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MECHANISM OF REDUCTIVE ELIMINATION OF BENZONITRILE IN CYANOPHENYL COMPLEXES OF NICKEL(II)

II. REACTIONS OF [CYANO(PHENYL)BIS(TRICYCLOHEXYLPHOSPHINE)NICKEL(II)] *

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Summary

The thermal decomposition of the complex $Ni(CN)(C_6H_5)(PCy_3)_2$ (Cy = cyclohexyl) in decalin has been examined. The complex reacts with $P(OC_2H_5)_3$ to give C_6H_5CN in quantitative yield. The mechanism of this reaction has been investigated and compared with that of the similar reaction shown by $Ni(CN)(C_6H_5)(PEt_3)_2$. The results indicate that the easiest path for the reaction involves a bimolecular attack of $P(OC_2H_5)_3$ at the metal atom before reductive elimination of C_6H_5CN.

Introduction

Arylnickel compounds $Ni(X)(Ar)(PR_3)_2$ (X = halide) by thermal decomposition or on treatment with tertiary phosphines give biaryls, often in quantitative yield [1]. Aryl halides are not produced and the available information does not allow one to decide whether carbon—carbon coupling is preferred to carbon—halide coupling for thermodynamic or for kinetic reasons. In contrast to this behaviour the cyanide organometal complexes $Ni(CN)(Ar)(PR_3)_2$ readily give aryl cyanides by reaction with a number of nucleophiles (tertiary or ditertiary phosphines [2], phosphites $P(OR)_3$, carbon monoxide [3]). Thus, a reaction path is available to the cyano complexes which is apparently closed to the halide derivatives. The elimination of aryl nitriles appears to involve the bimolecular attack of a suitable reagent upon the 4-coordinate substrate, and there is no indication that it can occur by a unimolecular process in which the cyanide and

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phenyl groups in the starting complex couple to form C_6H_5CN.

Reductive elimination reactions have not been investigated kinetically to any large extent. We recently investigated the mechanism of the reaction of $Ni(CN)(C_6H_5)(PEt_3)_2$ with the diphosphine $(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$ (DEE), affording C_6H_5CN and $Ni(DEE)_2$ [4]. We found that the kinetics are consistent with a bimolecular associative mechanism, and that the species which produces the C_6H_5CN is a 5-coordinate intermediate of the type $Ni(CN)(C_6H_5)P_3$ (P = phosphorus atom of a tertiary or ditertiary phosphine bound to nickel). As part of our studies of the reductive eliminations from organonickel(II) complexes, we report below the results of kinetic studies on the elimination of C_6H_5CN from the complex $Ni(CN)(C_6H_5)(PCy_3)_2$ (Cy = cyclohexyl) with emphasis on the effect of increasing the steric congestion about the nickel atom. It was hoped that a monomolecular dissociative path might be opened as a consequence of the increased steric hindrance.

Experimental

Materials. Most of the compounds used in this investigation were prepared by established methods. The preparation of the new complex $Ni(CN)(C_6H_5)(PCy_3)_2$ is described below.

All operations were carried out under argon. In the kinetic runs the temperature was controlled within 0.1°C by circulating water around the cell in the spectrophotometer.

Preparation of $Ni(CN)(C_6H_5)(PCy_3)_2$. 1 g (1.54 mmol) of $Ni(PCy_3)_2(C_2H_4)$, prepared by a standard method [5], and 3 ml (30.8 mol) of C_6H_5CN were refluxed for 4 h in 10 ml of boiling benzene under argon. After evaporation to a small volume the dark-red solution was stirred with n-hexane to give a yellow precipitate, which was filtered off and thoroughly washed with n-hexane. (Found: C, 69.8; H, 10.01; N, 2.21; $C_{43}H_{71}NNiP_2$ calcd.: C, 71.5; H, 9.90; N, 2.11%).

Results

Thermal decompositions of $Ni(CN)(C_6H_5)(PCy_3)_2$ (I). The decomposition of solutions of I (2×10^{-1} *M*) in decalin, were carried out under argon at 60—80°C. The infrared spectra of samples of the yellow solutions of the complex were investigated in the range 2300—1500 cm^{-1} (cell windows NaCl, path 0.5 mm). The intensity of the absorptions at the following wavenumbers were used to investigate the disappearance of the complex: 2105 cm^{-1} (ν(CN) stretching of the coordinated CN group), 1570 cm^{-1} (ν(CC) stretching of coordinated C_6H_5), 2230 cm^{-1} (ν(CN) stretch of free C_6H_5CN). Heating for 135 minutes at 70°C caused a 35% decrease in the intensity of the ν(CC) absorption and a 65% decrease in the intensity of the ν(CN) absorption. The amount of free C_6H_5CN present in solution (estimated from the intensity of the band at 2230 cm^{-1}) corresponded to less than 5% of the initial complex.

Solutions heated for 20 minutes at 80°C showed no band at 2105 cm^{-1}, but the intensity of the ν(CC) band at 1570 cm^{-1} had fallen by ca. 50%. The benzonitrile formed in the solution corresponded to about 7% of the initial complex (intensity of ν(CN) absorption at 2230 cm^{-1}). These results show that thermal decomposition of the complex in solution in the absence of accelerators affords only minor amounts of C_6H_5CN (probably as a result of side reactions). The decomposition mainly.gives other products, which were not investigated.

Decomposition induced by phosphines. The infrared spectral changes of decalin solutions of I (2×10^{-2} *M*) in the presence of tricyclohexylphosphine (2×10^{-1} *M*) were examined at 70—100°C. After 135 min at 70°C there was no evidence of decomposition of the starting complex. The infrared spectral patterns of the solutions after 20 min at 100°C indicated the disappearance of 45% of the coordinated cyanide and of 35% of the coordinated C_6H_5. The benzonitrile liberated in solution corresponded to only 10% of the initial complex.

The interaction of I (2×10^{-2} *M*) with the diphosphine DEE (5×10^{-2}—4×10^{-1} *M*) in decalin was monitored by recording the infrared and visible spectra (340—540 nm region) in the temperature range 25—70°C. The infrared spectra showed that the band at 2105 cm^{-1} (typical of the ν(CN) absorption of CN groups bound to nickel(II) in 4-coordinate planar complexes) was replaced by a doublet centered at 2105 cm^{-1} with the peaks separated by 10 cm^{-1}. The higher frequency peak was attributed to the ν(CN) absorption of a 4-coordinate complex; the lower frequency peak was assigned to the ν(CN) absorption of a 5-coordinate complex of the type $Ni(CN)(C_6H_5)P_3$ (P = phosphorus atom of a tertiary or ditertiary phosphine bound to the nickel atom) [4].

The changes in the infrared spectra were accompanied by a parallel change in the visible spectra: a new broad intense band with a maximum centered at 400 nm appeared on addition of DEE. This band was attributed to the 5-coordinate complex $Ni(CN)(C_6H_5)P_3$, and lies in the region where the absorption of the 4-coordinate species is very small (Fig. 1).

The system showed reversible changes when the temperature was varied. Temperature increase caused the intensity of the visible band at 400 nm and the ν(CN) absorption at 2100 cm^{-1} to decrease and the ν(CN) absorption at 2110 cm^{-1} to increase. Lowering of the temperature to the previous value restored the original spectrum. This behaviour is consistent with shifting of the equilibrium 1 to the right as the temperature is lowered.

$$Ni(CN)(C_6H_5)P_2 + P \rightleftharpoons Ni(CN)(C_6H_5)P_3 \qquad (1)$$

Reaction of I with triethylphosphite. The infrared spectra of 2×10^{-2} *M* solutions of I in decalin containing 4×10^{-1} *M* $P(OC_2H_5)_3$ showed that at 25°C the reductive elimination of C_6H_5CN was complete in about 10 min (disappearance of the ν(CN) absorption at 2105 cm^{-1} and of the ν(CC) at 1570 cm^{-1}, parallel development of a ν(CN) absorption at 2230 cm^{-1}). In agreement with the infrared spectra (single ν(CN) absorption), the visible spectra of this solution (path 1 mm) showed that no significant amounts of 5-coordinate intermediates or of products coming from replacements of PCy_3 by $P(OC_2H_5)_3$ in the starting complex had been formed. There was a decrease in the intensity of the absorption spectrum, but the shape of the spectrum remained unchanged.

The kinetic investigations were performed with an excess of phosphite present (>tenfold) to provide pseudo-first-order conditions. The constant substrate concentration was 7.5×10^{-4} *M* and that of the phosphite varied from $2.5 \times$

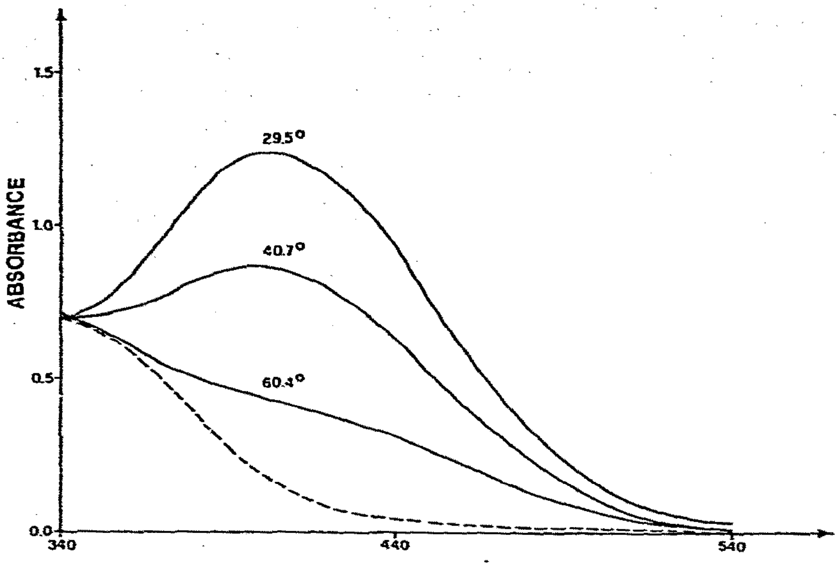

Fig. 1. Absorption spectra in decalin of 2×10^{-2} *M* $Ni(CN)(C_6H_5)(PCy_3)_2$ (broken line) in the presence of 4×10^{-2} *M* $(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$ (full line) at various temperatures. Cell path 1 mm.

10^{-2} to 5.2×10^{-1} *M*. The rates of the reaction were followed spectrophotometrically at 15, 25 and 35°C by measuring the intensity of the band at 357 nm appearing in the spectrum of I and absent in the spectrum of the solutions after reaction. The absorbance data showed that in these solutions the reaction always proceeded to at least 90%. No effect of the rates was observed on addition of PCy_3 or C_6H_5CN.

Excellent linear plots of $\log(A_t - A_\infty)$ versus time were obtained (A = absorbance at 357 nm). The values of the pseudo first order rate constants k_{obs} = rate/[complex] were found to increase linearly with the concentration of phosphite according to the equation $k_{obs} = k[P(OC_2H_5)_3]$ in the temperature range 288—308°K, The values of k thus determined were: 2.2×10^{-2} (288 K); 3.7×10^{-2} (298 K); 6.0×10^{-2} (308 K). The values of the activation parameters calculated from these data are: $\Delta H^{\neq} = 8.1 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\neq} = -38 \pm 2$ eu.

Discussion

The thermal decomposition of I in decalin at 60—80°C affords only minor amounts of C_6H_5CN. This shows that phenyl to cyanide coupling cannot take place in a simple monomolecular process in the starting 4-coordinate complex. Addition of 10 mol of PCy_3 does not substantially alter the decomposition pattern, but remarkably lowers the decomposition rate.

Addition of DEE to solutions of I in decalin causes an instantaneous change of colour from yellow to orange. The visible spectra (absorption bands in the 400 nm region) show, in agreement with the infrared spectra (two ν(CN) absorptions centered at 2105 cm^{-1}), that on addition of the diphosphine the equilibrium is instantaneously established (P indicates a phosphorus atom of

$$Ni(CN)(C_6H_5)P_2 + P \rightleftharpoons Ni(CN)(C_6H_5)P_3 \qquad (2)$$

PCy_3 or of DEE bound to nickel). The nature of the 5-coordinate complex may be inferred from the following considerations. The similar reactions between $Ni(CN)(C_6H_5)(PEt_3)_2$ and DEE has been shown [4] to involve the formation of the 5-coordinate intermediate $Ni(CN)(C_6H_5)(DEE)DEE$ (DEE not in parenthesis indicates a diphosphine ligand coordinated in a monodentate way). In the case of the system $Ni(CN)(C_6H_5)(PCy_3)_2$—DEE the visible bands of the 5-coordinate intermediate formed by addition of DEE to solutions of I show a blue shift of about 30 nm as compared to the spectrum of $Ni(CN)(C_6H_5)(DEE)DEE$, providing excellent evidence that the 5-coordinate complex cannot be the same. It may be $Ni(CN)(C_6H_5)(DEE)PCy_3$ or, less likely, $Ni(CN)(C_6H_6)(PCy_3)_2DEE$ (in the latter case the DEE molecule acts as a monodentate ligand). The ^{31}P NMR spectra reveal the presence of free cyclohexylphosphine, and consequently favour the formation of $Ni(CN)(C_6H_5)(DEE)PCy_3$.

The lack of reactivity of the intermediate containing PCy_3, in contrast to the relatively fast elimination of C_6H_5CN from $Ni(CN)(C_6H_5)(DEE)DEE$, shows that steric hindrance due to the bulky cyclohexyl groups stabilizes the phenyl-cyanide complex. This is easily understood if one accepts that the mechanism of elimination requires direct phenyl-cyanide interaction.

We shall now consider the kinetic results of the reaction of I with $P(OC_2H_5)_3$. The rate law found for this reaction is: rate = $k[P(OC_2H_5)_3][\text{Complex}]$. This can be interpreted only in terms of a bimolecular associative mechanism with a transition state of composition $Ni(CN)(C_6H_5)(PCy_3)_2P(OC_2H_5)_3$. This is in accord with the following observations: (i) no retardation in rate of reaction was observed in the presence of added PCy_3; (ii) no species other than the starting complex is detectable in the infrared and visible spectra of the reacting solution.

The negative value of the activation entropy (—38 eu) and the rather small enthalpy of activation (8 kcal mol^{-1}) are consistent with the formation of a transition state accompanied by net increase in bonding.

The situation recalls the bimolecular nucleophilic substitutions in planar complexes of d^8 transition metals. There is a close analogy in the first bond-making step in the two processes; addition of an entering group to form a 5-coordinate species. The two processes obviously differ in a subsequent step.

In conclusion, the easiest way for the reductive elimination of C_6H_5CN appears to be that involving bimolecular attack of an incoming group on the 4-coordinate substrate. Other possible decomposition pathways producing C_6H_4CN, for example an intramolecular decomposition of the type described by Morell and Kochi [6], are energetically unfavourable.

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