Substitution Reactions of Tricarbonyl-π-cyclopentadienylmolybdenum Chloride: the Cyclopentadienyl Ligand as Leaving Group

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ALTHOUGH the reactions of tricarbonyl-π-cyclopentadienylmolybdenum chloride, π-$C_5H_5Mo(CO)_3Cl$ (I), with many nucleophiles are recorded,[1–4] no study has been made of the kinetics and mechanism of these reactions. It has been suggested[5] that the π-cyclopentadienyl ligand is able to promote an S_N2 reaction mechanism in substitution reactions [as for example in carbon monoxide replacement reactions of π-$C_5H_5Rh(CO)_2$]. We wished to see whether reactions of the type (1), where L is a nucleophile,

$$\pi\text{-}C_5H_5Mo(CO)_3Cl + L \rightarrow \pi\text{-}C_5H_5Mo(CO)_2LCl + CO \qquad (1)$$

would proceed by an S_N2 mechanism or by an S_N1 mechanism similar to that observed for reactions of the manganese pentacarbonyl halides[6] where the π-cyclopentadienyl ligand is absent.

All reactions were carried out in foil-wrapped flasks (to avoid light-catalysis) under nitrogen, using dry air-free solvents. The concentration of the complex (I) was around 10^{-2}M; that of the nucleophile L was at least ten times greater. Reactions were followed by i.r. spectroscopy, using a Perkin–Elmer 257 spectrophotometer.

The rates of reaction of (I) with PPh_3, $P(OMe)_3$, and PPh_2Bu^n were found to be the same, and to be independent of ligand concentration. This, and the positive entropy of activation suggest an S_N1 mechanism; so does the lack of dependence of the rate on the solvent used (k_1 in tetrahydrofuran at 40° $10{\cdot}8 \times 10^{-5}$ sec.$^{-1}$; in benzene $9{\cdot}2 \times 10^{-5}$; in nitromethane $7{\cdot}1 \times 10^{-5}$). The only products of these reactions were mono-substituted compounds of the type shown in equation (1). Kinetic data for the reactions in tetrahydrofuran are given in Table 1.

TABLE 1

First-order rate constants for the reactions of (I) *with various ligands in tetrahydrofuran*

Ligand	Temperature	Ligand concentration (M)	10^5k_1 (sec.$^{-1}$)
PPh_3	40°	0·089	11·0
		0·343	10·5
		0·664	10·6
$P(OMe)_3$	40	0·096	10·6
		0·302	11·1
PPh_2Bu^n	40	0·372	10·8
		0·563	10·8
PPh_3	35	0·115	5·42
	30	0·115	2·48
	25	0·114	1·22

$E_a = 27{\cdot}2$ kcal./mole. $\Delta S^{\ddagger} = 8{\cdot}2$ e.u.

The reactions of (I) with $PPhBu^n_2$ and PBu^n_3 did not follow this simple pattern. The rates were faster than those for the other ligands, particularly in the case of PBu^n_3, and dependent on the concentration of the ligand. Other products besides the mono-substituted compounds, π-$C_5H_5Mo(CO)_2LCl$, were obtained, though only in small quantities in the case of $PPhBu^n_2$.

These other products have been isolated and shown to be compounds of the type $Mo(CO)_3L_3$ and $Mo(CO)_4L_2$. That these compounds were formed during the reaction and not during purification was shown by comparing the spectra of the isolated complexes (Table 2) with those of the reaction mixtures. We have also shown in independent experiments that these complexes are not formed from the mono-substituted compounds π-$C_5H_5Mo(CO)_2LCl$ under the reaction conditions, and hence must result from direct reaction of the starting material.

TABLE 2

Infrared spectra of products of the reactions between (I) *and* (a) L = $PPhBu^n_2$, (b) L = PBu^n_3

π-$C_5H_5Mo(CO)_2LCl$	(a)	1978, 1885†
	(b)	1977, 1884
$Mo(CO)_3L_3$	(a)	1945, 1854
	(b)	1939, 1845
$Mo(CO)_4L_2$	(a)	2018, 1920, 1904, 1898
	(b)	2015, 1918, 1903, 1892

† In $CHCl_3$ solution; remainder in n-pentane solution. All values are given in cm.$^{-1}$.

When the reactions of (I) with $PPhBu^n_2$ and PBu^n_3 were carried out in n-heptane, the only products were π-$C_5H_5Mo(CO)_2LCl$ and $Mo(CO)_3L_3$. In tetrahydrofuran the same two products were formed, but the concentration of $Mo(CO)_3L_3$ rose to a maximum and then decreased, with formation of $Mo(CO)_4L_2$. This appeared to be due to the reaction (2)

$$Mo(CO)_3L_3 + CO \rightarrow Mo(CO)_4L_2 + L \qquad (2)$$

where the carbon monoxide comes from reaction (1). We have shown that such a reaction does occur when the complexes $Mo(CO)_3L_3$ are dissolved in tetrahydrofuran and treated with carbon monoxide.

Hence a mechanism exists for a reaction of π-$C_5H_5Mo(CO)_3Cl$ with $PPhBu^n_2$ or PBu^n_3 in which both the chloride and cyclopentadienyl ligands are lost, being replaced by three molecules of the ligand L. We are studying this unusual reaction in the hope of clarifying its exact mechanism, and of determining the fate of the cyclopentadienyl ligand.

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