MECHANISM OF OXIDATIVE ADDITION OF BENZONITRILES TO DI(1,4-BIS(DIETHYLPHOSPHINO)BUTANE)NICKEL(0)

GIANCARLO FAVERO and ANTONINO MORVILLO

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., University of Padova (Italy)

(Received May 24th, 1983)

Summary

A kinetic study of the oxidative addition of RC_6H_4CN (R = H, *m*-CN, *p*-CN) to $Ni(DEPB)_2$ (DEPB = 1,4-bis(diethylphosphino)butane) suggests a template mechanism leading to the fission of one C–CN bond. The reaction products are *trans*-planar cyano-organonickel(II) complexes, $Ni_2(\mu\text{-}DEPB)_2(RC_6H_4)_2(CN)_2$ and $Ni(\eta^1\text{-}DEPB)(RC_6H_4)(CN)$, in equilibrium through exchange of DEPB.

Introduction

The oxidative addition of alkanenitriles $R(C_6H_5)CHCN$ (R = H, CH_3) to nickel(0) tricyclohexylphosphine complexes is a stereochemically controlled process, which implies mainly non-radical pathways [1]. We have found in several instances that the oxidative addition and, conversely, the reductive elimination of nitriles do not involve radicals (or one-electron steps), in contrast with the general behaviour of organic halides, which react by mechanisms involving monoelectronic activation steps [2].

Here we report on further evidence, arising from the study of the oxidative addition of benzonitriles RC_6H_4CN (R = H, *m*-CN, *p*-CN) to $Ni(DEPB)_2$ (DEPB = 1,4-bis(diethylphosphino)butane), in favour of the non-radical mechanism involved in the nitrile chemistry. We have already shown that the reaction of $Ni(DEPB)_2$ with C_6H_5CN affords the complex $Ni(DEPB)(C_6H_5)(CN)$ [3], which has been further investigated to aid understanding of the kinetic results.

The complex $Ni(DEPB)(C_6H_5)(CN)$

$Ni(DEPB)(C_6H_5)(CN)$ is a diamagnetic pale-yellow solid; it is sparingly soluble in hydrocarbons but the solubility is substantially increased by the presence of excess DEPB, and it is quite soluble in dichloromethane. The IR spectrum (Nujol or

dichloromethane) shows the $\nu(CN)$ absorption at 2100 cm^{-1} and the $\nu(CH)$ and $\nu(CC)$ (aromatic) absorptions at 3040 and 1565 cm^{-1}, respectively. The last absorption appears in a region which is typical of phenyl rings σ-bound to nickel(II) and to other metal centres [3]. The UV-VIS spectrum shows a strong absorption at 301 nm ($\epsilon = 6000$, shoulder at 325 nm) and a less intense band at 360 nm ($\epsilon = 1000$). The last absorption shifts to 390 nm ($\epsilon = 600$) when CN is replaced by Cl (the complex Ni(DEPB)(C$_6$H$_5$)(Cl) displays also an intense charge transfer band at 298 nm ($\epsilon = 9000$) [3]). On the basis of this spectrochemical shift, and in agreement with similar data reported for related organonickel(II) complexes for which a planar tetracoordinate structure has been established [4], we attribute the same structure to Ni(DEPB)(C$_6$H$_5$)(CN).

The ^{1}H NMR spectrum (CD$_2$Cl$_2$, 30°C) shows the resonances of the aromatic protons between τ 2.4 and 3.1 ppm, while the complex pattern of the aliphatic protons appears between τ 8.0 and 9.0 ppm. Very similar spectral patterns have been observed for the related organometallic complexes mentioned above [4]. The ^{31}P-$\{^1$H$\}$ spectrum (CH$_2$Cl$_2$, 30°C) consists of one sharp signal at 11.20 ppm (relative to H$_3$PO$_4$) which does not change upon cooling to -30°C, and is consistent with two equivalent phosphorus atoms mutually *trans*.

The observations collected indicate a regular *trans*-planar, tetracoordinate structure around the nickel atom. In view of the geometrical properties of the DEPB molecule, which preclude *trans*-chelation, and in agreement with the ascertained dimeric nature of Ni$_2$(μ-DPPB)$_2$(CN)$_4$ [5], the present complex is formulated as Ni$_2$(μ-DEPB)$_2$(CN)$_2$(C$_6$H$_5$)$_2$:
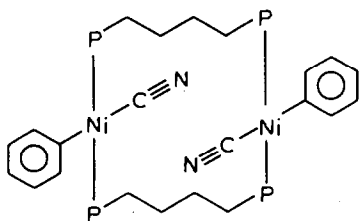
In hydrocarbon solutions containing excess DEPB (e.g. those obtained by oxidative addition of C$_6$H$_5$CN to Ni(DEPB)$_2$) the solubility of Ni$_2$(μ-DEPB)$_2$(CN)$_2$-(C$_6$H$_5$)$_2$ is greatly increased. This is attributable to the formation of a soluble adduct with DEPB, in agreement with the detection of new signals in the VIS (at 430 nm) and IR (at 2096 cm^{-1}, resolution 0.7 cm^{-1}) spectra. Also the ^{31}P-$\{^1$H$\}$ spectrum of these solutions shows new broad signals at 14.7 and -22.4 ppm whereas the signal of the parent complex is broadened and shifted to 11.9 ppm. The spectrum is (reversibly) temperature dependent, and at -40°C the signals are shifted to 15.1, -26.7, and 11.2 respectively (free DEPB has a signal at -26.70 ppm). The spectra remain broad at the lowest temperatures used, but the decrease in the solubility prevents investigation at even lower temperatures.

From these spectral features and in agreement with the stereochemistry of the DPPM complexes of Pd and Pt dicyanides [6], where the diphosphine acts as a monodentate ligand, which show a ^{31}P-$\{^1$H$\}$ spectrum similar to that under discussion, we tentatively attribute to our DEPB adduct the η^1 structure:
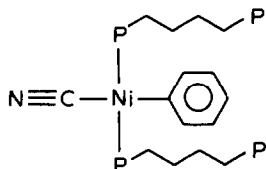
In the low resolution mode (3.5 cm^{-1}) the intensity of the composite ν(CN) absorption observed at 2100 cm^{-1} in toluene solutions of Ni$_2$(μ-DEPB)$_2$(CN)$_2$-(C$_6$H$_5$)$_2$ and DEPB is insensitive to the amount of excess DEPB ([Ni]$_{tot}$ = 2 × 10^{-2} M, [DEPB] up to 0.3 M). Therefore the absorbance and the apparent extinction coefficient (137) of this band were used for monitoring the total concentration of the cyanophenylnickel(II) complexes produced by oxidative addition of C$_6$H$_5$CN to Ni(DEPB)$_2$.

Kinetic study of the reaction of Ni(DEPB)$_2$ and C$_6$H$_5$CN

The kinetic study of the oxidative addition of benzonitrile to Ni(DEPB)$_2$ was performed in toluene at 60°C. A few runs in n-heptane at 60°C gave the same rates as those in toluene. The initial rate method was used to overcome the complexity arising from the participation of DEPB in various equilibria and from the reversibility of the overall oxidative addition process [3]. No CIDNP effects nor ESR signals could be observed during the reactions, and the rates were unaffected by the presence of galvinoxyl, duriquinone, or cyclooctadiene (up to 1 × 10^{-3} M).

The initial reaction rates and the concentration of Ni(DEPB)$_2$, benzonitrile and DEPB satisfactorily fit the rate equation:

$$\text{rate} = \frac{k_1[\text{DEPB}] + k_2 K}{[\text{DEPB}] + K}[\text{C}_6\text{H}_5\text{CN}][\text{Ni(DEPB)}_2] \tag{1}$$

Equation 1 is in agreement with the following mechanism:

$$\text{Ni(DEPB)}_2 \overset{K}{\rightleftarrows} \text{Ni(DEPB)} + \text{DEPB}$$

$$\text{Ni(DEPB)}_2 + \text{C}_6\text{H}_5\text{CN} \overset{k_1}{\rightarrow} \text{Products}$$

$$\text{Ni(DEPB)} + \text{C}_6\text{H}_5\text{CN} \overset{k_2}{\rightarrow} \text{Products}$$
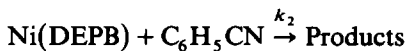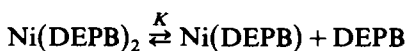
The values of the constants appearing in equation 1, estimated by a least-squares fitting of the experimental data, are: $k_1 = 2.9 \times 10^{-5}$ s^{-1}, $k_2 = 7.0 \times 10^{-4}$ s^{-1}, $K = 1.8 \times 10^{-3}$ mol l^{-1} all subject to a standard error of 10%.

Oxidative addition of RC$_6$H$_4$CN (R = m-CN, p-CN) to Ni(DEPB)$_2$

Under the experimental conditions used for C$_6$H$_5$CN, the nitriles RC$_6$H$_4$CN (R = m-CN, p-CN) react with Ni(DEPB)$_2$ to give cyanoorganonickel(II) complexes which analyze as Ni(DEPB)(RC$_6$H$_4$)(CN). The appearance in the IR spectrum of one sharp absorption at 2100 cm^{-1}, attributable to the CN group bound to nickel, and one sharp absorption at 2220 cm^{-1} (R = m-CN, free molecule 2235 cm^{-1}) or at

$2215\ cm^{-1}$ (R = p-CN, free molecule $2235\ cm^{-1}$), respectively, for the two nitriles, attributable to a CN group bound to the phenyl ring, show that only one C–CN bond is cleaved in the oxidative addition reaction. This is confirmed by the absence of reaction observed when these complexes are treated with excess nickel(0) complexes ($Ni(DEPB)_2$ or the more reactive $Ni(PCy_3)_2$). The complexes under discussion have an UV-VIS spectrum indistinguishable from that observed for $Ni_2(\mu\text{-}DEPB)_2(CN)_2(C_6H_5)_2$, and are suggested to be isostructural with that species.

An approximate value of k_2 for the oxidative addition of these nitriles to $Ni(DEPB)_2$ was estimated in the absence of added DEPB. The following values were obtained: k_2 (R = m-CN) $= 1.2 \times 10^{-2}\ s^{-1}$ and k_2 (R = p-CN) $= 3.5 \times 10^{-2}\ s^{-1}$.

Conclusions

The oxidative addition of benzonitriles to $Ni(DEPB)_2$ proceeds through the sequence shown in Scheme 1:

$$Ni(DEPB)_2\ +\ RC_6H_4CN\ \xrightarrow{\ k_1\ }\ Ni(\eta^1\text{-}DEPB)_2(RC_6H_4)(CN)$$

$$+DEPB\ \updownarrow\ -DEPB \qquad\qquad -DEPB\ \updownarrow\ +DEPB$$

$$Ni(DEPB)\ +\ RC_6H_4CN\ \xrightarrow{\ k_2\ }\ \tfrac{1}{2}\,Ni_2(\mu\text{-}DEPB)_2(RC_6H_4)_2(CN)_2$$
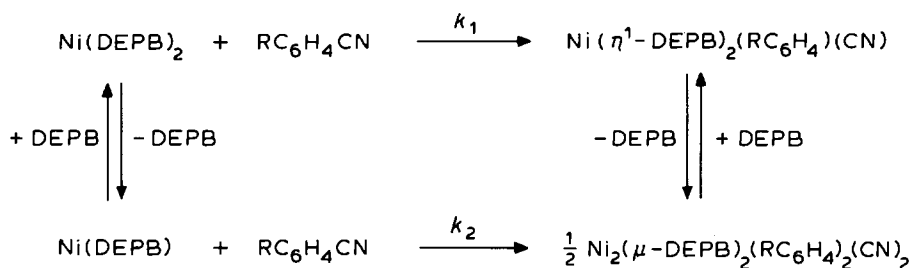
SCHEME 1

The value of 24 for the ratio k_2/k_1 confirms the higher reactivity of coordinatively unsaturated species, i.e. Ni(DEPB), than of three- or four-coordinated derivatives towards the oxidative addition reaction [7]. It is likely that the k_1 step has to be preceded by the dissociation of one diphosphine arm, and that both the k_1 and k_2 steps are preceded by the "end on" or "side on" coordination of the nitrile, as observed in the oxidative addition of alkanenitriles to $Ni(PCy_3)_2$ [1]. Although no IR kinetic evidence for these steps were obtained in the explored concentration range, their existence is suggested by the sudden color change from light-yellow to light-red observed upon nitrile addition. Moreover the coordination of the nitrile may promote the dissociation of the diphosphine, accounting for the abnormally high value of the dissociation constant $K = 1.8 \times 10^{-3}\ mol\ l^{-1}$ compared with those for other alkylphosphino complexes of nickel(0) producing formally dicoordinate species corresponding to Ni(DEPB) [8].

From the point of view of the nitrile, the absence of inhibition or retardation effects upon addition of radical-scavengers, coupled with the failure to observe CIDNP effects or ESR signals during the reaction argue against a simple radical-chain mechanism. There remains the possibility, which applies in the case of the oxidative addition of aryl halides to nickel(0) [9], that ion-pairs are involved which collapse prior to the diffusion of the aryl radicals out of the solvent cage. When this is the case an increase in reaction rate is observed when solvents of increasing polarity are used or when electron-withdrawing substituents are introduced into the benzene ring [7,9]. In particular, for the oxidative addition of RC_6H_4Cl to $Ni(PPh_3)_3$ a ratio of

1/650/6500 has been observed for the k_2 values when R = H, m-CN, p-CN, respectively [10]. These effects are found to be almost absent in the system studies here, the reaction rates bein unaffected on going from n-heptane to toluene as solvent and little changed on changing the nature of R (the ratio of k_2 for R = H, m-CN, p-CN is 1/17/50).

It has been demonstrated that the oxidative addition of alkanenitriles to nickel(0) is stereochemically controlled, and is non-radical [1]. A non-radical pathway seems also reasonable for the oxidative addition of benzenenitriles in view of all the results, of the higher energy required to obtain benzene radicals than alkane radicals from the relevant nitriles, and of the better accessibility, in contrast with the halide derivatives, of template intimate mechanisms [1].

Experimental

All reactions were carried out under argon in gas- and vapour-tight vessels from which aliquots of the reaction mixtures were withdrawn at appropriate times for the physical measurements. Infrared (Perkin–Elmer 599B), visible (Perkin–Elmer 576), NMR (Varian EM 360A and Bruker WP 60) and ESR (Jeol JES PE) were employed to study the reactions.

The ^{31}P-$\{^1H\}$ chemical shifts are reported with positive values downfield from H_3PO_4.

Preparation of the complexes

The nickel(0) complexes bearing the phosphine DEPB [3] and PCy_3[11] and the complex $Ni(DEPB)(C_6H_5)(CN)$ [3] were prepared by literature methods.

The complexes $Ni(DEPB)(RC_6H_4)(CN)$ (R = m-CN, p-CN) were prepared as follows. $Ni(DEPB)_2$ (250 mg, 0.5 mmol) in toluene (5 ml) was added to the nitrile (60 mg, 0.5 mmol) in dioxane and the mixture was stirred for 4 h at 60°C. Evaporation to small volume gave a white solid (80% yield), which showed the following IR absorptions (Nujol):

	ν(CH)(aromatic) (cm^{-1})	ν(CN)(nitrilic) (cm^{-1})	ν(CN)(Ni–CN) (cm^{-1})	ν(CC)(aromatic) (cm^{-1})
R = m-CN	3040–3080	2220	2100	1550
R = p-CN	3040	2215	2100	1570

It analyzed as $NiC_{20}H_{32}N_2P_2$: Found: R = m-CN: C, 57.1; H, 8.16; N, 6.74; R = p-CN: C, 57.4; H, 7.87; N, 6.83. Calcd.: C, 56.9; H, 7.64; N, 6.64%.

The complexes were recovered unchanged after treatment in toluene at 80°C with excess $Ni(DEPB)_2$ or $Ni(PCy_3)_2$.

Kinetic studies

The kinetics were performed at 60°C (± 0.1) in toluene with variable concentrations of [$Ni(DEPB)_2$] (1×10^{-2} M), RC_6H_4CN (0.1 to 1 M) and DEPB (2×10^{-2} to 0.23 M) corrected for the amount produced by the preequilibrium K. The absorbance of the ν(CN) absorption of the products (2100 cm^{-1}) measured at low resolution (3.5 cm^{-1}) and the relevant ϵ value (137) determined for pure samples of $Ni(DEPB)(C_6H_5)(CN)$ in the presence of excess phosphine were used to estimate the

total concentration of products. This absorption was monitored during the course of the reactions and the slope of the concentration versus time plots gave the initial rates, which were generally reproducible to within ±10%. The initial rate method was used to overcome the complications introduced by the participation of the diphosphine in concurrent equilibria.

Acknowledgements

References

1 G. Favero, A. Morvillo and A. Turco, J. Organomet. Chem., 241 (1983) 251.
2 J.A. Osborn in Y. Ishii and M. Tsutsui (Eds.), Organotransition Metal Chemistry, Plenum Press, New York, 1975, p. 65–80.
3 G. Favero, A. Frigo and A. Turco, Gazz. Chim. Ital., 104 (1974) 869.
4 R.G. Miller, R.D. Stauffer, D.R. Fahey and D.R. Parnell, J. Amer. Chem. Soc., 92 (1970) 1511.
5 P. Rigo, B. Corain and A. Turco, Inorg. Chem., 7 (1968) 1623.
6 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 956.
7 C.A. Tolman, Chem. Rev., 77 (1977) 313.
8 C.A. Tolman, W.C. Seidel and D.H. Gerlach, J. Amer. Chem. Soc., 94 (1972) 2269.
9 T.T. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 6319.
10 M. Foà and L. Cassar, J. Chem. Soc. Dalton, (1975) 2572.
11 G. Favero, A. Morvillo and A. Turco, Gazz. Chim. Ital., 109 (1979) 27.