Kinetics and Mechanism of the Substitution Reactions of the Four- (X = Cl) and Five-co-ordinate (X = I or SCN) Iridium Complexes [(Cyclo-octa-1,5-diene)Ir(1,10-phenanthroline)X]

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Summary The substitution reaction of the five-co-ordinate [(cod)Ir(phen)X] (cod = cyclo-octa-1,5-diene, phen = 1,10-phenanthroline, X = I or SCN) with ethylenediamine (en) proceeds *via* a dissociative mechanism; the reaction between $[(cod)Ir(phen)]^+$ and en shows the accumulation of either a four- or five-co-ordinate intermediate $[(cod)Ir(phen)(en)]^+$.

We have studied the substitution reactions of the four- and five-co-ordinate complexes[1] (a) to determine the mechanism of five-co-ordinate diamagnetic complex substitution reactions and (b) to attempt to generate a system pertaining to the build-up of a five-co-ordinate intermediate in the mechanism [equation (1); cod = cyclo-octa-1,5-diene; phen

$$[(cod)Ir(phen)X] + en \xrightarrow{MeOH} [(cod)Ir(en)]^+ + phen + X^- \quad (1)$$

= 1,10-phenanthroline; X = Cl, I, or SCN; en = ethylenediamine].

In the solid state the iodo- and thiocyanato-derivatives are pentaco-ordinate. In methanol K_e for the equilibrium in equation (2) is 600 and 126 l mol^{-1} for X = SCN and I,

$$[(cod)Ir(phen)]^+ + X^- \overset{K_e}{\rightleftharpoons} [(cod)Ir(phen)X] \quad (2)$$

respectively, while K_e for X = Cl is very small. Pseudo first order conditions with respect to complex concentration by X^- and en were maintained.

The rate law [equation (3)] derived from the reactions

$$k_{obs} = kK_1[en]/(1 + K_1[en] + K_e[X^-]) \quad (3)$$

shown in the Scheme corresponds to the experimental rate law. The stable intermediate $[(cod)Ir(phen)(en)]^+$ may either be a five-co-ordinate complex with one nitrogen of en co-ordinated or a four-co-ordinate complex with one nitrogen of each of the en and phen co-ordinated. It may also be an ion pair, but ion pairs are rather unique for square-planar complexes since the counter ion can enter the

$$\begin{tikzcd}
{[(cod)Ir(phen)]^+ + X^-} \arrow[r, leftrightharpoons, "K_e"] \arrow[d, leftrightharpoons, "K_1\ (en)"'] & {[(cod)Ir(phen)X]} \\
{[(cod)Ir(phen)(en)]^+} \arrow[r, "k"] & {[(cod)Ir(en)]^+ + phen}
\end{tikzcd}$$

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co-ordination sphere.[2] The K_e values calculated from the kinetic data are 587 and 116 l mol^{-1} for X = SCN and I, respectively. From reactions shown in the Scheme it is evident that the k and K_1 values should be the same for different X groups. This is the case; k = 18·2, 18·9, and 19·6 s^{-1} and K_1 = 14, 12, and 10 l mol^{-1} for X = Cl, I, and SCN, respectively.

When the sterically hindered ligand *NN'*-dimethylethylenediamine (*NN'*-en) is used, the stable intermediate $[(cod)Ir(phen)(NN'\text{-en})]^+$ disappears and the rate law changes to that shown in equation (4). The K_e values (572 and 134 l mol^{-1} for X = SCN and I, respectively) determined from this data once again agree with the previously determined values while the k_1 values are all the same as expected (k_1 = 1·39, 1·42, and 1·46 for X = Cl, I, and SCN, respectively).

$$k_{obs} = k_1\,[NN'\text{-en}]/(1 + K_e[X^-]) \tag{4}$$

With only one end of en sterically hindered as in the ligands *N*-methylethylenediamine (*N*-en) and *NN*-dimethylethylenediamine (*NN*-en), the rate law is the same as in equation (3). The k values decrease drastically with steric build-up (k = 14·3 and 0·16 for *N*-en and *NN*-en, respectively), while the K_1 value changes to 8 l mol^{-1} for both these amines.

A comprehensive paper will relate this work to previously reported claims[3] for the observation of an accumulation of a five-co-ordinate intermediate.

(*Received*, 13*th April* 1977; *Com.* 351.)

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[1] G. Mestroni, A. Camus, and G. Zassinovich, *J. Organometallic Chem.*, 1974, **73**, 119.

[2] W. J. Louw, D. J. A. de Waal, and G. J. Kruger, *J.C.S. Dalton*, 1976, 2364.

[3] A. J. Hall and D. P. N. Satchell, *J.C.S. Chem. Comm.*, 1976, **163**; L. Cattalini, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, 1968, **90**, 4800.