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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
IX*. THE SYSTEM 1,5-CYCLOOCTADIENERHODIUM(I) CHLORIDE AND TRIS[*p*-(DIMETHYLAMINO)PHENYL]ARSINE**

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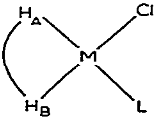
SUMMARY

Measurements of line-broadening in NMR spectra as a result of reactions involving the monomer (COD)Rh(L) in $CDCl_3$ are reported (COD = cyclooctadiene and $L = As[p\text{-}(C_6H_4N(CH_3)_2]_3)$. In the temperature region −20° to +25° the monomer exchanges L with the dimer $[(COD)RhCl]_2$ in the NMR time-scale. The kinetic characteristics differ from those previously found with L = triphenylarsine, thus showing that small variations in the ligand may give rise to completely different concentration dependences. The kinetic behaviour in fact resembles that found with the rhodium complex of triphenylphosphine, *i.e.* a reaction between the monomer and the dissociated dimer is observed. Almost the same parameters are found for the two systems, but the temperature required in the case of triphenylphosphine is slightly higher.

INTRODUCTION

Parts I-IV in this series[1-4] dealt with the conformational rearrangements and exchange reactions of π-allylpalladium(II) compounds containing group V donor ligands. They included a detailed study of the concentration dependences of the broadening of the NMR signals and thus provided some insight into the movements of the asymmetrically bonded allyl group. Parts V-VIII[5-8] subsequently dealt with the kinetics of exchange reactions of cyclooctadiene- and bicyclo[2.2.1]hepta-2,5-dienerhodium(I) and -iridium(I) chlorides with arsines and phosphines. In these compounds the metal ions have an electronic d^8 configuration. The so-called monomers consist of a metal ion with a square-planar configuration of four ligands: a chloride ion, a group V donor ligand (L) and a bidentate organic group occupying *cis*-positions. The general formula is:



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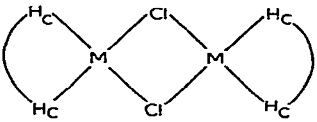
* For Part I-VIII see refs. 1–8 respectively.

** 1,5-Cyclooctadiene is represented by (COD) in formulas throughout this paper.

The free diene has a plane of symmetry and hence the protons in positions A and B are identical. There is no plane of symmetry in the monomer, however, and so the chemical shifts of A and B can differ, as indeed is found. The dimers contain two metal ions with square-planar configuration and the general formula is:



When a solution of monomer and dimer is heated the first reaction to occur in these systems, as indicated by the NMR spectrum, is the interchange of protons A and B in the monomer. This process may be intramolecular or intermolecular. In the latter case the other molecule involved may be the free ligand, the free diene, the dimer, the dissociated dimer, or a second monomer molecule. In the case of monomer–monomer reactions exchange of molecules or ions cannot be observed with NMR techniques since the final products of the reactions are identical with the starting monomers. The reaction with the free ligand is usually a ligand-exchange reaction, whereas in the reactions with dimers exchange of ligands or ions may occur. In this paper we are particularly interested in monomer–dimer reactions involving ligand exchange.

GENERAL REMARKS ON EXCHANGE MECHANISMS

Previous NMR studies[1-8] indicated the occurrence of the following reactions.
(*a*) Direct reaction between monomer (ML) and dimer (M_2):

$$MM^* + ML \rightarrow MM + M^*L \tag{1}$$

(*b*) Marked dissociation of the monomer:

$$ML \rightleftarrows M + L \tag{2}$$

The free ligand thus formed gives rise to the following equilibria and exchanges:

$$ML + L^* \rightarrow ML^* + L \tag{3}$$

$$M_2 + L \leftrightarrows M_2L \tag{4a}$$

$$M_2L + L \rightleftarrows 2\,ML \tag{4b}$$

Clearly, these reactions are more likely to be found in arsine systems than in phosphine systems since the dissociation constants of the latter are much smaller.
(*c*) Reactions involving the dissociated dimer:

$$M_2 \rightleftarrows 2\,M \tag{5}$$

According to the exchange reaction:

$$ML + M^* \rightarrow M^*L + M \tag{6}$$

the exchange rate of L is proportional to the concentration of M. This mechanism is often found in the case of phosphine compounds, *i.e.* where dissociation of ML is negligible.

(*d*) A simple reaction scheme may be the following, in which only dissociation reactions are assumed to occur:

$$\mathrm{ML} \rightleftarrows \mathrm{M}+\mathrm{L} \qquad (2)$$

$$\mathrm{M_2} \rightleftarrows 2\,\mathrm{M} \qquad (5)$$

With most of the triphenylphosphine and arsine compounds of $[(\mathrm{COD})\mathrm{RhCl}]_2$ one or other of these reactions was observed. For instance, mechanism (*c*), with reactions (5) and (6), was found for $(\mathrm{COD})\mathrm{RhCl}[\mathrm{P}(\mathrm{C_6H_5})_3]$. The behaviour of the corresponding arsine compound, however, was more complex[5,8]: in $\mathrm{CD_2Cl_2}$ mechanisms (*b*) and (*a*) were found, while in $\mathrm{CDCl_3}$ mechanism (*a*) was found, with a pre-equilibrium for the formation of a so-called activated monomer (7):

$$\begin{aligned} &\mathrm{ML} \rightleftarrows \text{"activated ML", or} \\ &(\text{solvent})+\mathrm{ML} \rightleftarrows \mathrm{ML}\,(\text{solvent}),\text{ or} \qquad (7)\\ &\mathrm{ML}\,(\text{solvent})_2 \rightleftarrows \mathrm{ML}\,(\text{solvent})+(\text{solvent}) \end{aligned}$$

The kinetics indicate that the formation of the activated monomer must be considerably slower than reaction (1)*, and speculation about the structure of this unknown species led to the conclusion that a solvent-exchange reaction was involved. Reaction (1) occurs in the NMR time-scale, *i.e.* 10–100 sec^{-1}, and hence it may be concluded that the solvent-exchange is slower. The monomer-solvent interaction, however, is very weak: even in polar media the solvent-exchange rate is considerably higher[9]. It is concluded therefore that the activated species is more complex and must involve more than a solvent-exchange reaction.

Another possible explanation is that mechanism (*d*) can account for the same concentration dependences if it is assumed that the species M is in a fast exchange with $\mathrm{M_2}$. In this instance the dissociation of ML will also be independent of the $\mathrm{M_2}$ concentration and the line-broadening of $\mathrm{M_2}$ will be proportional to $[\mathrm{ML}]/[\mathrm{M_2}]$, which has been found. This dependence can be visualized as follows. The combination of M with L can be observed in the collapsed signals of $\mathrm{M_2}$ and M, and the line-broadening is proportional to the fraction of the M signal in the $\mathrm{M_2}$ signal. If this fraction is replaced by chemical concentrations we obtain:

$$1/\tau(\mathrm{M_2}) = \frac{[\mathrm{M}]}{2[\mathrm{M_2}]}\cdot k_{-2}\cdot[\mathrm{L}] = 2k_2\cdot\frac{[\mathrm{ML}]}{[\mathrm{M_2}]}$$

It therefore seemed worthwhile to obtain more information about closely related systems.

EXPERIMENTAL

The $\mathrm{As}[p\text{-}\mathrm{C_6H_4N(CH_3)_2}]_3$ compound with $[(\mathrm{COD})\mathrm{RhCl}]_2$ was synthesized along the lines reported previously[1].

The measurements were carried out in $\mathrm{CDCl_3}$ in the temperature range −30° to +40°, on a Varian HA-100 spectrometer. Low temperatures were obtained with the Varian variable Dewar inserts. Tetramethylsilane was employed as internal

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* In reaction (1) the "activated ML" species must occur on both sides of the equation.

standard. The monomer and dimer were weighed in a sample tube, after which the necessary volume of $CDCl_3$ was added.

The rates of coalescence were usually calculated in the slow exchange limit. For the natural widths of the H_A, H_C and H_B signals we used values of 10.2, 10.1 and 10.0 Hz, respectively. Coupling between the protons A and B is not significant. The chemical shifts are 5.28 and 3.50 ppm, respectively. The concentrations were varied between 0.02–0.15 mole/l and 0.05–0.20 mole/l for M_2 and ML, respectively.

RESULTS

The lifetimes for protons A and C for chemical exchange were measured from the line-broadening. The results are plotted against the concentrations (based on weighed-in quantities) in Figs. 1 and 2, from which it may be deduced that:

$1/\tau(ML)$ is proportional to $[M_2]^{\frac{1}{2}}$ and independent of [ML];

$1/\tau(M_2)$ is linearly dependent on [ML] and proportional to $[M_2]^{\frac{1}{2}}$.

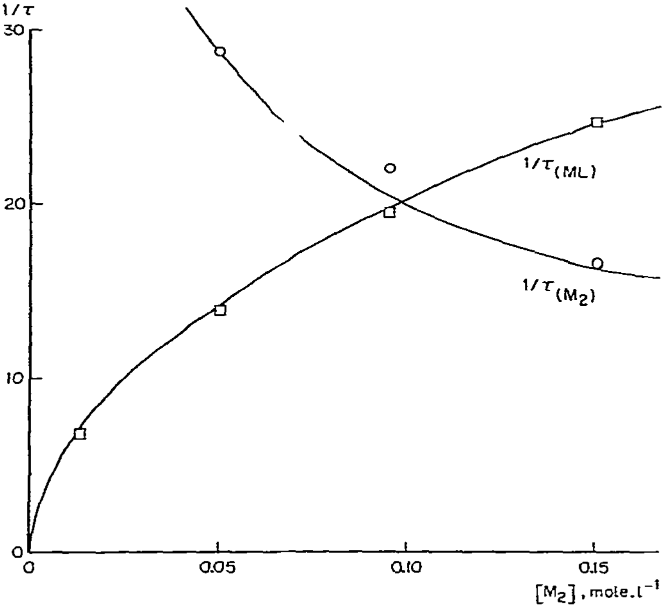

Fig. 1. The dependence of $1/\tau(M_2)$ and $1/\tau(ML)$ on $[M_2]_0$ for $[ML] = 0.20$ mole/l at 21° in $CDCl_3$. $[M_2]_0$ denotes weighed-in amounts; $ML = (COD)RhCl\{As[p\text{-}C_6H_4N(CH_3)_2]_3\}$; $M_2 = [(COD)RhCl]_2$.

The same constant *k* was found for both broadenings. Theoretically the curves should intersect at 0.10 mole/l in both figures, namely when $[ML] = 2[M_2]$. The activation parameters for *k* are $10^{7.3}$ and 8.3 kcal. In formulae:

$$1/\tau(ML) = 10^{7.3} \cdot e^{-8300/R \cdot T} \cdot [M_2]^{\frac{1}{2}}$$

$$1/\tau(M_2) = \tfrac{1}{2} \cdot 10^{7.3} \cdot e^{-8300/R \cdot T} \cdot \frac{[ML]}{[M_2]^{\frac{1}{2}}}$$

These results are in accord with mechanism (*c*), according to which exchange of L

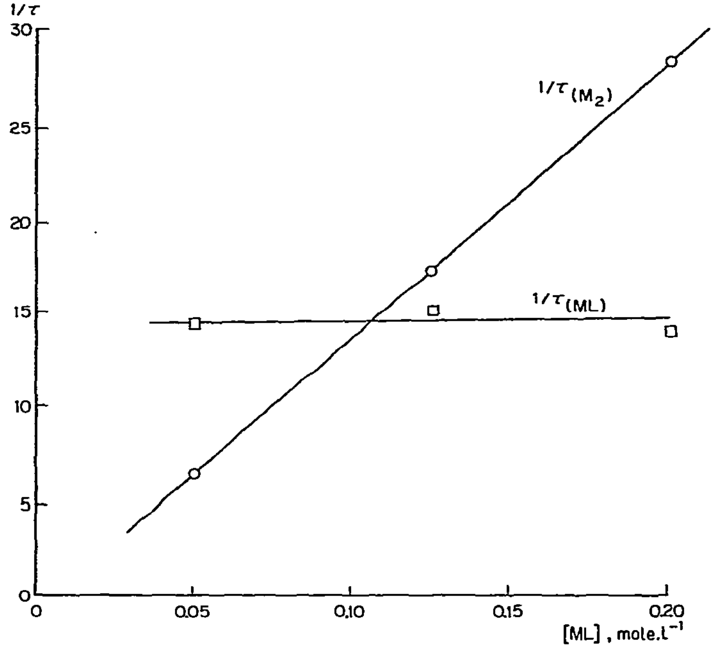

Fig. 2. The dependence of $1/\tau(M_2)$ and $1/\tau(ML)$ on $[ML]_0$ for $[M_2]=0.05$ mole/l at 21° in $CDCl_3$. ML = $(COD)RhCl\{As[p\text{-}C_6H_4N(CH_3)_2]_3\}$; $M_2 = [(COD)RhCl]_2$.

occurs via the dissociated dimer. For the above dependence of $1/\tau(M_2)$ to obtain, it is necessary for the exchange between M and M_2 to be very fast in NMR terms: the reaction (6) of dissociated dimer M is then observed as a line-broadening of the collapsed M and M_2 signals, this broadening being proportional to the fraction $p(M)$ of M occurring in the signal[10]. We do not see reaction (5) since M and M_2 have the same (average) NMR absorption:

$$1/\tau(M_2) = p(M)\cdot k_6\cdot[ML] = \frac{M}{M+M_2}\cdot k_6\cdot[ML]$$

This reduces to $(M/M_2)\cdot k_6\cdot[ML]$ when $[M] \ll [M_2]$; and when $k_{-5}\cdot[ML] > k_6\cdot[ML]$ the ratio (M/M_2) can be replaced by the chemical concentrations times the statistical factor. According to (5) we then obtain:

$$1/\tau(M_2) = \tfrac{1}{2}k_6\cdot K_5^{\frac{1}{2}}\cdot\frac{[ML]}{[M_2]^{\frac{1}{2}}}$$

The k measured is equal to $k_6\cdot K_5^{\frac{1}{2}}$.

DISCUSSION

The concentration dependences found here for the tris[p-(dimethylamino)-phenyl]arsine ligand have in the past also been found for the systems $(COD)RhCl[P(C_6H_5)_3]$ and $(Nor)RhCl[P(C_6H_5)_3]$*, for which mechanism (*c*) has been propo-

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* (Nor) = bicyclo[2.2.1]hepta-2,5-diene.

sed[1-8]. On the other hand, scheme (*b*) has been proposed[1-8] for other arsine complexes, namely (COD)IrCl[As(C_6H_5)$_3$], (Nor)Rh[As(C_6H_5)$_3$] and (COD)RhCl-[As(C_6H_5)$_3$] in CD_2Cl_2 at low temperatures. Besides the concentration dependences, however, there is also the equivalence of the rate constants for the ML and M_2 broadening in the present system, which is a very strong argument in favour of mechanism (*c*). On a qualitative basis it can easily be understood why (*c*) is found for phosphines and (*b*) is found for arsines complexes: mechanism (*b*) assumes a substantial dissociation of ML whereas (*c*) does not. At the same time it is seen that a very small modification, *i.e.* substitution of an amino group in triphenylarsine, is able to completely change the reaction pattern. Thus although we expected to find a mixture of simple dissociation (*d*) and some other reaction, as in the case of As(C_6H_5)$_3$, we found instead that the substituted arsine behaved similarly to phosphines. This is in agreement with our qualitative knowledge of the stabilities of the various complexes, from which it may be deduced that the dimethylamino donor group causes a slight increase in the stability of the arsine–metal bond. Admittedly, reactions (5) and (6) were observed at about 35° higher temperatures in (COD)RhCl[P(C_6H_5)$_3$], but this is also in accord with the known stabilities.

The importance of slight variations in the solvent has already been demonstrated[8] in connection with the (COD)RhCl[As(C_6H_5)$_3$] system in $CDCl_3$ and CD_2Cl_2. In the latter solvent, dissociation of the monomer was shown by the reaction of the dimer with free ligand.

It must be remembered, however, that in cases of slow exchange the NMR line-broadening technique is limited to the extent that:

(*a*) Only reactions between species with different chemical shifts and in concentrations of the same order of magnitude can be measured.

(*b*) As the sample is heated, only the first reaction to reach a rate in the NMR timescale (*i.e.* $k = 10$–100 sec^{-1}) can be observed.

Other reactions that occur at higher temperatures, and that may be relatively more important, cannot be studied. So, having found reaction (*c*) for the tris[*p*-(dimethylamino)phenyl]arsine ligand, we are not able to find mechanism (*b*) or (*d*) at higher temperatures, although in view of the different activation energies this may be possible in theory. On the other hand, with some of the other systems[1-8] we were able to study several reactions (inter- and intramolecular) in several different temperature regions, making use of different protons on the organic group.

No new indications have been found for a mechanism involving "activated" species or cage-effects. The system described here does appear to have a partly dissociative character, but dissociation of ML could not be found in the limited temperature range. Dissociation of ML may well contribute to the broadening of the M_2 signal but, as may be expected, the contribution is considerably smaller than in the normal arsine system (*d*).

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