.3	This work
$[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$	295	1	7

TABLE 3  
RATE AND ACTIVATION PARAMETERS FOR REACTIONS OF  $\pi$ -HYDROCARBON COMPLEXES WITH  $\text{Ph}_3\text{P}$  IN ACETONE

Complex	$k_{20^{\circ}\text{C}}$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	Ref.
$[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+{}^a$	7 460	$33.6 \pm 3.4$	$-50 \pm 10$	3
$[(\eta^3\text{-C}_8\text{H}_{11})\text{Co}(\eta\text{-C}_5\text{H}_5)]^+$	1 170	$21.0 \pm 1.2$	$-114 \pm 5$	5
$[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]^+$	115	$42.4 \pm 1.4$	$-63 \pm 5$	This work

<sup>a</sup>Rate constant in acetone, but activation parameters obtained in  $\text{CH}_3\text{NO}_2$  solvent.

reactivity of IV is associated with a very low  $\Delta H^\ddagger$  of  $21.0 \pm 1.2 \text{ kJ mol}^{-1}$ . This is counterbalanced to some extent by the large negative  $\Delta S^\ddagger$  value found for IV. In fact, the intermediate  $\Delta H^\ddagger$  value of  $33.6 \pm 3.4 \text{ kJ mol}^{-1}$  calculated for the most reactive cation II might suggest entropy-control in some of these reactions. However, the activation parameters for this latter complex were obtained in nitromethane (due to decomposition problems in acetone), and comparisons may be complicated by solvation effects.

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