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THE ELIMINATION OF BENZONITRILE IN THE REACTION OF [CYANO(PHENYL)BIS(TRIETHYLPHOSPHINE)NICKEL(II)] WITH 1,2-BIS(DIETHYLPHOSPHINO)ETHANE

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Summary

Mechanistic studies on the reaction in benzene of the complex $Ni(CN)(C_6H_5)[P(C_2H_5)_3]_2$ with the diphosphine $(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$ (DEE), leading to reductive elimination of C_6H_5CN, are reported. The results indicate that ready substitution of $P(C_2H_5)_3$ by DEE in the substrate complex precedes the rate-determining elimination step. The rate-law indicates that this process involves a 5-coordinate intermediate of the type $Ni(CN)(C_6H_5)(P)_3$ (P = coordinated ligand phosphorus atoms).

We recently reported [1] that the compound $Ni(DEB)_2$ (I) (DEB = 1,4-bis(diethylphosphino)butane) reacts with C_6H_5CN in solution to give $Ni(CN)(C_6H_5)(DEB)$ (II). We also showed that the oxidative reaction, formally depicted by the equation:

$$\underset{(I)}{Ni(DEB)_2} + C_6H_5CN \xrightarrow{-DEB} \underset{(II)}{Ni(CN)(C_6H_5)(DEB)}$$

is reversible, the reductive elimination of C_6H_5CN being easily induced by refluxing II in benzene in the presence of DEB.

In this work we report a kinetic study of the elimination of C_6H_5CN in the reaction of $Ni(CN)(C_6H_5)(PEt_3)_2$ (III) with DEE (DEE = 1,2-bis(diethylphosphino)ethane). The solvent was benzene at 24°C. The main objective was to elucidate the mechanistic role of the entering ligand in promoting the reaction.

Experimental

All experiments were carried out under argon. The complex $Ni(CN)(C_6H_5)(PEt_3)_2$ and the diphosphine DEE were prepared by published methods

[1,2], and had satisfactory elemental analyses and infrared spectra. The rates of reaction were followed spectrophotometrically by measuring: (a) the intensity of the ν(CN) absorption of the CN group bound to the nickel atom and that of the liberated C_6H_5CN (2230 cm^{-1}); (b) the visible spectra in the region of 300-500 nm. The ν(CN) absorption of the coordinated CN group, initially found at 2110 cm^{-1} for the solution of $Ni(CN)(C_6H_5)(PEt_3)_2$, immediately shifts to 2100 cm^{-1} on addition of the diphosphine DEE. This shift is in agreement [3] with the changes simultaneously observable in the visible spectra, which, on addition of DEE show the formation of a new band centered at 435 nm and are typical of the 5-coordinate tris(phosphine) complexes of nickel(II) [4]. This band is attributed to a complex of the type $Ni(CN)(C_6H_5)(P)_3$ (P = phosphorus atom of a tertiary or ditertiary phosphine) which forms immediately on addition of the diphosphine to solutions of $Ni(CN)(C_6H_5)(P)_2$.

The kinetic studies were performed with an excess of reagent present to provide pseudo-first-order conditions. The constant substrate concentration was 5×10^{-4} *M*, and the DEE concentration was varied from 10^{-2} to 4×10^{-1} *M*. Excellent linear plots of $\log(A_t - A_\infty)$ vs. time were obtained (A = absorbance at 435 nm, where the absorption of the 4-coordinate complex can be neglected). The values of the pseudo-first-order rate constants k_{obs} = rate/$[Ni(CN)(C_6H_5)(PEt_3)_2]$ were generally reproducible to within ± 4%.

At sufficiently great concentration of DEE a limiting rate is reached, and is independent of the concentration of the diphosphine. This suggests that the reactions proceed by a fast reagent—association preequilibrium followed by a slow rate-determining elimination step.

Parallel inspection of the infrared spectra of 3×10^{-2} *M* solutions of $Ni(CN)(C_6H_5)(PEt_3)_2$ showed that the elimination of C_6H_5CN initiated only for concentrations of DEE higher than 3×10^{-2} *M*. Moreover, the amount of C_6H_5CN formed was found to correspond to the excess of the diphosphine added. Addition of even large quantities of PEt_3 (up to 1.5×10^{-1} *M*) to the solutions of complex III, failed to promote the elimination.

The results suggest that the fast preequilibrium association step is preceded by an immediate replacement of PEt_3 by DEE in complex III. Thus the 5-coordinated species of the type $Ni(CN)(C_6H_5)(P)_3$ can be formulated as $Ni(CN)(C_6H_5)(DEE)DEE$, in which the DEE molecule not in brackets functions as a monodentate ligand. The association constant K for the equilibrium:

$$Ni(CN)(C_6H_5)(DEE) + DEE \rightleftharpoons Ni(CN)(C_6H_5)(DEE)DEE$$

was measured by using the Benesi—Hildebrand equation [5] in the form

$$\frac{1}{A_0} = \frac{1}{K\epsilon\alpha} \cdot \frac{1}{[DEE]} + \frac{1}{\epsilon\alpha} \qquad (1)$$

where ϵ is the molar absorptivity at 435 nm, α the constant concentration of the 4-coordinate complex and A_0 the absorbance at zero time. This was found by graphical extrapolation from the plots of $\log(A_t - A_\infty)$ versus time used in the kinetic runs.

A value of 54 ± 1 mol^{-1} for the association constant K could be calculated from the least-squares estimate of the intercept and slope for plots of the equation 1.

Results and discussion

The observed behaviour can be interpreted in terms of the reaction scheme 1

SCHEME 1

$$\mathrm{Ni(CN)(C_6H_5)(PEt_3)_2 + DEE \xrightarrow[\text{very fast}]{-2PEt_3} Ni(CN)(C_6H_5)(DEE) \underset{+\text{DEE fast}}{\overset{-\text{DEE}}{\rightleftharpoons}}}$$

$$\mathrm{Ni(CN)(C_6H_5)(DEE)DEE \underset{k_1\ \text{slow}}{\rightleftharpoons} Ni(DEE)DEE + C_6H_5CN \rightleftharpoons Ni(DEE)_2}$$

$$\mathrm{+\ C_6H_5CN}$$

The equation for the observed first order rate constant would be:

$$k_{\text{obs}} = \frac{k_1 K[\text{DEE}]}{1 + K[\text{DEE}]} \tag{2}$$

where k_1 is the rate constant for the rate-determining unimolecular act of elimination and K is the equilibrium constant for the formation of the 5-coordinate complex.

Equation 2 may be rewritten as:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{1}{k_1 K[\text{DEE}]} \tag{3}$$

The values of k_1 and K calculated from the least squares estimate of the intercept and slope for plots based on equation 3 were 4.5×10^{-3} sec^{-1} and 54.0 ± 3 l mol^{-1}, respectively.

The close agreement between the kinetic and spectroscopic values of K provides strong evidence for the corrections of the proposed mechanism.

The reaction scheme 1 shows that the mechanistic role of the diphosphine in promoting the elimination reaction is the same as that of a monodentate ligand. Therefore the kinetics indicate that the so called "*cis*-effect" [6] is non operative in the system investigated. This type of effect is expected to favour the cyanide—phenyl coupling by forcing the aryl and cyanide groups into a *cis* position, and has been invoked to explain the effectiveness of the diphosphine $\mathrm{Ph_2P(CH_2)_3PPh_2}$ in promoting the elimination of *o*-substituted aromatic nitriles from complexes of the type $\mathrm{Ni(CN)(aryl)(P)_2}$ [7].

Similarly, the fact that the diphosphine DEE induces a much faster elimination of $\mathrm{C_6H_5CN}$ from $\mathrm{Ni(CN)(C_6H_5)(DEB)}$ (DEB = $\mathrm{(C_2H_5)_2P(CH_2)_4\text{-}P(C_2H_5)_2}$) than does DEB has been discussed in terms of formation of a *cis* complex of the type $\mathrm{Ni(CN)(C_6H_5)(DEE)}$ in which the elimination reaction is favoured because the eliminated ligands are *cis* [1].

The results of the present study show that a simple monomolecular dissociative activation can be ruled out in the system investigated, and that the elimination actually involves a bimolecular attack leading to a 5-coordinate intermediate. In the light of this conclusion, the dependence of the rate on the nature of the incoming phosphine is more easily understood in terms of the simultaneous occurrence of the reverse oxidative addition path, which involves a bimolecular attack of C_6H_5CN to a 3-coordinate NiP_3 species. The rate of this reaction will depend on the concentration of the NiP_3 species in equilibrium with the NiP_4 complex, and hence on the chelating properties of the phosphine.

In the case of the nickel—DEE complex, this mechanism requires an equilibrium $Ni(DEE)_2$(4-coordinate) $\rightleftharpoons$ Ni(DEE)DEE(3-coordinate) in which one end of a diphosphine becomes detached from the metal centre. It is safe to assume that with a diphosphine such as DEE the equilibrium will lie far to the left, and this will result in relatively low rates for the oxidative addition and relatively high rates for the elimination.

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