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KINETICS AND MECHANISMS OF REACTIONS OF (CYCLOOCTATETRAENE)TRICARBONYLRUTHENIUM WITH PHOSPHORUS(III) LIGANDS

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SUMMARY

A kinetic investigation of the reaction of the complex $(C_8H_8)Ru(CO)_3$ with tertiary phosphines is reported. The results are interpreted in terms of a mechanism involving bimolecular attack of the entering phosphine on the substrate. The nucleophilic attack of the entering group is facilitated by electron delocalization by the cyclooctatetraene ligand.

INTRODUCTION

The reactivities of olefin metal carbonyl complexes and metal arene carbonyl complexes have been extensively studied as far as the metals of the Group VI are concerned (for reviews see ref. 1). The results indicate that the reactivity of the olefinic substrate is influenced not only by the ligands not directly involved in the substitution but also by the nature of the coordinated hydrocarbon.

The complex $Ru_3(CO)_{12}$ reacts with cyclooctatetraene to form, together with other products, the Ru^0 complex $(C_8H_8)Ru(CO)_3$. The latter reacts with mono and bidentate phosphines (L or L–L) to form *trans*-$Ru(CO)_3L_2$ and *cis*-$Ru(CO)_3$(L–L) (for a review see ref. 2). We have previously reported the analogous reactions of the complex $(C_8H_8)Fe(CO)_3$ and interpreted the results in terms of a mechanism involving a slow coordination of the phosphine to the substrate, followed by fast elimination of cyclooctatetraene from the resulting labile intermediate[3]. We now describe a kinetic investigation on the complex $(C_8H_8)Ru(CO)_3$, which has been carried out in order to elucidate to what extent the presence of the C_8H_8 ligand can facilitate bimolecular attack by the phosphines.

EXPERIMENTAL

The compound $(C_8H_8)Ru(CO)_3$ was prepared as previously described[4]. 1,2-Bis(diphenylphosphino)ethane was prepared by the method of Chatt and Hart[5]. Tributylphosphine and diphenylmethylphosphine were distilled before use. Triphenylphosphine, commercial reagent-grade, was recrystallized from petroleum ether (b.p. 40–70°).

The solvent methylcyclohexane was distilled from sodium under nitrogen and stored under nitrogen.

Determination of rates

The rates of substitution reactions were followed by observing the disappearance of the highest frequency CO stretching absorption of $(C_8H_8)Ru(CO)_3$ on a Perkin–Elmer 457 infrared spectrophotometer. Reactions were carried out in foil-wrapped flasks kept in constant-temperature baths. The kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent; the concentration of the complex was about 10^{-3} *M*.

A preliminary study showed that $(C_8H_8)Ru(CO)_3$ obeyed the Lambert–Beer law in the CO stretching region. All reactions proceeded to completion and the infinite spectra were in good agreement with those of the known products prepared independently.

Good linear plots were obtained by plotting $\log(\log T_b/T)$ *vs.* time, where T is the transmittance at time t and T_b is the transmittance of the time of the first measurement.

Product identification

The complexes *trans*-$Ru(CO)_3L_2$ $[L=P(C_6H_5)_3, P(n\text{-}C_4H_9)_3]$ were prepared as described in the literature[6,7]. No solid product could be isolated from the reaction of $(C_8H_8)Ru(CO)_3$ and $P(C_6H_5)_2(CH_3)$ but the fact that the changes in infrared spectra during the reaction were similar to those for the reaction with the other monodentate ligands is strong evidence for the formation of the complex.

The product *cis*-$Ru(CO)_3[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$ was obtained by treating a refluxing 4-methyl-2-pentanone solution of $(C_8H_8)Ru(CO)_3$ with a slight excess of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$. Its infrared spectrum, in saturated hydrocarbon, showed absorption bands $\nu(CO)$ at 2008 vs, 1943 s, 1922 vs.

RESULTS AND DISCUSSION

The reactions studied kinetically are the following:

$$(C_8H_8)Ru(CO)_3 + 2\,L \rightarrow trans\text{-}Ru(CO)_3L_2 + C_8H_8$$

and

$$(C_8H_8)Ru(CO)_3 + L\text{–}L \rightarrow cis\text{-}Ru(CO)_3(L\text{–}L) + C_8H_8$$

where $L=P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_2(CH_3)$, and $L\text{–}L=(C_6H_5)_2PC_2H_4\text{-}P(C_6H_5)_2$. Methylcyclohexane was used as the solvent for all the reactions.

The rate constants obtained under pseudo-first-order conditions, k_{obs} (sec^{-1}), are reported in Table 1. By plotting the experimental values of k_{obs} *vs.* the concentration of the entering phosphine linear plots are obtained, having zero intercept. Therefore, the rate law can be expressed by the equation:

$$k_{obs} = k_2 \cdot [\text{ligand}]$$

where k_2 is the second-order rate constant. The values of k_2 are summarized in Table 2.

The kinetic behaviour is consistent with a mechanism involving a direct

TABLE 1

PSEUDO-FIRST ORDER RATE CONSTANTS, k_{obs} (sec^{-1}) FOR REACTIONS IN METHYLCYCLOHEXANE:

$(C_8H_8)Ru(CO)_3 + 2\ L \rightarrow trans\text{-}Ru(CO)_3L_2 + C_8H_8$
$(C_8H_8)Ru(CO)_3 + L\text{–}L \rightarrow cis\text{-}Ru(CO)_3(L\text{–}L) + C_8H_8$

Entering ligand	L concn. (10^2 *M*)	Temp. (°C)	$10^3 \cdot k_{obs}$ (sec^{-1})
$P(C_6H_5)_3$	3.21	81.4	0.217
	4.73	81.4	0.333
	6.59	81.4	0.479
	9.82	81.4	0.723
	13.00	81.4	0.981
$P(C_6H_5)_2(CH_3)$	1.66	81.4	1.83
	2.55	81.4	2.83
	3.46	81.4	3.79
	5.15	81.4	5.44
	7.15	81.4	7.48
$P(n\text{-}C_4H_9)_3$	1.58	60.8	0.55
	4.35	60.8	1.37
	6.67	60.8	2.09
	12.42	60.8	3.99
	14.12	60.8	4.46
	0.47	70.1	0.21
	2.48	70.1	1.25
	5.38	70.1	2.76
	10.33	70.1	5.36
	12.25	70.1	6.31
	1.34	81.4	1.37
	3.74	81.4	4.02
	6.50	81.4	6.90
	8.83	81.4	9.30
$(C_6H_5)_2P\text{–}C_2H_4\text{–}P(C_6H_5)_2$	0.81	81.4	0.54
	2.27	81.4	1.65
	3.01	81.4	2.19
	5.10	81.4	3.70
	0.79	90.1	0.88
	1.83	90.1	2.45
	2.89	90.1	3.73
	4.12	90.1	5.30

bimolecular attack of the entering phosphine on the substrate followed by a fast elimination of C_8H_8 to give the products:

$$(C_8H_8)Ru(CO)_3 + L \xrightarrow{k_2} (C_8H_8)Ru(CO)_3L \xrightarrow[\text{fast}]{+L} trans\text{-}Ru(CO)_3L_2 + C_8H_8$$

This implies a transition state having a coordination number greater than that of the starting substrate.

We cannot exclude, *a priori*, a fast pre-equilibrium between the ligand L and the substrate followed by a slow rate determining dissociation of cyclooctatetraene.

TABLE 2

SECOND ORDER RATE CONSTANTS, k_2 ($M^{-1}\cdot\text{sec}^{-1}$), FOR REACTIONS IN METHYLCYCLOHEXANE:

$(C_8H_8)Ru(CO)_3 + 2\,L \rightarrow \textit{trans}\text{-}Ru(CO)_3L_2 + C_8H_8$

$(C_8H_8)Ru(CO)_3 + L\text{–}L \rightarrow \textit{cis}\text{-}Ru(CO)_3(L\text{–}L) + C_8H_8$

Entering ligand	Temp. (°C)	$10^2 \times k_2$ ($M^{-1}\cdot\text{sec}^{-1}$)
$P(C_6H_5)_3$	81.4	1.77
$P(C_6H_5)_2(CH_3)$	81.4	10.0
$P(n\text{-}C_4H_9)_3$	60.8	3.16
	70.1	5.19
	81.4	11.4
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	81.4	7.35
	90.1	13.14

TABLE 3

ACTIVATION PARAMETERS FOR REACTIONS OF $(C_8H_8)Ru(CO)_3$ WITH PHOSPHORUS(III) LIGANDS.

Ligand	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (e.u./mole)
$P(n\text{-}C_4H_9)_3$	14.5	−23.7
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	17.1	−18.2

If this mechanism is operating, the second-order rate constant determined will involve both the pre-equilibrium constant and the rate constant for the release of cyclooctatetraene from the intermediate. The negative activation entropies (Table 3) exclude this mechanism because the negative contribution of the pre-equilibrium stage should be more than compensated for by the positive contribution of the subsequent slow dissociative step.

A mechanism involving incomplete dissociation of the cyclooctatetraene in equilibrium conditions, followed by nucleophilic attack of the entering ligand L on the resulting intermediate and other rapid steps can be excluded because in this case a decreased dependence of the rate on the ligand concentration at high [L] would be observed.

The mass[4], infrared[8] and NMR[8,9] spectra and crystal structure data[10] of $(C_8H_8)Ru(CO)_3$ are consistent with a structure in which the hydrocarbon is bonded to the metal as a 1,3-diene. In solution the ring rotates with respect to the metal and the rate of rotation is temperature dependent. This demonstrates the similarity between this compound and the congener iron derivative, *i.e.* $(C_8H_8)Fe(CO)_3$.

It is possible now to discuss the influence of the coordinated olefin. Because of the nature of the bonding of the cyclooctatetraene ligand in the $(C_8H_8)M(CO)_3$ compounds (M = Ru, Fe) the approach of a nucleophile can cause delocalization of electrons from the metal onto the cyclooctatetraene molecule, and this would facilitate the nucleophilic attack.

There is information in the literature concerning the substitution of molybdenum olefin carbonyl complexes and molybdenum arene carbonyl complexes which shows that the mechanism is strongly affected by the nature of the hydrocarbon molecule[1]. The reactions of $Mo(CO)_4$(norbornadiene) with various entering groups obey a first order kinetic law[11]. $Mo(CO)_4$(1,5-cyclooctadiene) undergoes substitution with several mono- and bidentate neutral ligands according to a rate law where both first order and second order contributions are present[12,13]. The complexes $Mo(CO)_3$-(cycloheptatriene)[14] and $Mo(CO)_3$(arene)[15] undergo substitution according to a second order rate law. Moreover, there is evidence[16] that the π-cyclopentadienyl ligand may affect the mechanism of ligand displacement by promoting an S_N2 reaction path. Although further information is necessary, we are tempted to conclude that the delocalization of electrons which is possible in the cyclooctatetraene ligand is such as to facilitate the bimolecular nucleophilic attack.

The results reported in Table 2 indicate that on changing the nature of the entering phosphine the rate increases with the increasing σ-donor ability of the reagent. The fact that ligands of similar basicity to the phosphines used, having nitrogen as the donor atom, are not good nucleophiles for this substrate suggests that the polarizability of the ligand atom makes an appreciable contribution to the reactivity. This is in accord with a nucleophilic attack on the metal which in its low oxidation state is a solft Lewis acid[17].

It is also known[18] that the complex $RuI(\pi\text{-}C_5H_5)(CO)_2$ undergoes substitution reactions with ligands such as $P(OC_6H_5)_3$ with a rate constant which is roughly two orders of magnitude slower than that of the corresponding iron complex. In contrast, our results indicate a greater reactivity for the ruthenium than for the iron complexes.

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