Ligand Substitution at Five-co-ordinate Centres. Effect of Oxidation State Change on Mechanism

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Summary. The mechanism of replacement of tri-*p*-tolylphosphine by tri-n-butyl phosphite in the five-co-ordinate 1,2-dithiolene complex $[Co\{P(tolyl)_3\}\{S_2C_2(CF_3)_2\}_2]^z$ is associative when $z = 0$ and dissociative when $z = -1$.

The bis(trifluoromethyl)-1,2-dithiolene complex of cobalt is well known[1] for its ability to form five-co-ordinate adducts with phosphines and phosphites yielding $[Co(PR_3)\{S_2C_2(CF_3)_2\}_2]^z$ where z is 0 or -1. We recently reported[2] kinetic studies of other five-co-ordinate 1,2-dithiolene systems, finding either associative or mixed associative–dissociative pathways for ligand substitution. Preliminary results of kinetic studies of the bis(trifluoromethyl)-1,2-dithiolene system presented herein show how a change in oxidation state can affect the mechanism.

The kinetics of reaction (1) were followed in dichloromethane at 25 °C using a Durrum stopped-flow apparatus,

$$[Co\{P(tolyl)_3\}\{S_2C_2(CF_3)_2\}_2]^z + P(OBu)_3 \longrightarrow [Co\{P(OBu)_3\}\{S_2C_2(CF_3)_2\}_2]^z + P(tolyl)_3 \qquad (1)$$

under pseudo-first-order conditions, with a metal complex concentration of 2×10^{-5} M, $P(OBu)_3$ concentrations of 2—10 $\times 10^{-4}$ M, and $P(tolyl)_3$ concentrations of 2×10^{-5} M (no excess)—2×10^{-3} M (excess). The metal complexes were prepared by standard methods[3] and analysed satisfactorily.

With $z = 0$ the reaction is simply second order, equation (2). The addition of excess of $P(tolyl)_3$ (up to 2×10^{-3} M) has no effect on the kinetics. These results

$$k_{obs}/s^{-1} = 1{\cdot}4 \times 10^4\,[P(OBu)_3] \qquad (2)$$

are consistent with a simple associative mechanism, equation (3).

$$M\text{-}X + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L\text{-}M\text{-}X \xrightarrow{k_3} M\text{-}L + X \qquad (3)$$

$$k_{obs} = k_1k_3[L]/(k_2 + k_3) \qquad (4)$$

The results with the $z = -1$ complex are shown in the Figure. The addition of excess of $P(tolyl)_3$ has a pronounced retardation effect. The data agree quantitatively with the dissociative mechanism in equations (5) and (6). Thus

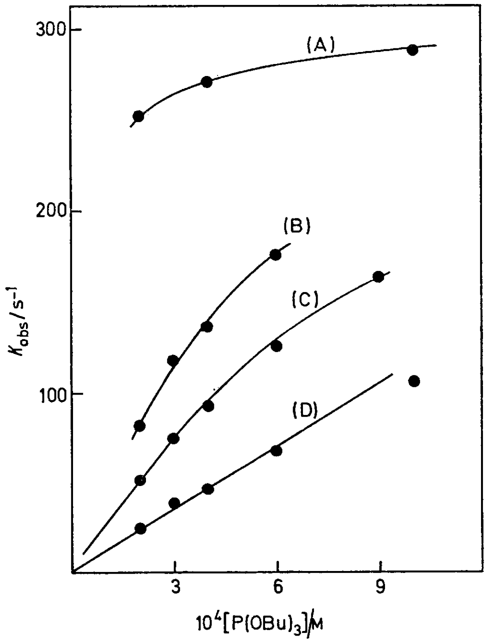

Figure. Kinetic results for the reaction of $P(OBu)_3$ with $[Co\{P(tolyl)_3\}\{S_2C_2(CF_3)_2\}_2]^{1-}$ in dichloromethane at 25 °C. Excess $P(tolyl)_3$ concentrations are (A) 0; (B) $0{\cdot}54 \times 10^{-3}$ M; (C) $1{\cdot}0 \times 10^{-3}$ M; (D) $2{\cdot}0 \times 10^{-3}$ M

$$\mathrm{M{-}X} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{M} + \mathrm{X} \tag{5}$$

$$\mathrm{M} + \mathrm{L} \xrightarrow{k_3} \mathrm{M{-}L} \tag{6}$$

$$k_{\mathrm{obs}} = k_1 k_3[\mathrm{L}]/(k_2[\mathrm{X}] + k_3[\mathrm{L}]) \tag{7}$$

plots of $1/k_{\mathrm{obs}}$ *vs.* $1/[\mathrm{L}]$ for fixed [X], *i.e.* $[\mathrm{P(tolyl)_3}]$, are linear with the same intercept within error. The intercept, $1/k_1$, yields $k_1 = 300 \pm 100\ \mathrm{s}^{-1}$, in agreement with the directly observed limit (Figure). Over the initial linear portions of the plots of k_{obs} *vs.* [L], we found that $k_{\mathrm{obs}} \propto 1/[\mathrm{X}]$ as required by equation (7).

Any significant contribution of a dissociative pathway for the $z = 0$ complex or an associative pathway for the $z = -1$ complex would easily have been detected because quantitative agreement with equations (4) and (7) respectively would not have resulted.

Thus there seems to be an abrupt change in mechanism of ligand substitution upon a one-electron reduction of the neutral complex. It has been shown previously[2] that some dithiolene complexes use both pathways simultaneously. In the case considered here the reduced complex contains sufficient additional electron density on the metal to weaken the M–X bond and thereby enhance the dissociation of X while inhibiting the direct attack of L on M–X. The result is a change to a dissociative mechanism. Although the assignment of oxidation state to the metal in dithiolene complexes is of dubious significance, we note that the complexes studied have cobalt formally in oxidation states III ($z = -1$) and IV ($z = 0$).

This work suggests that a single mechanism of ligand substitution at five-co-ordinate centres is not to be expected, except perhaps for 18-electron systems where it seems[4] that a dissociative mechanism is always followed.

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