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OXIDATIVE ADDITION OF ALKANENITRILES TO NICKEL(0) COMPLEXES VIA π-INTERMEDIATES

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Summary

The alkanenitriles $R(C_6H_5)CHCN$ ($R = H, CH_3$) coordinate rapidly and quantitatively through the CN group to the complexes $[Ni(PCy_3)_2]$ or $[\{Ni(PCy_3)_2\}_2N_2]$. Both the end-on $[Ni(PCy_3)_2(\sigma\text{-}R'CN)]$ and the edge-on $[Ni(PCy_3)(\pi\text{-}R'CN)]$ adducts are formed, and are present in an equilibrium the position of which is governed by the amount of added PCy_3. The π-complexes react to give the cyano-organometal complexes $[Ni(PCy_3)_n(R')(CN)]$ through an oxidative addition involving splitting of the C–CN bond. The complexes obtained are unstable and slowly decompose under the reaction conditions to give the coupling R′–R′ (R = H) or the β-elimination R′(–H) ($R = CH_3$) products. The kinetics of the reaction and the stereochemical result suggest a template mechanism in agreement with the findings above.

Introduction

During the last decade our interest in systems involving the rupture-formation of C–CN bonds has focused on benzonitrile. We studied its oxidative addition to phosphinenickel(0) complexes and the reductive elimination from the corresponding cyano-organometals [1].

Oxidative addition of alkanenitriles was discovered by us only recently in work with the reactive $[Ni(PCy_3)_2]$ and $[Ni(PEt_3)_4]$ complexes [2]. The reactions gave organic products which were suggested to be derived from intermediate cyano-organometals via β-elimination or phosphine metallation steps. However, information is lacking about the intimate mechanism of the reaction and about the nature of te cyano-organometals which are likely to be involved as intermediates. With the aim of defining the mechanism of the oxidative addition of alkanenitriles to nickel(0) complexes we have now studied the reactions between the nitriles $R(C_6H_5)CHCN$ ($R = H, CH_3$) and the complexes $[Ni(PCy_3)_2]$ and $[\{Ni(PCy_3)_2\}_2N_2]$.

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Reactions of $C_6H_5CH_2CN$ (BN)

When [Ni(PCy$_3$)$_2$] 10^{-1} *M* solutions in toluene at ambient temperature are made 10^{-1} *M* in BN (ν(CN) 2255 cm^{-1}; ν(CC) 1600, 1500 cm^{-1}; τ 2.98 (singlet, 5H, C_6H_5), 7.15 (singlet, 2H, CH_2) ppm, toluene-d_8, rel. TMS) there is an immediate color change from violet-brown to red. New absorptions appear in the IR (2250, 2240(sh), 1780 cm^{-1}) and PMR (τ 2.80 (br), 2.98 (br), 5.68 (br), 710 (br) ppm) spectra with complete disappearance of the peaks for the free nitrile. Identical spectral patterns are obtained starting from the [{Ni(PCy$_3$)$_2$}$_2$N$_2$] complex: the completeness of the reaction is confirmed in this instance by the evolution of about one mole of nitrogen for every two moles of nitrile and the disappearance of the 2080 cm^{-1} band of the coordinated N_2 [3].

Treatment of the solutions of the reaction with stoichiometric amounts of CO immediately removes the new signals; the IR and NMR patterns show the quantitative liberation of the nitrile and the production of [Ni(CO)$_2$(PCy$_3$)$_2$] (ν(CO) 1930, 1980 cm^{-1}) and, in lesser amount, [Ni(CO)$_3$(PCy$_3$)] (ν(CO) 1980, 2060 cm^{-1}) [4].

Addition of excess nitrile (even in the presence of excess PCy$_3$) up to 1 *M* causes no significant changes in the intensity of the new IR and PMR signals, confirming the completeness of the reaction at the concentrations employed. Additions of excess PCy$_3$ up to 0.5 *M* increase the intensities of the signals at 2250, 2240(sh) cm^{-1} and at τ 2.98, 7.10 ppm at the expense of those at 1780 cm^{-1} and τ 2.80, 5.68 ppm which are thus attributable to a different species. Attempts to isolate the two species revealed by the spectral patterns were thwarted by their rapid conversion into the final reaction products (see later). Nevertheless it is possible to formulate them safely on the basis of the following arguments.

The nitriles possesse two sites for coordination, namely the nitrogen lone pair (end-on coordination) and the CN π-electrons (edge-on coordination) [5]. Both types have been confirmed for a number of complexes including those of nickel(0) with triphenylphosphine [6]. The end-on coordination is found to involve a change of the ν(CN) frequency in the range -100, $+100$ cm^{-1} with respect to the free nitrile, but it usually implies a smaller change of frequency (-60, $+40$ cm^{-1}) [5]. Correspondingly, very small or negligible changes are observed in the values of the chemical shifts of the α-protons [7]. By contrast, edge-on coordination is found to involve a large decrease in ν(CN) (-100, -500 cm^{-1} and around -480 cm^{-1} for a π-benzonitrile-nickel(0) complex) [6b], and a marked deshielding of the α-protons is expected.

To account for the observed features we attribute the end-on structure to the species absorbing at 2250, 2240(sh) cm^{-1}. This species is formulated as [Ni(PCy$_3$)$_2$(σ-BN)] on the basis of the lack of any effects on its concentration of addition of BN, and of the results of the equilibrium studies (see Experimental). On a similar basis an edge-on structure is attributed to the species absorbing at 1780 cm^{-1}, which is formulated as [Ni(PCy$_3$)(π-BN)].

In the presence of 0.5 *M* PCy$_3$ the complex [Ni(PCy$_3$)$_2$(σ-BN)] (10^{-1} *M*) is the predominant species, and is stable at room temperature. In the absence of added phosphine the predominant species is [Ni(PCy$_3$)(π-BN)]. The π-complex decomposes slowly at ambient temperature yielding products which show absorptions at 2100(br) and 1590 cm^{-1} attributable to the ν(CN) stretch of coordinated CN and to aromatic CC stretching. The presence of increasing amounts of PCy$_3$ (0.1 to 0.5 *M*) progressively lowers the initial concentration of the π-complex and the reaction rate. These facts suggest the overall mechanism:

$$\begin{array}{ll}[\mathrm{Ni(PCy_3)_2}] + \mathrm{BN} \overset{K_1}{\rightleftarrows} [\mathrm{Ni(PCy_3)_2}(\sigma\text{-}\mathrm{BN})] \overset{K_2}{\rightleftarrows} & [\mathrm{Ni(PCy_3)}(\pi\text{-}\mathrm{BN})] + \mathrm{PCy_3} \\ & \qquad \downarrow k_1 \\ & \qquad \text{products}\end{array}$$

Under the conditions used the formation of the nitrile complexes from $[\mathrm{Ni(PCy_3)_2}]$ is practically complete and the value of K_1 is estimated to be $> 10^5$. The kinetic study was performed in toluene at 50°C, with variable BN (10^{-1} to 1 M) and $\mathrm{PCy_3}$ (2×10^{-2} to 10^{-1} M) concentrations. The values of k_{obs}, estimated from the initial slope of the $[\mathrm{Ni(PCy_3)}(\pi\text{-}\mathrm{BN})]$ concentration versus time plots, fit the equation:

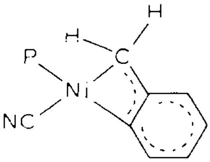
$$k_{\mathrm{obs}} = \frac{k_1 K_2}{K_2 + [\mathrm{PCy_3}]}$$

The rates calculated from this equation fit the observed disappearance of the reagents and the formation of the products (absorption at 1590 cm^{-1} alone) if $K_2 = 1.2 \times 10^{-2}$ mol l^{-1} and $k_1 = 1.4 \times 10^{-3}$ s^{-1}. The best fit value of K_2 is in fair agreement with the value (1.5×10^{-2}) found independently from equilibrium studies (see Experimental) and this provides support for the proposed mechanism.

The nature of the products present in solution during the course of the reaction was investigated by ESR, PMR and GLC. The ESR spectra fail to reveal paramagnetic species present in concentration higher than the limiting value (ca. 10^{-6} M). The PMR spectra between τ 0 and τ 50 ppm (rel. TMS), registered at ambient temperature and at −70°C, showed no resonances attributable to hydridic hydrogens.

Gas-liquid chromatography of the reaction mixture after treatment with $\mathrm{CF_3COOH}$ or with CO gave the following results: (i) Initially, acidolysis quantitatively liberates the coordinated nitrile. As the reaction proceeds smaller amounts of nitrile are liberated and toluene is found in amounts corresponding to the missing nitrile. (ii) The carbonylation of the reaction mixture initially yields the free nitrile along with the complexes $[\mathrm{Ni(CO)}_n(\mathrm{PCy_3})_{4-n}]$ ($n = 2, 3$). Later treatments with CO produce a species absorbing at 2110 and 1650 cm^{-1} which increase at the expense of decreases in the amounts of the nitrile and the carbonyls. From these solutions a yellow-brown impure solid separates which shows bands at 2115 and 1650 cm^{-1} (Nujol). The infrared spectrum of this product is identical to that of the solid produced by carbonylation of $[\mathrm{Ni(PCy_3)(C_6H_5CH_2)(CN)}]$ (see later) in the same solvent. Both spectra are similar to that of the complex $[\mathrm{Ni(PCy_3)(C_6H_5CO)(CN)}]$ (ν(CN) 2120 cm^{-1}; ν(CO) 1645 cm^{-1}) [8]. The compound produced by the carbonylation of the reaction mixture is thus formulated as the acyl complex $[\mathrm{Ni(PCy_3)(C_6H_5CH_2CO)(CN)}]$.

Finally, a yellow-brown diamagnetic solid precipitates on standing at 50°C. This analyzes for $[\mathrm{Ni(PCy_3)(C_6H_5CH_2)(CN)}]$ and is insoluble in common solvents. The IR spectrum of the complex shows aromatic CH stretchings at 3080–3020 cm^{-1}, the CN stretching at 2105 cm^{-1} (2100 cm^{-1} in toluene) (vs), and the monosubstituted aromatic CC stretchings at 1590, 1490 cm^{-1}. The UV-VIS spectrum shows an intense charge transfer absorption with the maximum at 300 nm and a shoulder at 370 nm. A planar tetracoordinate structure can be assigned to the complex on the basis of the ascertained diamagnetism of the nickel atom. This stucture can be accounted for in terms of a di-hapto coordination of the benzyl moiety:



This mode of bonding is well kown for benzyl complexes, especially of the nickel triad; for example the species $[\mathrm{Ni(PPh_3)(\pi\text{-}C_6H_5CH_2)(Cl)}]$, has been characterized and is analogous to the species under discussion [9].

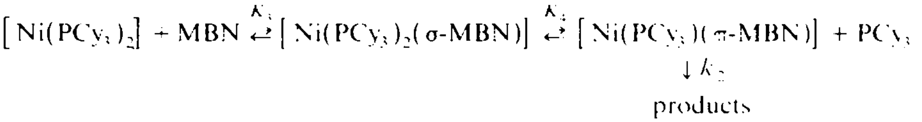
The complex $[\mathrm{Ni(PCy_3)(C_6H_5CH_2)(CN)}]$ must be regarded as a relatively labile intermediate, since it decomposes in the solid state in a few days at ambient temperature to give $\mathrm{C_6H_5CN}$. This decomposition is of obvious interest because it involves the rupture of the phenyl $\mathrm{CH_2}$ bond and the simultaneous formation of a phenyl CN bond. Work is in progress to elucidate the mechanism of this reaction. In toluene or benzene at 50°C under argon the complex decomposes according to the following scheme, similar to the thermal decompositions observed for the halide-benzyl complexes of nickel(II) and palladium(II) [10]:

$$2[\mathrm{Ni(PCy_3)(C_6H_5CH_2)(CN)}] \rightleftarrows \mathrm{Ni}^0_s + [\mathrm{Ni(PCy_3)_2(CN)}] + \mathrm{C_6H_5CH_2CH_2C_6H_5}$$

In decalin, toluene is also found as a product.

Reactions of $\mathrm{C_6H_5(CH_3)CHCN}$ (MBN)

The reactions were studied by the methods used for the nitrile BN. Complete coordination of the nitrile was observed when $[\mathrm{Ni(PCy_3)_2}]$ or $[\{\mathrm{Ni(PCy_3)_2}\}_2\mathrm{N_2}]$ 10^{-1} *M* solutions in toluene at room temperature were made 10^{-1} *M* in MBN (ν(CN) 2240 cm^{-1}; ν(CC) 1600, 1500 cm^{-1}; τ 2.91 ppm (singlet, 5H, $\mathrm{C_6H_5}$), 6.80 (quartet, ^3J 7 Hz, 1H, CH), 8.80 (doublet, ^3J 7 Hz, 3H, $\mathrm{CH_3}$), toluene-d_8; rel. TMS). The data were consistent with the following equilibria, analogous to those found for the nitrile BN:



$$[\mathrm{Ni(PCy_3)_2}] + \mathrm{MBN} \overset{K_3}{\rightleftarrows} [\mathrm{Ni(PCy_3)_2(\sigma\text{-}MBN)}] \overset{K_4}{\rightleftarrows} \underset{\substack{\downarrow k_2 \\ \text{products}}}{[\mathrm{Ni(PCy_3)(\pi\text{-}MBN)}]} + \mathrm{PCy_3}$$

with $K_3 > 10^5$ mol l^{-1} and $K_4 \approx 6 \times 10^{-2}$ mol l^{-1}. The nitrile coordinated end-on showed ν(CN) 2240 cm^{-1} and τ 8.83(br) ppm (doublet, ^3J 7 Hz, $\mathrm{CH_3}$); the nitrile bound edge-on showed ν(CN) 1760 cm^{-1} and τ 8.15(br) ppm (doublet, ^3J 7 Hz, $\mathrm{CH_3}$).

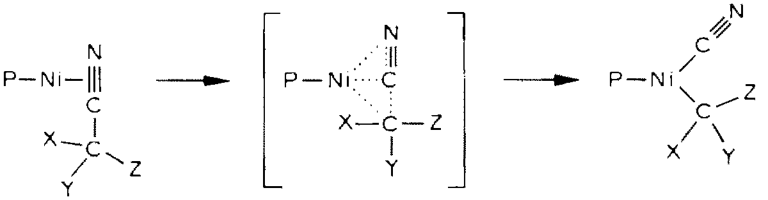
The kinetic studies confirmed the similarity in the behaviour of the nitriles BN and MBN. Again the π-adduct $[\mathrm{Ni(PCy_3)(\pi\text{-}MBN)}]$, is unstable, and it decomposes (k_2) according to the expression:

$$k_{\mathrm{obs}} = \frac{k_2 K_4}{K_4 + [\mathrm{PCy_3}]}$$

The best fit value of k_2 is 4.5×10^{-2} s^{-1} and that of K_4 is 4.3×10^{-2} mol l^{-1}, the latter value agreeing with that found spectrophotometrically (6.0×10^{-2} mol l^{-1}).

The decomposition of the π-adduct yields species which show ν(CN) absorptions at 2100 and 2050 cm^{-1} and ν(CC) absorptions at 1600, 1495 cm^{-1}. By analogy with the spectral behaviour observed in the reactions with BN, it is suggested that these species are cyano-organometal complexes produced in the final oxidative addition step. The ratio of the intensity of the absorptions ν_{2100}/ν_{2050} was found to depend linearly on $1/[PCy_3]$. It is concluded that the cyano-organo complexes differ in the number of coordinated PCy_3 molecules. These species were not further investigated owing to their very low stability. Repeated attempts to isolate them failed because they decompose with liberation of styrene, most likely through a β-elimination process. Reaction of CO with the solution of the complexes yields styrene and nickel-phosphine carbonyls.

Use of optically active MBN in which the *S* enantiomer was slightly predominant, produced organometallic complexes displaying positive CD with a maximum near 370 nm, where the UV spectra of the solution shows a shoulder on the tail of an intense charge transfer band centered at 300 nm. This stereochemical result rules out radical addition and is in accordance with the template mechanism depicted in eq. 1 postulated for the oxidative additions of benzonitrile [1] and benzoyl cyanide [8] to phosphinenickel(0) complexes:



(1)

Other mechanisms are less plausible in view of the observed intermediates.

Experimental

The solvents were dried by standard methods and distilled under argon. The nitriles $R(C_6H_5)CHCN$ ($R = CH_3$, H), obtained from EGA, were distilled carefully under argon. The complexes $[Ni(PCy_3)_2]$ and $[\{Ni(PCy_3)_2\}_2N_2]$ were prepared by literature methods [2a].

Reactions

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 360 A and Bruker WP 60) and ESR spectra (Jeol JES PE) were employed to study the reactions. The organic products were identified by GLC (Perkin–Elmer Sigma 3B) by comparison with authentic samples.

Preparation of $[Ni(PCy_3)(C_6H_5CH_2)(CN)]$. Phenylacetonitrile (0.23 g, 2 mmol) was added to $[Ni(PCy_3)_2]$ (0.62 g, 1 mmol) in decalin (10 ml) at ambient temperature and the mixture was set aside for several days. A yellow-brown solid separated (0.1 g, 25% yield) which was insoluble in common solvents and unstable even under argon (the decomposition gave benzonitrile, identified by GLC, SE 30 on Chromosorb A 2m × 3mm OD). Analyses: Found: C, 68.69; H, 8.94; N, 2.97; Ni, 12.81; P, 6.58. $NiC_{26}H_{40}NP$ calcd.: C, 68.44; H, 8.84; N, 3.07; Ni, 12.87; P, 6.79%. The IR spectrum (Nujol) shows bands at 3080, 3060, 3040, 3020 cm^{-1} (aromatic CH stretchings); 2105 cm^{-1} (CN stretching); 1590, 1490 (aromatic monosubstituted CC stretchings), and bands typical of coordinated PCy_3. The UV-VIS spectrum shows at 370 nm a shoulder on an intense absorption with a maximum at 300 nm.

Upon suspension in benzene or decalin and treatment with CF_3COOH, the complex loses about one mole of toluene per mole. When suspensions in toluene or benzene are treated with a stoichiometric amount of CO the complex reacts rapidly to give a yellow solid. Owing to the poor solubility of the complex in the useful solvents we were unable to purify it, and obtained erratic analyses. The IR spectrum of the product (Nujol) shows bands at 2115 and 1650 cm^{-1} (vs) attributable to $\nu(CN)$ and $\nu(CO)$ (acyl derivative), respectively.

Kinetic studies

The kinetics were performed at 50°C (±0.1) in toluene with $[Ni(PCy_3)_2]$ 5×10^{-2} or 10^{-1} *M* and variable concentrations of nitriles (10^{-1} to 1 *M*) and phosphine (10^{-1} to 2×10^{-2} *M*, corrected for the amount produced by the rapid dissociation of the σ-nitrile adducts). The concentrations of the σ- and π-nitrile adducts were estimated from the NMR spectra (vide infra) of the initial solutions at 50°C. The apparent extinction coefficients of the π-adducts $\nu(CN)$ absorptions, were determined by their initial intensities and the relevant initial concentrations ($\varepsilon_{BN(1780\ cm^{-1})}$ 130 $cm^{-1}\ mol^{-1}\ l$; $\varepsilon_{MBN(1760\ cm^{-1})}$ 80 $cm^{-1}\ mol^{-1}\ l$). These absorptions were 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 phosphine in concurrent equilibria.

Equilibrium constants

The values of the dissociation constants for the equilibria:

$$[Ni(PCy_3)_2(\sigma\text{-nitrile})] \rightleftarrows [Ni(PCy_3)(\pi\text{-nitrile})] + PCy_3$$

encountered in the study were estimated at 50°C in solutions containing various amounts of PCy_3 from the equilibrium concentrations of the various species calculated as follows:

$[Ni(PCy_3)(\pi\text{-nitrile})]$ = calculated from absorbance and apparent extinction coefficient of the $\nu(CN)$ absorption

$[Ni(PCy_3)_2(\sigma\text{-nitrile})] = [Ni^0]_{total} - [Ni(PCy_3)(\pi\text{-nitrile})]$

$[PCy_3] = [PCy_3]_{added} + [Ni(PCy_3)(\pi\text{-nitrile})]$

The constants thus obtained ($[PCy_3]$ ranging for 0.02 to 0.07 *M*) were generally reproducible to within ± 10%, and gave the mean values: $K_{BN} = 1.5 \times 10^{-2}\ mol\ l^{-1}$ (0.2×10^{-2} standard deviation); $K_{MBN} = 6.0 \times 10^{-2}\ mol\ l^{-1}$ (0.8×10^{-2} standard deviation).

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