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NOTE

NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
XI*. A KINETIC STUDY OF EXCHANGE REACTIONS IN ClD_2C–CD_2Cl INVOLVING 1,5-CYCLOOCTADIENERHODIUM(I) CHLORIDE TRIPHENYLARSINE AND THE PARENT DIMER

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INTRODUCTION

Studies on the effect of solvents on exchange reactions in square-planar complexes have continued with the system $[(COD)RhCl]_2$ (dimer) and (COD)-$RhCl(AsPh_3)$ (monomer) in ClD_2C–CD_2Cl (COD = 1,5-cyclooctadiene).

In Part VIII[2] of this series we described how exchange reactions involving the same dimer and monomer were affected by the solvents $CDCl_3$ and CD_2Cl_2. It was found that in CD_2Cl_2 the behaviour is that normally found with arsines, *i.e.* reactions of the monomer with the free ligand and reactions of the dimer with the free ligand, the free-ligand concentration being dependent on the monomer and dimer concentrations. In $CDCl_3$, however, the line-broadening observed for the monomer appeared to be independent of the monomer and dimer concentrations while the lifetime-broadening of the dimer was linearly dependent on the monomer concentration and inversely proportional to the dimer concentration. As a result the following reaction scheme was put forward:

$$\text{ML} \rightleftarrows \text{“ML”} \qquad \text{(slow)} \qquad (1)$$

$$\text{“ML”} + \text{M}^*\text{M} \rightarrow \text{“M}^*\text{L”} + \text{M}_2 \qquad \text{(fast)} \qquad (2)$$

where ML is the monomer, MM or M_2 is the dimer, and "ML" is an unknown species presumably generated by intramolecular rearrangement or a change in solvation. This scheme requires that reaction (1) must be slow in NMR terms and that (2) must be fast.

The reason for investigating the same system in $(CD_2Cl)_2$ was that the properties of this solvent lie between those of $CDCl_3$ and CD_2Cl_2. The behaviour was expected to be similar to that found in $CDCl_3$ since at low M_2 concentrations the behaviour in CD_2Cl_2 resembles the $CDCl_3$ case.

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* For Part X see ref. 1.

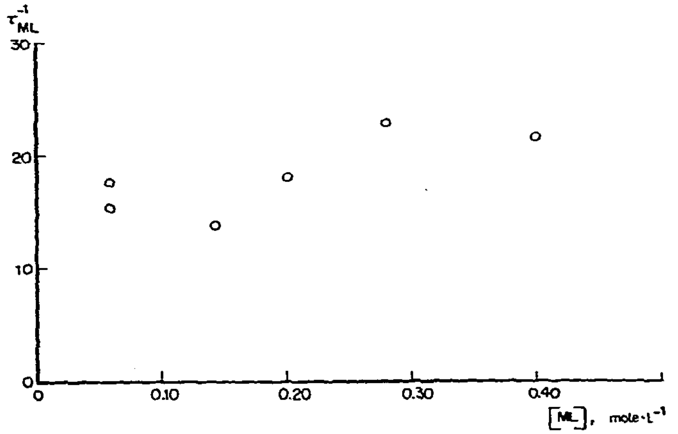


Fig. 1. The dependence of τ_{ML}^{-1} on [ML] in $(CD_2Cl)_2$ at 5° for ML=(COD)RhCl(AsPh$_3$).

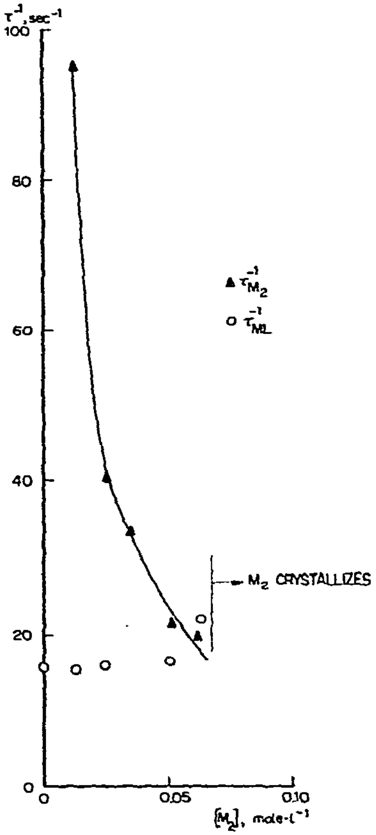


Fig. 2. The dependence of $\tau_{M_2}^{-1}$ and τ_{ML}^{-1} on [M$_2$] at [ML]=0.20 mole·l^{-1} in $(CD_2Cl)_2$ at 5° for ML=(COD)RhCl(AsPh$_3$).

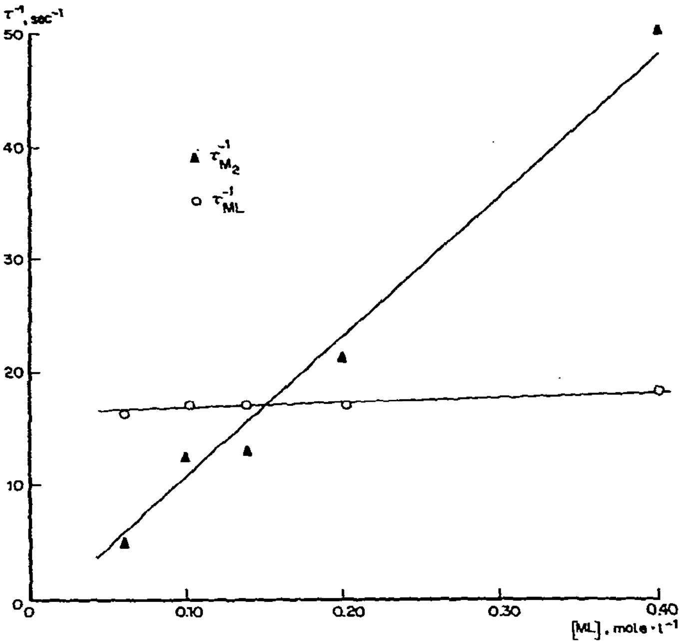
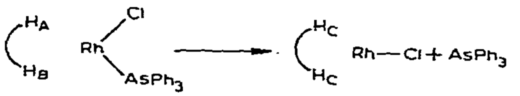


Fig. 3. The dependence of $\tau_{M_2}^{-1}$ and τ_{ML}^{-1} on [ML] at $[M_2]=0.05$ mole·l^{-1} in $(CD_2Cl)_2$ at 5° for ML= (COD)RhCl(AsPh$_3$).

RESULTS AND DISCUSSION

The experimental details are given in Part VIII[2]. The concentration dependences are given in Figs. 1–3. In Fig. 1 it is seen that the left-right interchange of the square-planar complex is almost independent of the monomer concentration itself. Hence the exchange reaction is a simple monomolecular process (3) or a dissociation process (4):

(3)



(4)

Mixtures of monomer and dimer (Figs. 2 and 3) give the following results for the exchange line-broadening (τ^{-1}):

$$\tau_{ML}^{-1} = k + \text{other, small contributions}$$

$$\tau_{M_2}^{-1} = k \cdot \frac{[ML]}{2[M_2]}$$

Unfortunately, the insolubility of M_2 made measurement at concentrations above

0.07 mole·l^{-1} impossible. A slight increase of τ_{ML}^{-1} was observed at $[M_2]=0.06$ mole·l^{-1}.

The rates of ML are slightly higher than expected and some other reactions must contribute to τ_{ML}^{-1}. The kinetic parameters are $k=10^{10.5}\cdot e^{-12000/RT}$ (activation energy in cal/mole). The absolute rates in $ClD_2C{-}CD_2Cl$ are one-third higher than the rates in $CDCl_3$.

The mechanism may well be the one mentioned in the introduction, or, assuming dissociation, it may be as follows. The dissociation reaction is relatively fast ($\tau_{ML}^{-1}=18$ sec^{-1} at 5°) but the amount of L formed must remain very small since the reaction:

(5)

would have a τ_{ML}^{-1} in the order of 20 when $[L]=10^{-2}$ mole·l^{-1} at 5° (Part VIII[2]). The concentration dependence of this reaction has not been found. The dissociation reactions responsible for the kinetics found are:

$$ML \leftrightarrows M+L \tag{6}$$

$$M_2 \rightleftarrows 2\,M \quad \text{(fast)} \tag{7}$$

The species M is in fast exchange with M_2 and hence the reverse reaction in eqn. (6) is observed in the collapsed signal of M_2 and M. The resulting reciprocal lifetimes are:

$$\tau_{ML}^{-1} = k_6$$

$$\tau_{M_2}^{-1} = \frac{[M]}{2[M_2]+[M]}\cdot k_{-6}\cdot[L] = k_6\frac{[ML]}{2[M_2]}$$

The derivation of the latter equations will be found in Part II[3] of this series and a recent review[4].

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