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Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES

XII*. ADDITION OF TRIPHENYLPHOSPHINE TO $[(C_8H_{11})Co(C_5H_5)]BF_4$

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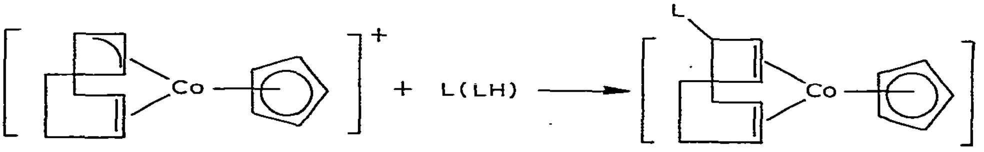
Summary

A stopped-flow investigation of the reversible addition of Ph_3P to $[(C_8H_{11})Co(C_5H_5)]^+$ indicates the rate law, $k_{obs} = k_1[Ph_3P] + k_{-1}$. The low $\Delta H_1^{\ddagger}$ of 21.0 ± 1.2 kJ mol^{-1} and the negative $\Delta S_1^{\ddagger}$ of –114 ± 5 J K^{-1} mol^{-1} are consistent with rapid addition to the enyl ligand. The higher $\Delta H^{\ddagger}_{-1}$ of 86.2 ± 5.1 kJ mol^{-1} and the positive $\Delta S^{\ddagger}_{-1}$ of +60 ± 17 J K^{-1} mol^{-1} are as expected for the reverse dissociation. Preliminary studies show that the related complex $[(C_7H_9)Co(C_5H_5)]^+$ is at least 65 times more electrophilic towards Ph_3P.

The cation $[(C_8H_{11})Co(C_5H_5)]^+$ (I) is known [1] to react with a variety of nucleophiles (L = H^-, acetylacetone, CN^-; LH = morpholine) according to eq. 1. In pursuing our interest in the formation of metal-stabilized *C*-phosphonium ions we recently observed [2] analogous additions on I with L = Ph_3P and i-Pr_3P. Herein we report kinetic data for the addition of Ph_3P to I, which provide the first quantitative information on nucleophilic addition at a π-hydrocarbon co-



(1)

(I)

(+H$^+$)

TABLE 1

KINETIC DATA FOR THE REACTION OF $[(C_8H_{11})Co(C_5H_5)]BF_4$

Temperature (°C)	k_1 (mol dm^{-3} s^{-1})	k_{-1} (s^{-1})
0.15	696 ± 6	0 ± 0.16
6.2	776 ± 26	0.48 ± 0.69
19.4	1150 ± 40	3.82 ± 0.64
23.9	1330 ± 19	5.10 ± 0.50
27.0	1560 ± 7	7.24 ± 0.18
28.9	1690 ± 55	8.30 ± 1.41

ordinated to a metal in the cobalt triad. As far as we are aware it is also the first kinetic investigation of nucleophilic attack on an enyl ligand.

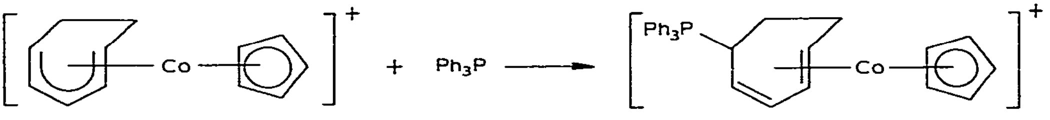
Reaction 1 ($L = Ph_3P$) is rapid in acetone solvent and is accompanied by a large decrease in absorbance at 490 nm. It was conveniently monitored at this wavelength using a thermostatted stopped-flow spectrophotometer. The rate law 2 was observed in the concentration range $[Ph_3P] = 3–50 \times 10^{-3}$ mol dm^{-3}, which is consistent with the equilibrium process 3. Derived values for the forward addition (k_1) and the reverse dissociation (k_{-1}) are collected in Table 1.

$$k_{obs} = k_1[Ph_3P] + k_{-1} \qquad (2)$$

$$[(C_8H_{11})Co(C_5H_5)]^+ + Ph_3P \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(Ph_3PC_8H_{11})Co(C_5H_5)]^+ \qquad (3)$$

Activation parameters associated with k_1 are $\Delta H_1^\ddagger = 21.0 \pm 1.2$ kJ mol^{-1} and $\Delta S_1^\ddagger = -114 \pm 5$ J K^{-1} mol^{-1}. The large negative $\Delta S_1^\ddagger$ is as expected for an associative process, and is similar to values found [3—5] for related reactions considered to involve direct addition of phosphines to coordinated π-hydrocarbons. The rapidity of k_1 is reflected in the very low enthalpy of activation. On the other hand, the much larger $\Delta H_{-1}^\ddagger$ value of 86.2 ± 5.1 kJ mol^{-1} is consistent with bond cleavage in dissociation k_{-1}, as is the positive $\Delta S_{-1}^\ddagger$ of +60 ± 17 J K^{-1} mol^{-1}.

Preliminary studies of the related reaction of $[(C_7H_9)Co(C_5H_5)]^+$ (II) with Ph_3P (eq. 4) show that it is complete within the time of mixing at 20°C and $[Ph_3P] = 3 \times 10^{-3}$ mol dm^{-3}. This indicates a k_1 value larger than 75 000 mol dm^{-3} s^{-1} for reaction 4, showing that the dienyl ligand in II is at least 65 times more electrophilic than the closely related enyl ligand in I.



(II)

(4)

Comparison with previous [3,4] kinetic data for addition of Ph_3P to other organometallic cations allows one to place the cobalt complexes I and II in a general reactivity order towards nucleophiles. $[(C_7H_9)Co(C_5H_5)]^+ >$ $[(C_6H_7)Fe(CO)_3]^+ > [(2\text{-}MeOC_6H_6)Fe(CO)_3]^+ > [(C_7H_7)Cr(CO)_3]^+ >$

$[(C_8H_{11})Co(C_5H_5)]^+ > [(C_7H_9)Fe(CO)_3]^+$ (relative rates at 20°C ca. 400/40/8/6/6/1).

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