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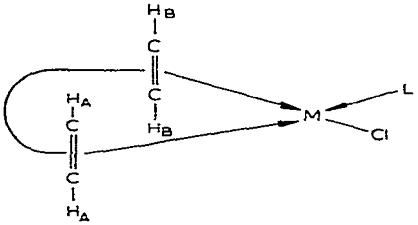
PRELIMINARY COMMUNICATION

NMR studies of ligand exchange reactions involving diolefin complexes of Rh^I and Ir^I

In continuation of our NMR studies[1,2] on the temperature dependent behaviour of organic groups bonded to a metal atom, we wish to report some preliminary data on ligand exchange reactions* with diolefin complexes of Rh^I and Ir^I. The compounds investigated are (COD)IrCl(L), (COD)RhCl(L) and (Nor)RhCl(L) (COD = 1,5-cyclooctadiene; Nor = bicyclo[2,2,1]hepta-2,5-diene and L = Group-V donor ligand *e.g.* R_3P, R_3As, R_3Sb, in which R = aryl and/or alkyl). The compounds were prepared in a manner analogous to procedures described by Winkhaus and Singer[3], Chatt and Vananzi[4], and Bennett and Wilkinson[5]. The yellow to dark orange compounds are monomeric, non-electrolytes in nitrobenzene and 1,2-dichloroethane. Both double bonds of the diolefin are coordinated to the metal, as is evidenced by the absence of stretching frequencies in the infrared of uncoordinated double bonds and by the chemical shifts of the olefinic protons which are at higher field than those of the free diolefin (Table 1). The olefinic protons H_A and H_B absorb at different magnetic field owing to the asymmetry of the complex. Tentatively, we assign the low field

TABLE 1

CHEMICAL SHIFTS (δ) OF THE PROTONS IN ppm FROM TMS



Complex[a]	δ(H_A) (in ppm from TMS)	δ(H_B) (in ppm from TMS)	T °C
COD	5.58		+20
(COD)IrCl(PPh_3)	5.15[b]	2.73[c]	+20
(COD)IrCl($AsPh_3$)	4.92	3.12	−60
(COD)RhCl(PPh_3)	5.52	3.10	0
(COD)RhCl($AsPh_3$)	5.25	3.52	0
Nor	6.82		+20
(Nor)RhCl(PPh_3)	5.20	2.92	−20
(Nor)RhCl($AsPh_3$)	4.80	3.40	−80

[a] In $CDCl_3$ solution (Varian HA 100). [b] $J(P\text{-}H_A) = 4.6$ cps. [c] $J(P\text{-}H_B) = 3.4$ cps (both derived from double resonance measurements)

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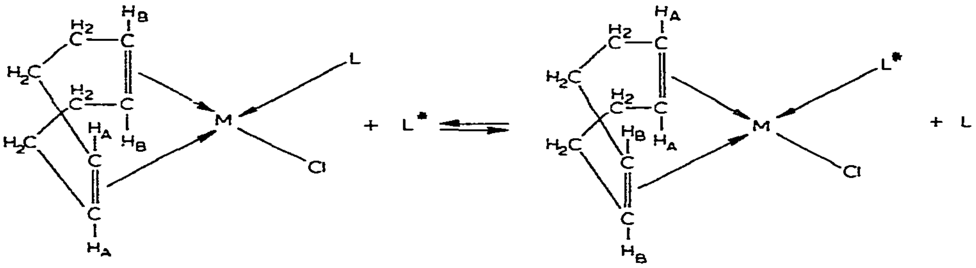
* Professor J. Lewis kindly informed us that he and co-workers have also been working on ligand exchange reactions of diolefin rhodium complexes (COD)RhCl(L).

absorption to protons H_A (attached to the double bond *trans* to L), since protons *trans* to strong electron donor ligands (L) in general absorb at lower magnetic field than protons *trans* to Cl*. At elevated temperatures the H_A and H_B absorptions broaden and finally coalesce to approximately their weighted mean. The interchange process of H_A and H_B is interpreted as being due to a ligand exchange reaction, if free ligand is present, for example:



The exchange scheme is supported by the following evidence:

(*a*) the rate of interchange increases with increasing ligand concentration and appears to be first order in L and in (diolefin)MClL in the temperature range of −70 to −10°.

(*b*) addition of free diolefin does not exert a measurable effect on the broadening of the signals.

(*c*) the interchange process in the case of the phosphine complex is accompanied by the disappearance of the P–H coupling.

For the system $(\mathrm{COD})\mathrm{RhCl}(\mathrm{AsPh_3})$ and $\mathrm{AsPh_3}$ a frequency factor of $10^5\ \mathrm{l\cdot mole^{-1}\cdot sec^{-1}}$ and an activation energy of about 4.0 $\mathrm{kcal\cdot mole^{-1}}$ were found. The activation energies for the other reactions in general lie between 4–10 $\mathrm{kcal\cdot mole^{-1}}$.

The reaction presumably proceeds via a five-coordinate short-lived intermediate (diolefin) $\mathrm{MCL(L)_2}$ $(=\mathrm{ML_2})$ and can be schematically pictured as:

$$\mathrm{ML}+\mathrm{L}^* \underset{k_{+1}}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{MLL}^* \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{ML}^*+\mathrm{L}\,.$$

The occurrence of $\mathrm{ML_2}$ is supported by the fact that in the case of iridium, the complexes $(\mathrm{COD})\mathrm{IrCl(L)_2}$ could be isolated from ethanol solutions. In 1,2-dichloroethane these complexes are completely dissociated into (COD)IrCl(L) and L.

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1 K. VRIEZE, P. COSSEE, C. W. HILBERS AND A. P. PRAAT, *Rec. Trav. Chim.*, 86 (1967) 769.
2 K. VRIEZE AND H. C. VOLGER, *J. Organometal. Chem.*, 9 (1967) 537.
3 G. WINKHAUS AND H. SINGER, *Chem. Ber.*, 99 (1966) 3610.
4 J. CHATT AND L. M. VENANZI, *J. Chem. Soc.*, (1957) 4735.
5 M. A. BENNETT AND G. WILKINSON, *J. Chem. Soc.*, (1961) 1418.

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* The assignment is irrelevant for the study of the reactions.