Intramolecular and Intermolecular Ligand Exchange in Five-co-ordinate Cobalt(I) Complexes

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Summary Five-co-ordinate Co^I isonitrile complexes are subject to rapid intra- and inter-molecular ligand exchange.

N.M.R. studies on five-co-ordinate complexes with identical ligands indicate very low (*ca.* 5 kcal mol^{-1}) barriers to intramolecular exchange.[1,2] The complex ion $Co[CNCMe_3]_5$, reported to be stereochemically rigid at $-30°$,[3] is of interest because of the implication that steric factors contribute to the surprisingly high barrier. We report that isonitrile complexes of cobalt(I) are stereochemically labile with respect to intra- and inter-molecular ligand exchange.

There is no evidence (from ^{13}C and ^1H n.m.r.) of ligand inequivalence in $Co[CNCMe_3]_5^+$ and in $Co[CNMe]_5^+$ down to $-160°$. Similarly, the isonitrile ligands (L) in monophosphine and arsine derivatives, $CoL_4(MR_3)^+$, are equivalent down to $-120°$. Thus, these complexes appear to be highly fluxional structures.

Ligand lability through dissociation is evident in the complexes but the processes are complex. Exchange of ligand between $Co[CNCMe_3]_5^+$ and $CNCMe_3$ occurs at a rate of *ca.* 10 s^{-1} at 85°; the analogous exchange in the phosphine derivatives is slower. Exchange of Me_3C groups through the carbonium ion is a still slower process. A catalysed ligand exchange does occur for all these compounds. A dichloromethane or tetrahydrofuran solution of $Co[CNCMe_3]_5^+$ and $Co[CNCMe_3]_3[(p\text{-}MeC_6H_4)_3P]_2^+$ shows no evidence of reaction or ligand exchange to give $Co[CNCMe_3]_4[(p\text{-}MeC_6H_4)_3P]^+$. However, an equilibrium (equation 1) mixture of all three species forms within 1—3 min on exposure of the solution to trace amounts of oxygen. Hence, it is exceedingly difficult to isolate the pure monophosphine complex. Dimethyl sulphoxide greatly inhibits

$$CoL_5^+ + CoL_3L_2'^+ \rightleftharpoons 2CoL_4L'^+ \quad (K\ ca.\ 3\ \text{at}\ 40°) \qquad (1)$$

the catalysed exchange through complexation of a cobalt complex.

The arsine system is significantly different from the phosphine. For example, the equilibrium constant at 40°

for (2) is small ($<0{\cdot}01$), and it is necessary to remove the isonitrile by distillation to form substantial amounts of the

$$\mathrm{Co[CNCMe_3]_5^+ + AsPh_3 \rightleftharpoons Me_3CNC + Co[CNCMe_3]_4AsPh_3^+} \qquad (2)$$

monoarsine derivative. Accordingly, some of the chemistry reported for such arsine derivatives is based on mixtures.[3] Equilibrium (3) lies far to the right at 40°. The forward reaction to give the monoarsine is fast (time of mixing).

$$\mathrm{Co[CNCMe_3]_3[AsPh_3]_2^+ + Co[CNCMe_3]_5^+ \rightleftharpoons 2Co[CNCMe_3]_4AsPh_3^+} \qquad (3)$$

The n.m.r. data establish that dissociation (4) has a relatively low activation energy and that the analogous process in $\mathrm{Co(CNR)_3(PR_3)_2^+}$ is more activated. These four-co-ordinate complexes are probably key intermediates

$$\mathrm{CoL_5^+ \rightleftharpoons CoL_4^+ + L} \qquad (4)$$

in solution reactions of the isonitrile complexes. In the oxygen catalysis of ligand exchange (1), it is proposed that the first step is formation[4] of $\mathrm{CoL_4O_2^+}$ which is suppressed in donor solvents like dimethyl sulphoxide (S) through solvation of $\mathrm{CoL_4^+}$ to give $\mathrm{CoL_4S^+}$. Fast ligand exchange may be effected in the oxygen complex through an equilibrium $\mathrm{Co^{I}L_4(O_2^{0})^+ \rightleftharpoons Co^{II}L_4(O_2^{-})^+}$ where exchange would be fast in the cobalt(II) form. Alternatively, or additionally, $\mathrm{CoL_4O_2^+}$ may form bridged $\mathrm{Co^{I}L_4O_2Co^{II}L_5^{2+}}$ complexes. Another alternative is some conventional $\mathrm{Co^{I}}$–$\mathrm{Co^{II}}$ equilibrium. Addition of $\mathrm{Co^{II}}$ compounds such as $\mathrm{Co^{II}}$ isonitrile complexes does, in fact, give a rapid catalysed exchange. Since this specific catalysis is effective in dimethyl sulphoxide solution, the blocking role of the sulphoxide in oxygen addition to $\mathrm{CoL_4^+}$ seems clearly indicated. Oxygen reacts with mixtures of $\mathrm{CoL_5^+}$ and $\mathrm{CoL_4^+}$ to give a pale green solution; addition of dimethyl sulphoxide regenerates the yellow colour characteristic of the cobalt(I) complexes. Demonstration of the individual steps is being sought through isolation of pure $\mathrm{CoL_4^+}$ and $\mathrm{CoL_4O_2^+}$ complexes.

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[4] Analogous rhodium(I) complexes of the type $\mathrm{Rh(PR_3)_4O_2^+}$ have been isolated: L. M. Haines, *Inorg. Chem.*, 1972, **10**, 1685.