

Kinetics of Nucleophilic Addition to Co-ordinated Cyclobutadiene

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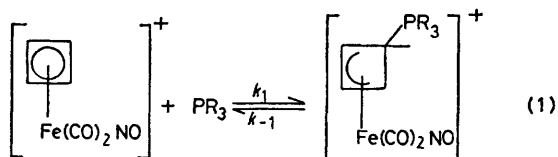
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Summary A kinetic study in acetone of the equilibrium addition of tris-(*p*-chlorophenyl)phosphine to the cyclobutadiene ring in cyclobutadienedicarbonylnitrosyliron hexafluorophosphate suggests that the mechanism of addition does not involve initial attack at the metal.

We report herein the first quantitative kinetic study of nucleophilic addition to co-ordinated cyclobutadiene. It has recently been shown^{1,2} that phosphines, PR₃, rapidly add to cyclobutadienedicarbonylnitrosyliron hexafluorophosphate to yield the corresponding *exo*-phosphonium-cyclobutenyliron complexes according to reaction (1). We have studied the kinetics of reaction (1) in acetone with

(*p*-ClC₆H₄)₃P as the nucleophile. A Durrum stopped flow apparatus was used (λ 455 nm) and the concentrations were [C₄H₄Fe(CO)₂NO⁺] = 1 × 10⁻⁴M and [PR₃] = (1.0—5.0) × 10⁻³M. We found that with most phosphines reaction (1) went essentially to completion and at a rate too fast to measure using the stopped-flow method. (*p*-ClC₆H₄)₃P was chosen as the nucleophile because its rate of addition is slow enough to be measured and i.r. spectra show that reaction (1) does not go to completion unless this phosphine is in extremely large excess. This means that both forward and reverse rates can be measured. The observed rate constants obeyed the rate law [equation (2)] expected for reaction (1). The results are given in the Table.

$$k_{\text{obs}} = k_1[\text{PR}_3] + k_{-1} \quad (2)$$



The activation parameters obtained from data in the Table are: for k_1 : $\Delta H^\ddagger = 5.92 \pm 0.15$ kcal mol⁻¹ and $\Delta S^\ddagger = -22 \pm 2$ cal K⁻¹ mol⁻¹; for k_{-1} : $\Delta H^\ddagger = 17.6 \pm 1$ kcal mol⁻¹ and $\Delta S^\ddagger = +3.2 \pm 4$ cal K⁻¹ mol⁻¹.

Kinetic studies of nucleophilic addition to co-ordinated cyclic π -hydrocarbons have been reported for only three

systems.^{3,4} These results, along with fairly extensive synthetic and structural studies, suggest that the most likely mechanism of addition is simply bimolecular or direct attack on the ring. Brown *et al.*⁵ have recently suggested, however, that in some cases nucleophilic addition may be preceded by attack at the metal. This does not seem to be the case with co-ordinated cyclobutadiene since the full absorbance change calculated for reaction (1) was observed experimentally with no evidence for an intermediate. This, coupled with the known *exo*-configuration of the product,¹ is suggestive of direct attack on the ring. Similar conclusions apply to co-ordinated arene systems.⁴

The activation parameters are very reasonable for a bond formation step (k_1) and a bond breaking step (k_{-1}) and are similar to the activation parameters obtained for co-ordinated arene complexes.⁴

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² A. Efraty, D. Liebman, J. Sikora, and D. Z. Denney, *Inorg. Chem.*, 1976, **15**, 886.

³ L. A. P. Kane-Maguire, *J. Chem. Soc. (A)*, 1971, 1602; K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1975, **102**, C4; G. R. John, L. A. P. Kane-Maguire, and D. A. Sweigart, *ibid.*, 1976, **120**, C47.

⁴ L. A. P. Kane-Maguire and D. A. Sweigart, *Inorg. Chem.*, submitted for publication.

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TABLE. Rate constants for reaction (1)^a.

$T/^\circ\text{C}$	$k_1/\text{l mol}^{-1} \text{s}^{-1}$	k_{-1}/s^{-1}
0.5	1840 (90)	—
7.5	2580 (40)	0.58 (0.07)
13.5	3180 (70)	1.33 (0.19)
19.5	4010 (100)	2.01 (0.22)
27.0	5380 (200)	5.19 (0.40)

^a Acetone solvent; standard deviations in parentheses.

Data available to date imply the following tentative order of reactivity towards ring addition: $[(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_2\text{NO}]^+ > [(\text{C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+ > [(\text{C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+ > [(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$.

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