

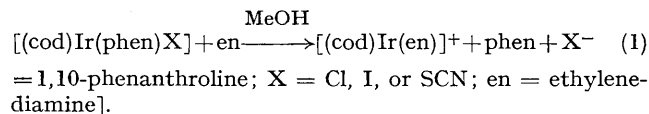
**Kinetics and Mechanism of the Substitution Reactions of the Four- (X = Cl)
and Five-co-ordinate (X = I or SCN) Iridium Complexes
[(Cyclo-octa-1,5-diene)Ir(1,10-phenanthroline)X]**

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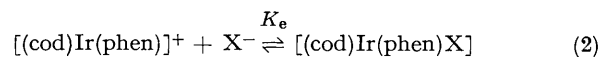
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Summary The substitution reaction of the five-co-ordinate [(cod)Ir(phen)X] (cod = cyclo-octa-1,5-diene, phen = 1,10-phenanthroline, X = I or SCN) with ethylenediamine (en) proceeds *via* a dissociative mechanism; the reaction between [(cod)Ir(phen)]⁺ 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 complexes¹ (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



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,

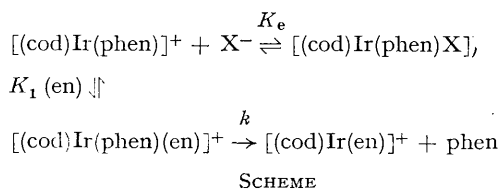


respectively, while K_e for X = Cl is very small. Pseudo first order conditions with respect to complex concentration by X⁻ and en were maintained.

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

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

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



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 $[(\text{cod})\text{Ir}(\text{phen})(\text{NN}'\text{-en})]^+$ disappears and the rate law changes to that shown in equation (4). The K_e values (572

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

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).

With only one end of en sterically hindered as in the ligands *N*-methylethylenediamine (*N*-en) and *N,N*-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 claims³ for the observation of an accumulation of a five-co-ordinate intermediate.

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