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Preliminary communication

Kinetic studies of the reactions of h^4-1,2,3,6-$C_8H_{12}Fe(CO)_3$ with tertiary phosphines and phosphites

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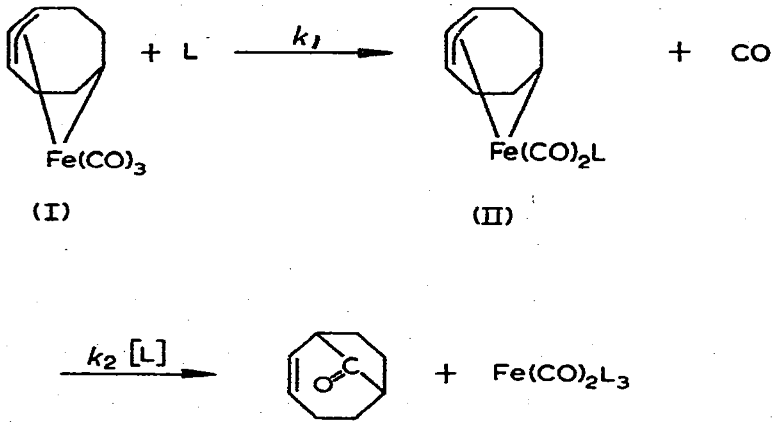
A feature of the molecule (I)[1,2] is the ease with which it reacts with carbon monoxide, tertiary phosphines and phosphites to produce the *trans*-annular ketone (III). We have now examined these reactions in greater detail and have been able to characterize two distinct reaction pathways (see Scheme 1).



Scheme 1 (III) (IV)

The kinetics of the reaction of (I) with a number of substituted phosphines and phosphites have been examined under pseudo first order conditions in heptane solution using IR spectroscopy. With the relatively poor nucleophiles PPh_3 and $P(OPh)_3$, substitution of the carbon monoxide molecule *trans* to the iron—carbon bond takes place via a CO dissociative mechanism. At a given temperature, pseudo first order rate constants rise to a limiting value with increasing concentration of the ligand, and the limiting rate is independent

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of the nature of the entering ligand. The reaction is inhibited by carbon monoxide (1 atm.) and the activation parameters ($\Delta H_1^{\neq} = 29.2 \pm 0.2$ kcal/mole, $\Delta S_1^{\neq} = 15.2 \pm 0.5$ e.u.) are typical for a CO dissociative reaction. No evidence for further reaction of (II) was found at 80°.

Reaction of (I) with more nucleophilic ligands (alkyl phosphines and phosphites) takes place by two paths, and under pseudo first order conditions the kinetics obey a two term rate law:

$$k_{\text{obs}} = k_1 + k_2\,[\text{L}]$$

The k_1 term corresponds to the formation of (II). Its value is the same for all of the ligands used (at 60°) and identical with the limiting rate constant obtained with PPh_3 or $P(OPh)_3$. The second order path results in removal of the organic moiety from the iron centre as the *trans* annular ketone (III) and formation of $FeL_3(CO)_2$. Carbon monoxide (1 atm.) reacts only very slowly with (I) at these temperatures to form (III) in low yield and iron carbonyl species. It is therefore likely that a carbon monoxide molecule bound to the iron becomes inserted into the iron—carbon bond during or after the bimolecular process. Activation parameters for this reaction with $P(OEt)_3$ ($\Delta H_2^{\neq} = 13.7 \pm 0.5$ kcal/mole, $\Delta S_2^{\neq} = -27.0 \pm 1.6$ e.u.) are typical for a bimolecular reaction and are similar to those recently obtained[3] for methyl migration reactions of $C_5H_5Mo(CO)_3CH_3$ and $C_9H_7Mo(CO)_3CH_3$.

Because of the large difference between $\Delta H_1^{\neq}$ and $\Delta H_2^{\neq}$, nearly quantitative conversio of (I) to (III) and (IV) can be achieved using a high ligand concentration at room temperature.

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