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Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES

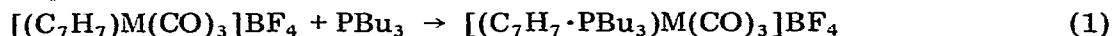
VI*. MECHANISM OF ADDITION OF TRI-*n*-BUTYLPHOSPHINE TO $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, W) AND RELATED CATIONS

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Summary

Phosponium adduct formation via attack of tri-*n*-butylphosphine on the cations $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W) obeys the rate law, Rate = k [complex] [PBu₃]. The very similar rate constants for the Cr, Mo and W complexes confirm the similar electrophilicities of the tropylium rings in these cations, and also support the view that there is direct addition to the rings. The related complexes $[(C_6H_7)Fe(CO)_3]BF_4$ and $[(C_6H_6)Mn(CO)_3]BF_4$ also form adducts with PBu₃, and the quantitative reactivity order $[(C_6H_7)Fe(CO)_3]^+ > [(C_7H_7)Cr(CO)_3]^+ \gg [(C_6H_6)Mn(CO)_3]^+$ (160:60:1) has been established.

The formation of phosponium adducts via the addition of tertiary phosphines to coordinated π -hydrocarbons has been the subject of considerable recent interest [1–7]. Although a variety of such additions have now been reported no kinetic studies have appeared. We report here preliminary kinetic data for the reactions of tri-*n*-butylphosphine with $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, W; eq. 1) which throw some light on the mechanisms of these additions.



Reaction 1 in acetone involves a rapid colour change from orange to red in each instance [6] and can be readily followed by stopped-flow techniques. Stoichiometry 1 has been established for Cr over a wide range of PBu₃ concentrations, but for the Mo and W analogues excess phosphine gives initial adduct formation followed by ring displacement [6]. However, ring removal (involving a colour change from red to yellow) is too slow to interfere with the study of eq. 1.

*Part V see ref. 12.

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TABLE 1

KINETIC DATA FOR ADDITION OF PBu_3 TO ORGANOMETALLIC CATIONS IN ACETONE AT 0°C

Substrate	k ($\text{l mol}^{-1} \text{s}^{-1}$)
$[(\text{C}_7\text{H}_7)\text{Cr}(\text{CO})_3]\text{BF}_4$	17 400
$[(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_3]\text{BF}_4$	7 500
$[(\text{C}_7\text{H}_7)\text{W}(\text{CO})_3]\text{BF}_4$	8 400
$[(\text{C}_6\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$	47 000
$[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]\text{BF}_4$	295

Each of the phosphine additions was shown to obey rate law 2, and their second-order rate constants k at 0°C in acetone are compared in Table 1.

$$\text{Rate} = k [\text{complex}][\text{PBu}_3] \quad (2)$$

Significantly, the rates for reaction 1 are seen to depend very little on the nature of the metal. A factor of only two separates the fastest Cr complex from the Mo and W compounds which have similar k values. These results confirm our previous conclusion [8] that the tropylium rings in $[(\text{C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) have similar electrophilicities. Furthermore, the close similarity in rates supports direct addition by tri-*n*-butylphosphine to the tropylium ligand in each case. An alternative mechanism involving initial rate-determining attack by the phosphine nucleophile at the metal followed by rearrangement to the ring would be expected to lead to large rate differences ($\text{Mo} > \text{W} \gg \text{Cr}$, e.g. 2200:350:1; for ring-displacement from $[(\text{C}_7\text{H}_8)\text{M}(\text{CO})_3]$ by trimethylphosphite [9]). Interestingly, this latter two-step mechanism has recently been suggested for addition of tri-*n*-butylphosphine to the cycloheptadienyl ring in $[(\text{C}_7\text{H}_9)\text{Fe}(\text{CO})_3]\text{BF}_4$ [10].

Included in Table 1 for comparison are k values obtained for addition of PBu_3 to the isoelectronic cations $[(\text{C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+$ and $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$. These reveal the quantitative electrophilicity order: $[(\text{C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+ > [(\text{C}_7\text{H}_7)\text{-Cr}(\text{CO})_3]^+ \gg [(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$ (160:60:1). The sequence $[(\text{C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+ > [(\text{C}_7\text{H}_7)\text{-Cr}(\text{CO})_3]^+$ has been previously noted with acetylacetone as nucleophile [11], but the present study is the first time that the arene complex $[(\text{C}_6\text{H}_6)\text{-Mn}(\text{CO})_3]^+$ has been placed in a quantitative reactivity order. Its low electrophilicity is reflected by its failure to react with heterocyclic aromatic species such as indole.

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