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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
VI. KINETIC STUDIES OF REACTIONS INVOLVING [(1,5-CYCLOOCTADIENE)IrCl]$_2$ AND TRIPHENYLARSINE OR TRIPHENYLPHOSPHINE

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SUMMARY

NMR kinetic investigations have been carried out on systems containing the 1,5-cyclooctadiene complexes (COD)IrCl(L) as such or in combination with [(COD)IrCl]$_2$ or L (L = AsPh$_3$ or PPh$_3$).

The results for mixtures of (COD)IrCl(L) and L indicate that at low temperatures (−70 to −40°) an exchange of L occurs via the five-coordinate species (COD)IrCl(L)$_2$, which is in equilibrium with much smaller amounts of the ionic species [(COD)Ir(L)$_2$]$^+$Cl$^-$.

With (COD)IrCl(AsPh$_3$) and [(COD)IrCl]$_2$ reactions of dissociated triphenylarsine with both the monomeric and dimeric complexes are observed. Line-broadening was not noted when triphenylarsine was replaced by triphenylphosphine.

Furthermore, it was found that (COD)IrCl(AsPh$_3$) reacts with Cl$^-$ and 1,5-cyclooctadiene. The reaction with 1,5-cyclooctadiene does not involve exchange between the coordinated and the free diolefin.

The results are compared with those of the isoelectronic and isostructural rhodium systems.

I. INTRODUCTION

Recently[1] NMR kinetic studies on the influence of the ligand L on reactions of the monomeric diene complex (COD)RhCl(L) (COD = 1,5-cyclooctadiene; L = AsPh$_3$, PPh$_3$) have been reported. These systems were investigated by studying the broadening and/or coalescence of the olefinic protons of the coordinated diene in CDCl$_3$ solution. It was observed that exchange reactions occur in mixtures of (COD)RhCl(L) and L, *i.e.*:

$$\text{(COD)RhCl(L)} + \text{L}^* \leftrightarrows \text{(COD)RhCl(L}^*\text{)} + \text{L}$$

Interesting differences were found for mixtures of the monomer and the dimer [(COD)RhCl]$_2$. In the case of the arsine system the kinetics strongly indicate the occurrence of the following equilibria:

$$(COD)RhCl(AsPh_3) \rightleftarrows (COD)RhCl(AsPh_3)\,(S)$$

$$(COD)RhCl(AsPh_3)(S) + [(COD)Rh^+Cl_2Rh(COD)] \rightleftarrows$$
$$\rightleftarrows [(COD)RhCl_2Rh(COD)] + (COD)Rh^+Cl(AsPh_3)S$$

The formation of the five-coordinate species $(COD)RhCl(AsPh_3)$ (S) ($S = CDCl_3$) from the monomer was found to be rate-determining.

For the phosphine system, however, the results were analogous to those obtained for the system containing the π-methallyl complexes $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ and $[(\pi\text{-}C_4H_7)PdCl]_2$ in the temperature region of +20 to +80°, *i.e.* a fast dissociation of the dimer[2]:

$$[(COD)RhCl]_2 \rightleftarrows 2\,(COD)RhCl$$

and subsequently a rate-determining exchange step:

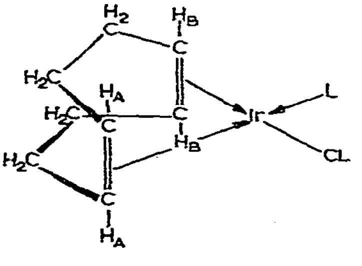
$$(COD)RhCl + (COD)Rh^+Cl(PPh_3) \rightleftarrows (COD)RhCl(PPh_3) + (COD)Rh^+Cl$$

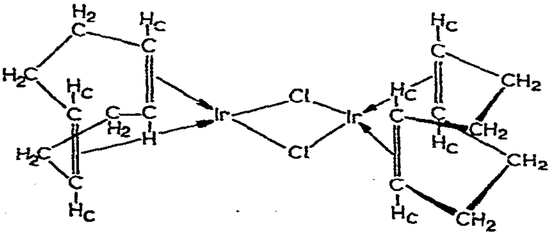
We have now investigated the reactions of the isoelectronic and isostructural iridium complexes. The results obtained are compared with those of the rhodium systems.

II. EXPERIMENTAL

The preparation and properties (IR, conductivity etc.) of this type of complexes have been reported before[1,3-5]. The NMR spectra were measured with a Varian spectrometer (HA100 and DP60) with $CDCl_3$ as solvent. The concentrations of (COD)IrCl(L), $[(COD)IrCl]_2$ and L were between 0.1–0.5 mole/l, 0.1–0.5 mole/l and 0.01–0.05 mole/l, respectively. Tetramethylsilane (TMS) was employed as an internal standard. All measurements were carried out on oxygen-free solutions.

The pseudo first-order rate constants $1/\tau$ (τ is the lifetime of the protons concerned) were calculated for mixtures of the monomer and the dimer, from the broadening of the signals (slow exchange limit[6]) of the olefinic protons H_A and H_B of (COD)-IrCl(L) and of H_C of the dimer.





In the case of exchange reactions of (COD)IrCl(L) with L we had to use formulas for the fast exchange limit[6] of the coalesced signal of H_A and H_B.

Double resonance experiments showed that the protons H_A and H_B do not couple with each other. They do couple with the adjacent CH_2 groups; the coupling constants $J(H_A\text{–}CH_2)$ and $J(H_B\text{–}CH_2)$ are about 2–3 cps. The protons H_A and H_B may also couple with the phosphorus nucleus[1]. In the latter case appropriate corrections for the line width were made.

The use of simple Bloch equations including exchange for an AB system is justified for the slow exchange limit, as the coupling constants between H_A (H_B, H_C) and the CH_2 groups are small as compared with the chemical shift differences between the signals H_A, H_B and H_C. For the fast exchange case a correction may be needed. Application of the more accurate density matrix treatment[7,8] for the fast exchange case was, however, impossible, as we could not determine the coupling constants with sufficient accuracy. However, from the results it is clear that for the determination of the reactions occurring the use of the Bloch equations for the calculation of the rates is sufficiently accurate.

The contribution to the line width due to exchange of the signals H_A, H_B and H_C was obtained by subtracting the line width, in the absence of exchange, from the actual line width. This is a good approximation, since a line shape analysis of overlapping Lorentz curves for multiplets of the type observed for H_A, H_B and H_C shows that the measured exchange contribution to the line width (when it exceeds ~2 cps) is approximately equal to the broadening of the component line widths.

For the line widths in the absence of exchange we used for the signals H_A, H_B and H_C values of 10.0, 9.5 and 10.0 cps, respectively. These values are independent of the temperature (−20° to +80°) for $L = PPh_3$. We have assumed that this is also the case for $L = AsPh_3$.

The conductivities were measured with the aid of a Philips Philoscope G.M.4249 with platinum electrodes. Dichloromethane and nitromethane were used as solvents.

III. RESULTS AND DISCUSSION

In the following we will discuss the kinetics obtained, in section *A* for mixtures of the monomer (COD)IrCl(L) (=ML) and L($L/Ir > 1$), and in *B* for mixtures of (COD)IrCl(L) and the dimer [(COD)IrCl]$_2$ (=M_2) ($L/Ir < 1$) and for solutions of the monomer proper ($L/Ir = 1$). In section *C* the influence of added chloride ion and 1,5-cyclooctadiene is discussed.

Table 1 summarizes the chemical shifts of the olefinic protons of coordinated cyclooctadiene in the complexes involved.

A. L/Ir > 1

The NMR spectrum of a mixture of (COD)IrCl($AsPh_3$) and $AsPh_3$ shows above −70° one coalesced signal at 3.98 ppm at approximately the weighted mean

TABLE 1

RELEVANT NMR DATA OF 1,5-CYCLOOCTADIENE (COD) AND OF THE IRIDIUM COMPLEXES
$CDCl_3$, chemical shifts in ppm from TMS.

	$\delta(H_A)$		$\delta(H_B)$	Temp. (°C)
COD		5.58		+20
(COD)IrCl(PPh_3)	5.15[a]		2.73[a]	+20
(COD)IrCl($AsPh_3$)	4.92		3.12	−60
[(COD)IrCl]$_2$		4.22[b]		+20

[a] $J(P\text{-}H_A)$ 4.6 cps; $J(P\text{-}H_B)$ 3.4 cps. [b] $\delta(H_C)$.

of signals H_A and H_B (Fig. 1). Fig 2 shows that $1/\tau(ML)$ is proportional to the weighed-in amount of $AsPh_3$ ($[L]_0$); Fig. 3 shows that $1/\tau(ML)$ decreases with increasing concentrations (*i.e.* weighed-in amounts) of the monomer ($[ML]_0$). The results obtained in the range of −70° to −40° (fast exchange) gave a value of 4.5 kcal/mole for the activation energy.

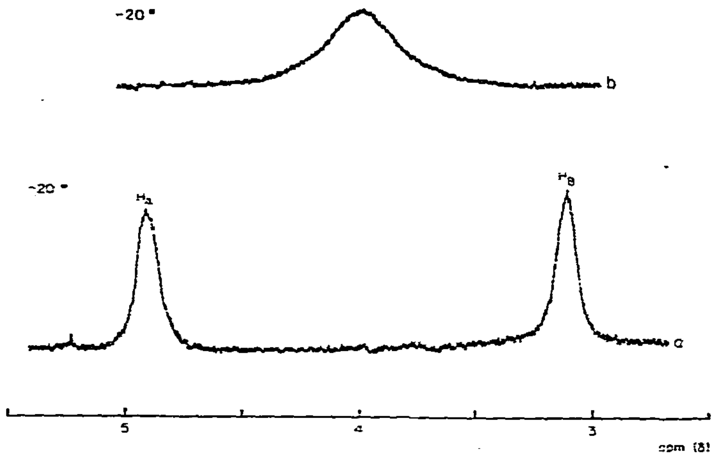


Fig. 1. Spectrum of (COD)IrCl($AsPh_3$) (0.30 mole/l) in $CDCl_3$; a. without $AsPh_3$ at −20°. b. in the presence of 0.010 mole/l $AsPh_3$ at −20°. (Shown are only the signals of the olefinic protons H_A and H_B).

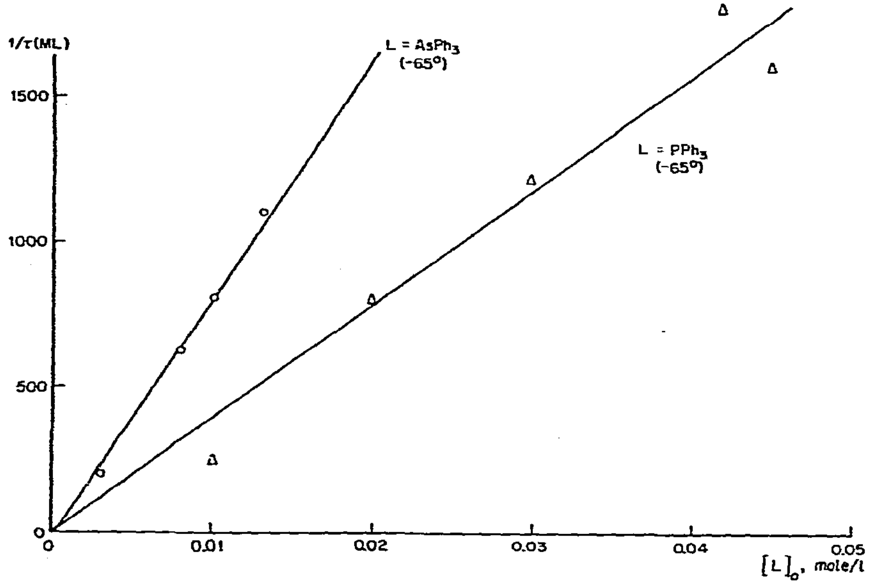
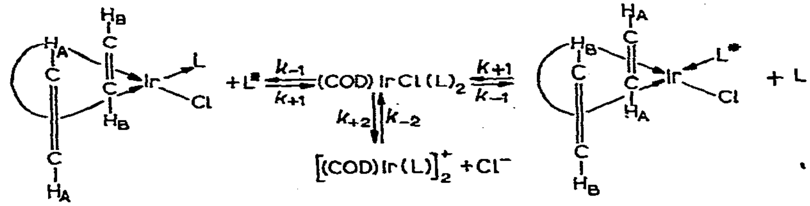


Fig. 2. Dependence of $1/\tau(ML)$ for $L{=}AsPh_3$ and $L{=}PPh_3$ on $[L]_0$ for $[ML]_0{=}0.30$ mole/l [(COD)-IrCl(L)=ML].

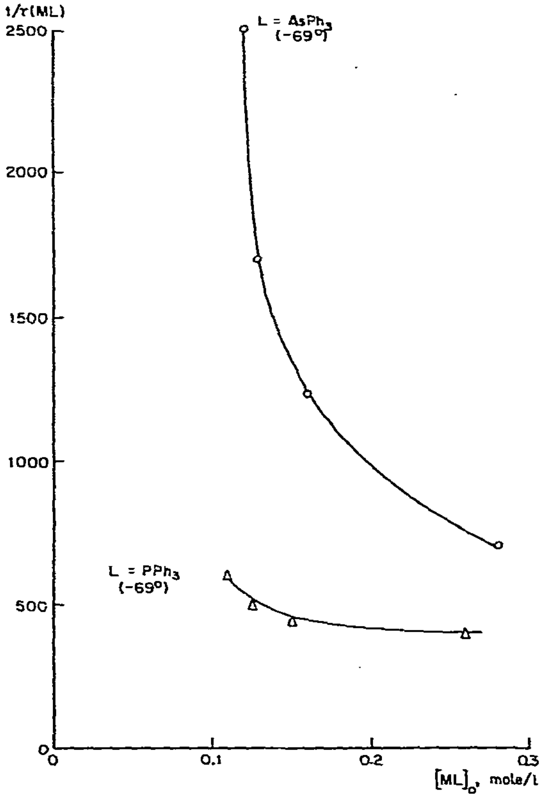
We suggest the following reaction scheme for L=$AsPh_3$:



(1,2)

The presence of the proposed species $(COD)IrCl(L)_2$ and the ionic compound $[(COD)Ir(L)_2]^+Cl^-$* is indicated by the following experimental evidence.

Complex $(COD)IrCl(AsPh_3)_2$ could be isolated in suitable solvents, such as alcohols; the presence of the ionic species could be shown by conductance measurements of mixtures of $(COD)IrCl(AsPh_3)$ and $AsPh_3$ in nitromethane (Fig. 4). Anothe



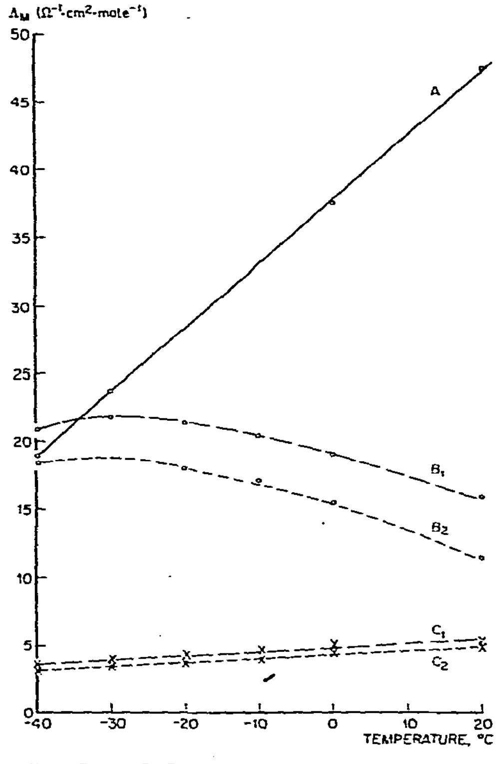


Fig. 3. Dependence of $1/\tau(ML)$ for L=$AsPh_3$ and PPh_3 on $[ML]_0$ for $[L]_0$=0.030 mole/l (L=PPh_3) and for $[L_0]$=0.010 mole/l (L=$AsPh_3$).

Fig. 4. Conductance measurements with nitromethane as solvent. A: a uni-univalent electrolyte $[(DP)_2Rh]^+$-Cl^- [DP=1,2-bis(diphenylphosphino)ethane]; B_1: a mixture of $(COD)IrCl(PPh_3)$ and PPh_3 in the ratio 1:10; B_2: a mixture of $(COD)IrCl(PPh_3)$ and PPh_3 in the ratio 1:5; C_1: a mixture of $(COD)IrCl(AsPh_3)$ and $AsPh_3$ in the ratio 1:10; C_2: a mixture of $(COD)IrCl(AsPh_3)$ and $AsPh_3$ in the ratio 1:5.

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* These salts have been isolated by J. Lewis and coworkers by another route (private communication).

interesting observation was that at −80° the solutions of (COD)IrCl(L) and L are deep-red, but yellow-orange at 0°. The yellow-orange solution of the (COD)IrCl(L) proper did not change with temperature. Further evidence was provided by the NMR spectra of (COD)IrCl($AsPh_3$) with a fivefold excess of $AsPh_3$ between −75° and 0°. At −75° the signal of the olefinic protons was observed at 3.44 ppm with a small shoulder at 3.70 ppm. On the temperature being raised these bands coalesced and subsequently the coalesced band shifted to 3.98 ppm (which is the coalesced signal of H_A and H_B of (COD)IrCl($AsPh_3$).

For the triphenylphosphine case we found similar dependencies as for triphenylarsine, *i.e.* $1/\tau(ML)$ on $[L]_0$ and on the monomer concentration $[ML]_0$ (Fig. 2 and 3). The activation energy, however, appeared to depend on $[ML]_0$. For instance, we found for $[ML]_0=0.11$ mole/l an activation energy of 5.9 kcal/mole, whereas for $[ML]_0=0.26$ mole/l the energy was found to be 14.5 kcal/mole.

In this case, too, arguments can be advanced for the presence of five-coordinate partly ionized species (COD)IrCl$(L)_2$. For instance, the five-coordinate complex can be prepared in suitable solvents.

Furthermore, in nitromethane an ionic species is observed for 1:5 and 1:10 molar mixtures of (COD)IrCl(PPh_3) and PPh_3; the amount of ionic species is larger than in the arsine case (Fig. 4). The NMR spectra of a 1:5 molar mixture of (COD)-IrCl(PPh_3) and PPh_3 showed at −75° a peak at 4.03 ppm, which sharpened upon the temperature being raised and moved upfield to 3.80 ppm (at ~−50°) and subsequently downfield to 4.02 ppm (−10°), which is approximately the weighted mean of the chemical shifts of H_A and H_B of (COD)IrCl(PPh_3)*.

The dependencies of $1/\tau(ML)$ on $[L]_0$ and $[ML]_0$ observed for both the arsine and the phosphine case, can be derived from the reaction scheme [equilibria (1) and (2)]. Using the abbreviations ML_2 and ML_2^+ for the species (COD)IrCl$(L)_2$ and $[(COD)Ir(L)_2]^+$, respectively, we can express the rate of interchange as:

$$\text{Rate} = k_{+1}\cdot[ML]\cdot[L]\cdot\frac{k_{-1}}{2k_{-1}+k_{+2}}$$

or:

$$1/\tau(ML) = k_{+1}\cdot\frac{k_{-1}}{2k_{-1}+k_{+2}}[L] \tag{a}$$

The concentration of L is determined by equilibria (1) and (2). Since the electrical conductivity for both L=$AsPh_3$ and PPh_3 is very small, even for large excess of L, we only consider the case for which $[ML_2^+]\ll[ML_2]$. [L] can be derived from

$$K_1 = [ML_2]/[ML]\cdot[L] \tag{b}$$

Furthermore:

$$[ML]_0 = [ML]+[ML_2]$$

and:

$$[L]_0 = [L]+[ML_2]^{**}$$

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* It is relevant to note that for mixtures of (COD)IrCl(L) and very small amounts of L the coalesced peaks of H_A and H_B did not change their chemical shifts with a variation of the temperature.

** These expressions still hold for $[ML_2]^+$ and $[ML_2]$ in the ratio 1:10.

Substitution in (b) yields:

$$K_1 = ([L]_0 - [L])/([ML]_0 - [L]_0 + [L]) \cdot [L] \qquad \text{(c)}$$

Since:

$$[L]_0 \ll [ML]_0, \; [ML]_0 \gg ([L]_0 - [L])$$

(c) becomes:

$$K_1 = ([L]_0 - [L])/[ML]_0 \cdot [L]$$

or:

$$[L] = [L]_0/(K_1 \cdot [ML]_0 + 1) \qquad \text{(d)}$$

Substitution of (d) into (a) leads to:

$$1/\tau(ML) = k_{+1} \cdot \frac{k_{-1}}{2k_{-1} + k_{+2}} \cdot \frac{[L]_0}{(K_1 \cdot [ML]_0 + 1)},^{*} \qquad \text{(e)}$$

which fits in with the experimental results (Figs. 2 and 3). The dependency of the activation energy on the concentration of $[ML]_0$ for $L = PPh_3$ is not explained by equation (e). Reactions other than mentioned in the reaction scheme must occur.

B.1. L/Ir < 1

The reactions involving (COD)IrCl(L) (=ML) and $[(COD)IrCl]_2$ ($=M_2$) were measured only for $L = AsPh_3$, as too high temperatures were needed to study the phosphine system. The arsine system was investigated from the line widths of the signals H_A and H_B of ML and of H_C of M_2 (at 4.22 ppm) in the slow exchange limit. At sufficiently high temperatures they coalesce to one absorption at the weighted mean (Fig. 5).

The following concentration dependencies of the rates were observed:

$$1/\tau(ML) = \frac{d[ML]}{dt}/[ML] = k' \cdot [ML]_0/[M_2]_0^{\frac{1}{2}}$$

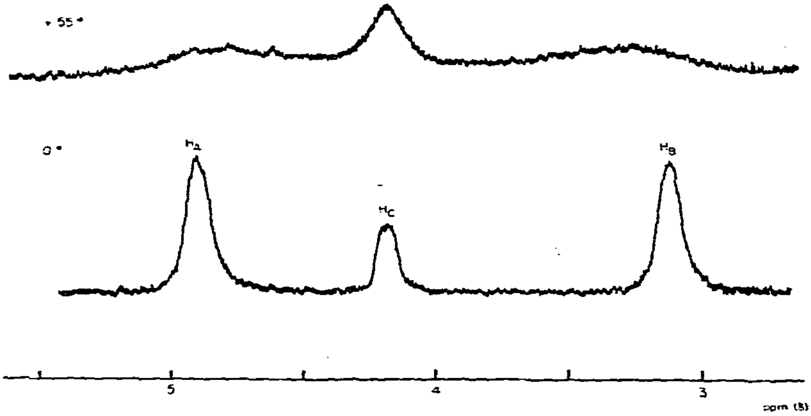

Fig. 5. NMR spectra of $(COD)IrCl(AsPh_3)$ (0.47 mole/l) and of $[(COD)IrCl]_2$ (0.05 mole/l) as a function of the temperature. (Shown is the broadening of the signals H_A, H_B and H_C).

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* For $[ML_2^+] \gg [ML_2]$ the concentration dependence of $1/\tau(ML)$ is different (see ref. 2 where L/Pd > 1).

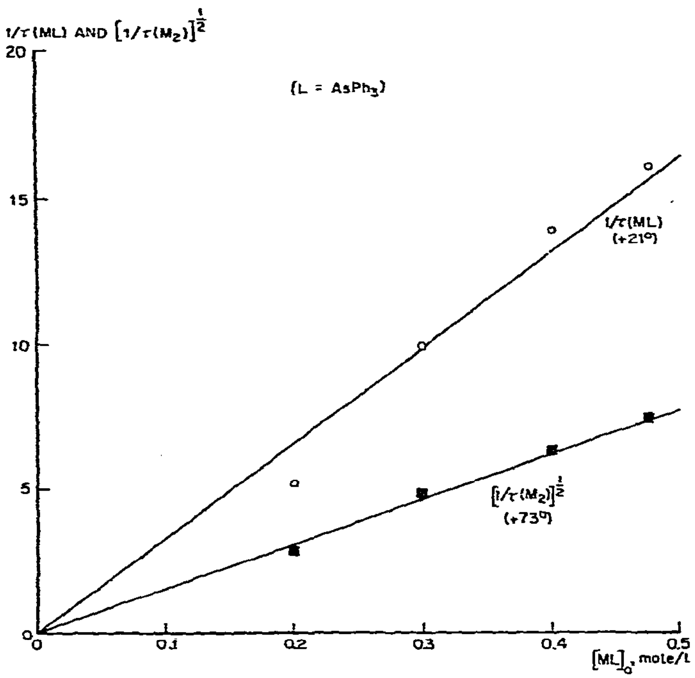
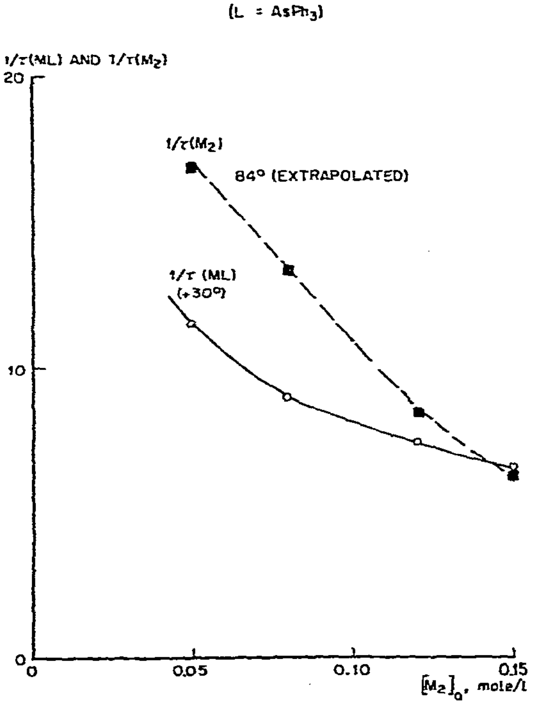


Fig. 6. Dependence of $1/\tau(ML)$ and $[1/\tau(M_2)]^{\frac{1}{2}}$ on $[ML]_0$ for $[M_2]_0 = 0.05$ mole/l ($L = AsPh_3$).



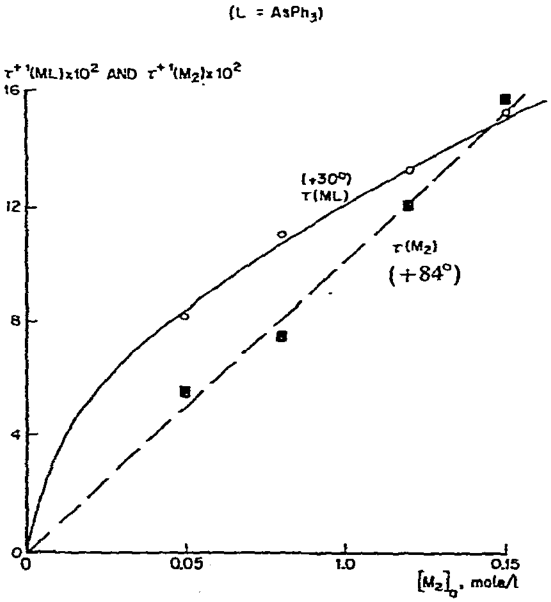


Fig. 7. Dependence of $1/\tau(ML)$ and $1/\tau(M_2)$ on $[M_2]_0$ for $[ML]_0 = 0.20$ mole/l ($L = AsPh_3$).
Fig. 8. Dependence of $\tau(ML)$ and $\tau(M_2)$ on $[M_2]_0 = 0.20$ mole/l ($L = AsPh_3$).

and:

$$1/\tau(M_2) = \frac{d[M_2]}{dt}/[M_2] = k'' \cdot [ML]_0^2/[M_2]_0{}^{*} \qquad \text{(Figs. 6, 7 and 8)}$$

This result can be explained by the following reaction scheme *i.e.* dissociation of the monomer**:

$$\underset{ML}{(COD)IrCl(AsPh_3)} \underset{k_3}{\rightleftharpoons} \underset{M}{(COD)IrCl} + \underset{L}{AsPh_3} \qquad (3)$$

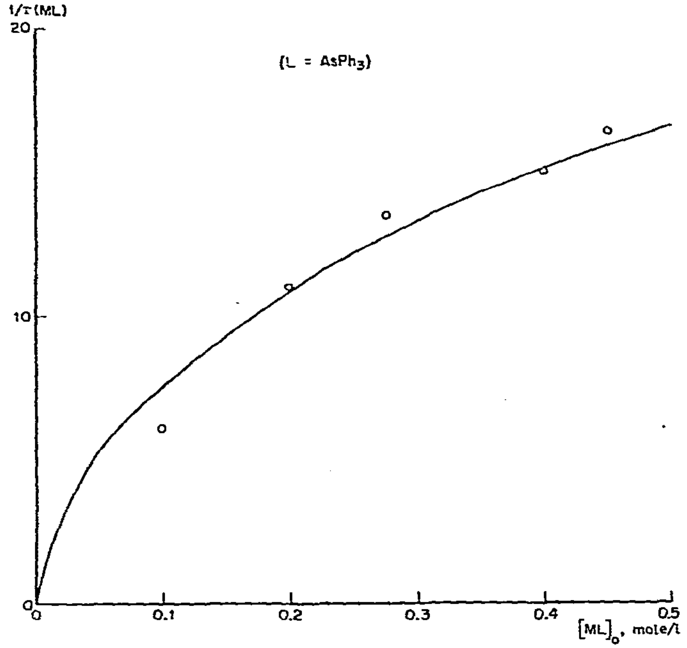


Fig. 9. Dependence of $1/\tau(ML)$ on $[ML]_0$ for solutions of $(COD)IrCl(AsPh_3)$.

The dissociated $AsPh_3$ reacts with dimer and monomer***, respectively;

$$\underset{M_2}{[(COD)IrCl]_2} + \underset{L}{AsPh_3} \underset{k_{4a}}{\rightleftharpoons} \underset{M_2L}{[(COD)IrCl(AsPh_3)IrCl(COD)]} \qquad (4)$$

$$\underset{M_2L}{[(COD)IrCl(AsPh_3)IrCl(COD)]} + \underset{L}{AsPh_3} \underset{k_{4b}}{\rightleftharpoons} 2\,\underset{ML}{(COD)IrCl(AsPh_3)}$$

$$\underset{ML}{(COD)IrCl(AsPh_3)} + \underset{L^+}{AsPh_3^+} \underset{k_5}{\rightleftharpoons} \underset{ML^+}{(COD)IrCl(AsPh_3^+)} + \underset{L}{AsPh_3} \qquad (5)$$

and dissociaton of the dimer:

$$\underset{M_2}{[(COD)IrCl]_2} \underset{k_6}{\rightleftharpoons} 2\,\underset{M}{(COD)IrCl} \qquad (6)$$

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* Since [L] and [M] are very small $[M_2] \cong [M_2]_0$ and $[ML] \cong [ML]_0$.

** The species M_2L may be a dimer with one of the chloride bridges broken by a ligand molecule L.

*** The same concentration dependencies were observed for mixtures of $[NorRhCl(AsPh_3)]$ and $[NorRhCl]_2$ (Part VII, to be published).

In principle it is possible that reaction (+3) as well as reactions [(−4a) and (−4b)] are responsible for the formation of $AsPh_3$. However, from measurements for solutions of ML proper it is concluded that $AsPh_3$ is formed by step (+3) (see *B*.2). The expression for [L] is:

$$[L] = K_3 \cdot [ML]/[M]^{**}$$

Since $[M]^2 = K_6 \cdot [M_2]$, the expression for [L] becomes:

$$[L] = K_3 \cdot [ML]/K_6^{\frac{1}{2}} \cdot [M_2]^{\frac{1}{2}}$$

If again reaction (+5) is rate-determining we find:

$$1/\tau(ML) = k_5 \cdot (K_3/K_6^{\frac{1}{2}}) \cdot [ML]/[M_2]^{\frac{1}{2}}$$

and

$$1/\tau(M_2) = \tfrac{1}{2} k_4 \cdot (K_3^2/K_6) \cdot [ML]^2/[M_2]^{*}$$

which is observed experimentally.

The observed reaction constants k' and k'' are:

$$k' = k_5 \cdot (K_3/K_6^{\frac{1}{2}}) = 10^{13} e^{-15500/(R \cdot T)} l^{\frac{1}{2}} \cdot mole^{-\frac{1}{2}} \cdot sec^{-1}$$
$$k'' = k_4 \cdot (K_3^2/K_6) = 10^{11} e^{-17000/(R \cdot T)} l \cdot mole^{-1} \cdot sec^{-1}$$

It should be emphasized that the difference between the starting and equilibrium concentrations of M_2 is so small that it cannot be observed from the integration of the appropriate NMR signals.

The second-order behaviour in [L] for equilibrium (4) implies a two-step mechanism (4a) and (4b), since a termolecular reaction of M_2 and 2L is unlikely.

B.2. *L*/*Ir* = 1

For (COD)IrCl($AsPh_3$) proper in $CDCl_3$ solution it was observed that:

$$1/\tau(ML) = k''' \cdot [ML]_0^{\frac{1}{2}} \text{ (studied between } -10 \text{ and } +20^\circ) \quad \text{(Fig. 9)}.$$

The observed concentration dependency can be explained by equilibria (3) and (5). The other reactions can be neglected, because $[M_2]$, [M] and [L] are all very small.

It will be seen that:

$$[L] = \sqrt{K_3 \cdot [ML]}$$

and thus:

$$1/\tau(ML) = k_5 \sqrt{K_3 \cdot [ML]}, \quad ([ML] = [ML]_0)$$

where

$$k''' = k_5 \sqrt{K_3} = 10^{13} e^{-15000/(R \cdot T)} l^{\frac{1}{2}} \cdot mole^{-\frac{1}{2}} \cdot sec^{-1}$$

We further see that reaction (+3) is faster than either (−4a) or (−4b). In case of the reverse we would find that $1/\tau(ML)$ is proportional to [ML].

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* $k_4 = k_{4b} K_{4a}$

** For [M] = [L] we would find that $1/\tau(ML)$ and $1/\tau(M_2)$ are proportional to $[ML]_0^{\frac{1}{2}}$ and $[ML]_0$ respectively[14].

C. Influence of added Cl^- and 1,5-cyclooctadiene

Addition of Cl^- (in the form of benzylhexadecyldimethylammonium chloride) or of 1,5-cyclooctadiene had little or no effect on the phosphine case.

Addition of Cl^- (at −25°) to $(COD)IrCl(AsPh_3)$ caused the signals of H_A and H_B to coalesce to their weighted mean. In the presence of $[(COD)IrCl]_2$ the dimer signal of H_C coalesced with H_A and H_B, which does not occur in the absence of Cl^-.

Similar effects of chloride ions were already observed for the analogous rhodium complexes. The following tentative reaction model is proposed:

$$\begin{tikzcd}
\mathrm{(COD)IrCl(AsPh_3)} + \mathrm{Cl^-} \arrow[r, leftrightarrows] & \mathrm{[(COD)IrCl_2(AsPh_3)]^-} \arrow[r, leftrightarrows] \arrow[d, shift left, "-\mathrm{AsPh_3}"'] & \mathrm{(COD)IrCl(AsPh_3)} + \mathrm{Cl^-} \\
\tfrac{1}{2}\mathrm{[(COD)IrCl]_2} + \mathrm{Cl^-} \arrow[u, "+\mathrm{AsPh_3}"'] \arrow[r, leftrightarrows] & \mathrm{[(COD)IrCl_2]^-} \arrow[u, shift left] &
\end{tikzcd}$$

Again, direct reactions of $[(COD)IrCl_2(AsPh_3)]^-$ and $[(COD)IrCl]_2$ with exchange of $AsPh_3$ cannot be excluded.

Broadening and coalescence of the signals of H_A and H_B of the arsine complex can also be caused by addition of 1,5-cyclooctadiene*. The rate of coalescence is, however, much lower than for Cl^-. An interesting point is that this reaction does *not* involve exchange of diolefin, as evidenced by the absence of broadening of the olefinic protons of the free diolefin. It is likely that the attacking diolefin becomes attached with one olefinic double bond to Ir. In the resulting five-coordinate intermediate the protons H_A and H_B of the bidentate diolefin may interchange their positions. Subsequently the attacking diolefin, which is much more weakly bonded to Ir than the bidentate olefin, leaves the complex again. The kinetics of this reaction and of exchange reactions of 1,5-cyclooctadiene with $[(COD)IrCl]_2$ will be reported in the future.

IV. COMPARISON OF THE IRIDIUM AND RHODIUM SYSTEMS

The coalescence of the signals of non-equivalent olefinic protons in the 1,5-cyclooctadiene complexes of iridium(I) and rhodium(I)** is due to a ligand exchange reaction via the intermediate formation of a five-coordinate metal complex. This species may be formed by reaction of the starting complex (COD)M(Cl)(L) with triphenylarsine, triphenylphosphine, chloride ions, 1,5-cyclooctadiene and even with the dimer $(COD)_2M_2Cl_2$ or the dissociated dimer.

Comparison of the rate constants for the reaction between (COD)M(Cl)(L) and L reveals that the iridium complexes react faster than the rhodium ones. For both metals the triphenylarsine complex reacts faster than the phosphine complex.

The more rapid ligand exchange is considered to be due to the greater tendency to form and stabilize the five-coordinate species. The faster rate for iridium relative to rhodium can be explained by the greater effective nuclear charge on the former metal atom, thus favouring nucleophilic attack of the ligand. In addition, the five-coordinate species is also better stabilized as appears from the formation of these

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* $[(COD)IrCl]_2$ itself reacts with 1,5-cyclooctadiene. A similar exchange was noted for mixtures of $[(norbornadiene)RhCl]_2$[9] and norbornadiene, but not for the COD–Rh system[10].

** Similar phenomena were observed for $(\pi\text{-}C_4H_7)Pd(Cl)(L)$ (ref. 2).

complexes in suitable solvents and from its existence in solution at low temperatures.

The favourable effect of the triphenylarsine ligand relative to triphenylphosphine—clearly demonstrated by the reaction of (COD)M(Cl)($AsPh_3$) with Cl^- or 1,5-cyclooctadiene, whereas with (COD)M(Cl)(PPh_3) no reaction occurs in the NMR time scale—is twofold: (*i*) triphenylarsine stabilizes the five-coordinate species[11-13] by its greater π-backbonding ability (relative to PPh_3); (*ii*) the effective positive charge on the metal atom is larger in triphenylarsine than in the phosphine complexes, which makes the arsine complexes the most reactive ones towards nucleophilic attack.

Comparison of iridium and rhodium for the systems containing (COD)M(Cl)(L) and $[(COD)M(Cl)]_2$ is more difficult, since the rate-determining steps in the two systems are different. For the rhodium-arsine case the rate-determining step is the conversion of (COD)RhCl($AsPh_3$) into an activated species, tentatively depicted as five-coordinate (COD)RhCl($AsPh_3$)(solvent). The rate-determining step for the iridium–arsine system is the ligand exchange of (COD)IrCl($AsPh_3$) and $AsPh_3$.

Finally, for the rhodium–phosphine case the rate is determined by the reaction of (COD)RhCl (formed by dissociation of the dimer $[(COD)RhCl]_2$) with (COD)RhCl(PPh_3)[1]. For the iridium system reactions were too slow to be observed in the NMR time scale; apparently, the Ir–P bond is so strong that exchange of PPh_3 does not occur below +90°.

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