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CARBONYLATION OF CYANO(PHENYL)BISLIGAND-NICKEL(II) COMPLEXES AND RELATED REACTIONS OF BENZOYL CYANIDE WITH NICKEL(0) COMPLEXES

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Summary

Carbonylation of the complexes $Ni(CN)(C_6H_5)(P)_2$ ($P = P(C_2H_5)_3$; $P(cyclo\text{-}C_6H_{11})_3$; $\frac{1}{2}(C_2H_5)_2P{-}(CH_2)_4{-}P(C_2H_5)_2$) affords the acyl-derivatives $Ni(CN)(COC_6H_5)(P)_n$ ($n = 1, 2$) which, in the presence of excess CO, undergo reductive elimination of C_6H_5COCN. It has been shown that C_6H_5COCN reacts with the NiP_n ($n = 2, 4$) complexes to give molecular adducts in which the organic reagent is coordinated to the nickel atom through the CO double bond. These adducts are unstable under ambient conditions and decompose to $Ni(CN)(C_6H_5)(P)_2$ and carbonyl(phosphino)nickel(0) complexes.

Introduction

Carbon monoxide insertion into a transition metal—carbon bond is one of the most important reactions of organo-transition metal compounds, and its relevance to many organic syntheses is well established [1]. Elucidation of the mechanism of this reaction is useful for understanding how different ligands bound to the metal can affect the course of the reaction, and for assisting in the tailoring of new catalysts for carbonylations.

The ligands normally employed in mechanistic studies are phosphines and amines, halides and organic anions [2]. Nothing was known about the influence of the metal-coordinated cyanide ligand on the mechanism of the CO insertion. We present below the results of a study of the reaction between CO and the complexes $Ni(CN)(C_6H_5)(P)_2$ (P: $PEt_3 = P(C_2H_5)_3$; $PCy_3 = P(cyclo\text{-}C_6H_{11})_3$; $\frac{1}{2}$ deb $= \frac{1}{2}(C_2H_5)_2P{-}(CH_2)_4{-}P(C_2H_5)_2$).

The reactions of C_6H_5COCN with the corresponding nickel(0) phosphine complexes have also been investigated.

Experimental

Instruments

Infrared spectra were recorded on a Perkin Elmer 257 spectrophotometer. Proton NMR spectra were recorded on a Varian 360 A spectrometer operating at 60 MHz. Gas chromatographic analyses were performed with a Hewlett Packard 5750 instrument fitted with SE 30/Chromosorb 10% (2 m) and Lac 728 (2 m) columns.

Materials

The complexes $Ni(CN)(C_6H_5)(PEt_3)_2$ [3], $Ni(CN)(C_6H_5)(PCy_3)_2$ [4], $Ni(CN)(C_6H_5)(deb)$ [5], $Ni(PEt_3)_4$ [6], $Ni(PCy_3)_2$ [7] and $Ni(deb)_2$ [5] were prepared by literature methods.

The solvents used were anhydrous and oxygen-free. The benzoyl cyanide was from Schuchardt and was recrystallized from ethyl ether. The carbon monoxide was UP grade (SIO).

General procedure for the reactions

The solid reactants were weighed (in a dry box when necessary) in a Teflon container, which was inserted into a valve for solids fitted to a three necked flask also equipped with a vacuum stopcock and a rubber serum cap. Known volume of solvents and stock solutions of the more reactive complexes were introduced into the vessel from air-tight hypodermic syringes. At various times small amounts of the reaction solutions were drawn off through the rubber cap and the appropriate analyses were performed.

The identification of the carbonyl-nickel complexes bearing the phosphines PEt_3 and PCy_3 was based on the observation of their characteristic $\nu(CO)$ infrared absorptions [8]. The $\nu(CO)$ bands of the carbonyl-complexes bearing the diphosphine deb were monitored during the carbonylation of $Ni(deb)_2$ and assigned by reference to the very similar bands displayed by the complexes containing the diphosphine 1,2-bis(diethylphosphino)ethane [8].

The amounts of the various reactants and products present in a reaction mixture were estimated by GC or by measuring the intensity of their infrared absorptions appearing in the range 2300—1500 cm^{-1} and comparing them under identical instrumental conditions with the absorptions of standard solutions. The absorbances of the two bands of the $Ni(CO)_2(P)_2$ complexes were determined from the fully reacted solutions formed from the relevant nickel(0) complexes under pure CO, when the concentration of other species as $Ni(CO)(P)_3$ and $Ni(CO)_3P$ were negligible.

Preparation of $Ni(CN)(COC_6H_5)(deb)$

$Ni(CN)(C_6H_5)(deb)$ (10^{-1} *M*) in CH_2Cl_2 was treated with the stoicheiometric amount of CO in the presence of free deb (10^{-2} *M*). After a few minutes stirring at room temperature the mixture was cooled to —10°C and the solvent removed in vacuo. The resulting orange oil was crystallized from ethyl ether to give a yellow solid showing infrared absorptions at 2105s ($\nu(CN)$), 1605vs, ($\nu(CO)$), 1590m ($\nu(CC)$), 1575s ($\nu(CC)$) cm^{-1} and bands due to coordinated phosphine. Anal. Found: C, 56.11; H, 7.66; N, 3.41; P, 14.89, $C_{20}H_{33}NNiOP_2$ calcd.: C, 56.64; H, 7.60; N, 3.30; P, 14.60%.

Preparation of Ni(CN)(COC$_6$H$_5$)PCy$_3$

Ni(CN)(C$_6$H$_5$)(PCy$_3$)$_2$ (10^{-1} *M*) was treated with the stoicheimetric amount of CO in n-hexane or THF. Upon standing overnight, a yellow solid separated; this was insoluble in the common solvents. The infrared spectrum showed absorptions at 2120s (ν(CN)) and 1645vs (ν(CO)) cm^{-1} and bands due to coordinated phosphine. Analyses differed from batch to batch as the crude products could not be recrystallized and probably contained some solvent: Found: C, 65.4—63.5; H, 8.68—7.99; N, 2.99—2.79, $C_{26}H_{38}NNiOP$ calcd.: C, 66.4; H, 8.10; N, 2.98%.

Results

Carbonylation reactions

Solutions of Ni(CN)(C$_6$H$_5$)(P)$_2$ complexes (10^{-1} to 10^{-2} *M* in n-hexane, benzene, THF or CH_2Cl_2 depending on the best solubility) in the presence of free phosphine (5×10^{-1} to 10^{-2} *M*, the highest value being that for PCy$_3$) rapidly absorb one molar equivalent of CO at ambient conditions in the initial step of the reaction (Fig. 1). The infrared spectra of the reacting solutions reveal the disappearance of the starting complex (monitored through the ν(CC) absorption, Table 1) and the parallel formation of a species displaying one strong absorption in the range 1605—1610 cm^{-1} (see Table 1). In accord with the literature [9—11] this absorption is attributed to the ν(CO) of the benzoyl complexes Ni(CN)(COC$_6$H$_5$)(P)$_2$ (Table 1), thus indicating the insertion of CO in the nickel—phenyl bond, eq. 1.

$$\mathrm{Ni(CN)(C_6H_5)(P)_2 + CO \rightleftharpoons Ni(CN)(COC_6H_5)(P)_2} \qquad (1)$$

In keeping with this, pure samples of Ni(CN)(COC$_6$H$_5$)(deb) are isolated from CH_2Cl_2 solutions. Attempts to crystallize the oils given by the PEt$_3$ and PCy$_3$ analogues were thwarted by decomposition of the samples to materials containing nickel carbonyl complexes.

The reversibility of the reaction 1 was demonstrated for all the phosphines examined by pumping off the CO and filling the reaction flask with argon. This

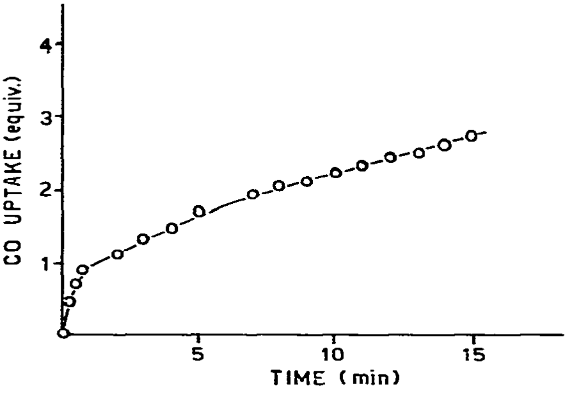


Fig. 1. Carbonylation of the complex Ni(CN)(C$_6$H$_5$)(PEt$_3$)$_2$ (10^{-2} *M*) in decalin at 25°C in the presence of 10^{-2} *M* PEt$_3$.

TABLE 1

INFRARED ABSORPTIONS (cm^{-1}) IN THE RANGE 2300—1500 cm^{-1} IN 10^{-2} *M* SOLUTIONS OF THE COMPLEXES SPECIFIED AND USED FOR MONITORING THE REACTIONS STUDIED

Complex	ν(CN)	ν(CO)	ν(CC)	Solvent [a]
$Ni(CN)(C_6H_5)(PEt_3)_2$	2105m		1565m [b]	D, M
$Ni(CN)(COC_6H_5)(PEt_3)_2$	2105m	1605vs	1585m, 1570s	D, M
$Ni(CN)(C_6H_5)(deb)$	2100m		1565m [b]	B, M
$Ni(CN)(COC_6H_5)(deb)$	2105m	1610vs	1595m, 1580s	B, M
$Ni(CN)(C_6H_5)(PCy_3)_2$	2105m		1570m [b]	M, T
$Ni(CN)(COC_6H_5)(PCy_3)_2$	2100m	1610vs	1590m, 1575s	M, T
$Ni(CN)(COC_6H_5)PCy_3$	2120m	1645vs		M, T

[a] B: benzene; D: decalin; M: methylene chloride; T: tetrahydrofuran. [b] Complex absorption.

procedure partially restored the starting complex at the expense of the benzoyl derivative. A further supply of CO displaces the equilibrium to the right again.

The solutions of the benzoyl complexes also show two absorptions of medium-strong intensity in the 1600—1570 cm^{-1} region (Table 1) which fall in the range typical of C$\overline{\ldots}$C stretching modes of phenyl groups bound to coordinated CO [12]. The cyanide stretching frequencies of the phenyl and benzoyl complexes involved in equation 1 are very close each other (Table 1) and only a slight broadening of the 2100—2105 cm^{-1} absorption present in the spectra of the starting complexes is observed in this reaction step, the intensity remaining nearly unchanged.

If the reaction is carried out in the absence of added phosphine, new species absorbing at 2120(br) and 1645 cm^{-1} are observed along with the benzoyl complexes described (or as the only detectable species for P = PCy_3) as products of the first reaction step. The quenching of the reaction at this stage by pumping off the CO followed by addition of excess phosphine (up to 5 × 10^{-1} in the case of PCy_3) caused the disappearance of the 2120 and 1645 cm^{-1} absorptions and produced the benzoyl complexes described in eq. 1. These facts suggest the existence of an equilibrium involving a phosphine dissociation of the type depicted in eq. 2 and known to occur in the carbonylation of organoplatinum complexes [9].

$$Ni(CN)(COC_6H_5)(P)_2 \rightleftharpoons Ni(CN)(COC_6H_5)P + P \qquad (2)$$

For P = PCy_3 the formally three-coordinate acyl complex is the predominant species in solution and slowly separate as a yellow solid, probably polymeric, containing bridging cyanide ligands.

In the presence of excess CO all the benzoyl complexes examined behave as reactive intermediates. Thus the initial reaction step considered above is followed by a slower one (Fig. 1) involving further CO absorption and giving products which differ in nature and/or relative quantity depending on the phosphine coordinated in the starting complex and on the presence of added phosphine.

The complex $Ni(CN)(C_6H_5)(PCy_3)_2$ (10^{-2} *M* in THF) absorbs overall more than 3.5 equivalents of CO, producing C_6H_5COCN in 90% yield (estimated from the absorptions at 2225m (ν(CN)), 1685vs (ν(CO)), 1600m (ν(CC)), 1580w

(ν(CC)) cm^{-1}) and $Ni(CO)_3PCy_3$, in accord with equation 3.

$$Ni(CN)(C_6H_5)(PCy_3)_2 + 4\,CO \rightleftharpoons Ni(CO)_3PCy_3 + C_6H_5COCN + PCy_3 \tag{3}$$

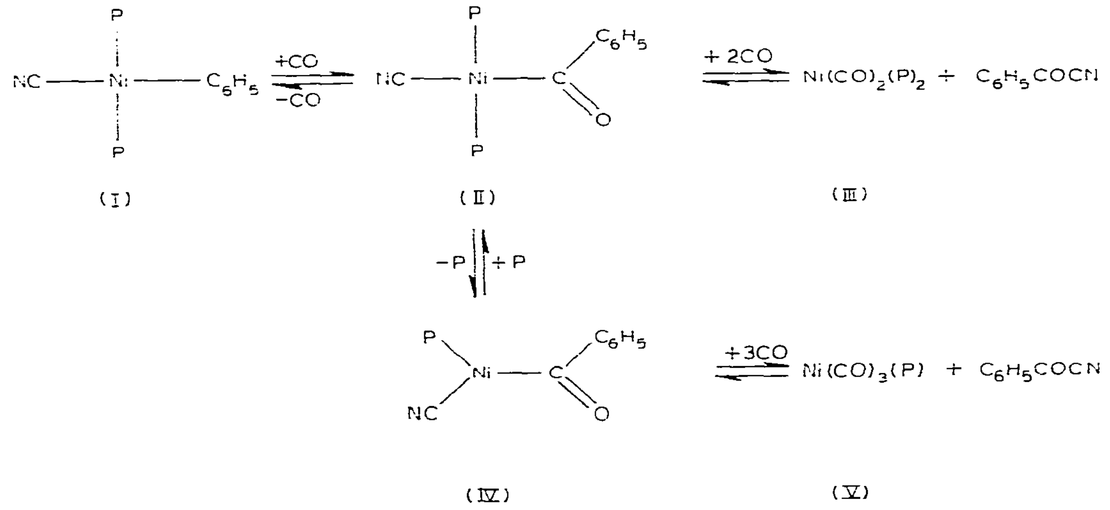
After this process, a further step, completed in a few days, takes place between C_6H_5COCN and PCy_3, leading to a product which absorbs strongly at 1740 cm^{-1} *. If 5×10^{-2} *M* phosphine is present at the start of the whole reaction, $Ni(CO)_2(PCy_3)_2$ is also observed among the products and the rate of consumption of the benzoyl cyanide is raised, so that the maximum yield of C_6H_5COCN reached in solution is lowered to 60%.

The complex $Ni(CN)(C_6H_5)(PEt_3)_2$ (10^{-2} *M* in n-hexane) reacts with about 3.2 equivalents of CO producing C_6H_5COCN (60%), $Ni(CO)_3PEt_3$, minor but significant amounts of $Ni(CO)_2(PEt_3)_2$, and a product absorbing at 1720 cm^{-1} *. The benzoyl cyanide is consumed in a subsequent slow stage producing a species absorbing at 1720 cm^{-1} with concomitant growth of $Ni(CO)_3PEt_3$ at the expense of $Ni(CO)_2(PEt_3)_2$. If the reaction is carried out in the presence of PEt_3 the yields of $Ni(CO)_2(PEt_3)_2$ and the species absorbing at 1720 cm^{-1} are proportionally increased.

The complex $Ni(CN)(C_6H_5)$(deb) (10^{-2} *M* in benzene) reacts with CO to give C_6H_5COCN (70%) and $Ni(CO)_2$(deb). In the presence of excess phosphine (up to 10^{-1} *M*) the pattern is not substantially altered.

The reactions observed and the other experimental evidence can be accomodated by Scheme 1:

SCHEME 1.



Low steric hindrance at the phosphorus atom of the phosphines (cone angles: PCy_3 = 170°; PEt_3 = 132°; deb ≃ 130° [15]) and the presence of excess phosphine will favour the route through the tetracoordinate acyl complex II to

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* A species displaying the same infrared band can be obtained in the reaction between the phosphine (10^{-2} *M*) and C_6H_5COCN (10^{-2} *M*) in THF. Work is in progress to elucidate the nature of this product.

the carbonyl III. Greater bulkiness of the ligand and the occurrence of the reaction of P with C_6H_5COCN will shift the equilibria through the acyl complex IV towards the carbonyl V.

Reactions of C_6H_5COCN with nickel(0) complexes

The reaction between C_6H_5COCN and excess of $Ni(P)_n$ ($n = 2, 4$) in decalin (10^{-1} *M*) occurred with rapid disappearance of the benzoyl cyanide to give red-brown solutions which showed medium intensity infrared absorptions at 2195 (ν(CN)), 1490, 1160, 1135 and 640 cm^{-1} (0.1 mm cell). The ^1H NMR spectra of these solutions showed the disappearance of the multiplets due to C_6H_5COCN aromatic protons (about 2.1 τ) and the appearance of new overlapping resonances, one broad and one sharp, at about 2.6 τ.

The absence of infrared absorptions around 2100 and 1600 cm^{-1} rule out a formulation of the new species as cyanobenzoyl complexes. The infrared, NMR spectra and chemical behaviour (vide infra) are analogous to those displayed by the molecular adduct $Ni(C_6H_5COCN)(t\text{-}BuNC)_2$, in which the benzoyl cyanide is known to be π-bonded to the metal through the carbonyl group double bond [13]. The shift in the ν(CN) frequency reported for this complex (—10 cm^{-1}) is in agreement with those observed in the complexes under discussion (—30 cm^{-1}) and contrasts with substantially higher shift (—110 cm^{-1}) observed when C_6H_5CN is coordinated to $Ni(PEt_3)_4$ through the nitrogen lone pair *. If an "end-on" coordination of this type is present in the benzoyl cyanide adducts, the CO stretching frequencies should undergo only minor changes from those of the free molecule but in fact no infrared absorption of significant intensity assignable to ν(CO) can be observed in the range of ±190 cm^{-1} around the value for the free reagent.

On the basis of these considerations we suggest that the initial reaction products are molecular adducts of benzoyl cyanide bound to the nickel atom through the CO double bond, a type of coordination which, while rare, is well established [13,14]. Attempts to isolate pure samples of these adducts failed because under the conditions used they behave as reactive species leading to products the nature of which depends on the nature of the phosphine bound to the nickel atom.

In the presence of excess $Ni(PCy_3)_2$ (1.5×10^{-2} *M* in decalin), the benzoyl cyanide (0.7×10^{-2} *M*) undergoes quantitative coordination. The adduct then slowly (60°C) gives $Ni(CN)(C_6H_5)(PCy_3)_2$ and $Ni(CO)_2(PCy_3)_2$ in a 2 : 1 molar ratio. Appreciable concentrations of $Ni(CN)(COC_6H_5)(PCy_3)_n$ ($n = 1, 2$) could not be detected with certainty owing to the overcrowding of absorptions near 1600 cm^{-1}. Moreover GC measurements reveal that CO does not accumulate during the reaction. If equimolar amounts of the reagents are mixed (1.5×10^{-2} *M* in decalin) about 85% of the benzoyl cyanide undergoes immediate coordination. Subsequently a slow release of the organic reagent takes place, so that after ca. 1 hour the 35% of the employed benzoyl cyanide is free. This release of C_6H_5COCN is accompanied by the formation of $Ni(CN)(C_6H_5)(PCy_3)_2$ and $Ni(CO)_2(PCy_3)_2$ in 2 : 1 molar ratio. The observed behaviour is accounted

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* We also detected in the green solutions of C_6H_5CN and $Ni(PEt_3)_4$ an absorption at 1765 cm^{-1}, which can be attributed to a benzonitrile "side-on" adduct, i.e. π-bonded through the CN triple bond [16].

for by the following equations:

$$Ni(PCy_3)_2 + C_6H_5COCN \rightleftharpoons Ni(C_6H_5COCN)(PCy_3)_2 \quad (4)$$

$$Ni(C_6H_5COCN)(PCy_3)_2 \rightarrow Ni(CN)(C_6H_5)(PCy_3)_2 + CO \quad (5)$$

$$Ni(C_6H_5COCN)(PCy_3)_2 + 2\ CO \rightarrow Ni(CO)_2(PCy_3)_2 + C_6H_5COCN \quad (6)$$

Over longer reaction times, and more rapidly in the presence of an excess of the organic reagent, two side reactions involving the benzoyl cyanide take place:

(i) with the phosphine, to form $Ni(CO)_3PCy_3$ and a product absorbing at 1740 cm^{-1};

(ii) with the $Ni(CN)(C_6H_5)(PCy_3)_2$ complex to produce C_6H_5CN and $Ni(CN)_2(PCy_3)_2$ (as shown by independent tests on $Ni(CN)(C_6H_5)(PCy_3)_2$).

The formation of $Ni(CO)_3PCy_3$, C_6H_5CN and $Ni(CN)_2(PCy_3)_2$ is evident after almost one day and complete after 3—4 days.

The reddish adducts formed by $Ni(PEt_3)_4$ and $Ni(deb)_2$ with C_6H_5COCN give not only the $Ni(CO)_2(P)_2$ species but apparently also the monocarbonyl species $Ni(CO)(P)_3$ together with the $Ni(CN)(C_6H_5)(P)_2$ complexes. In these instances it is impossible to define the stoichiometry as the monocarbonyl complexes cannot be estimated quantitatively because it is impossible to obtain them free from bis- and tris-carbonylated species. The presence of excess benzoyl cyanide lead to formation of C_6H_5CN, $Ni(CN)_2(P)_n$ ($n = 2, 3$) and $Ni(CO)_2(P)_2$.

Conclusions

The findings of the study can be summarized as follows:

(i) A cyanoacyl-nickel(II) complex has been detected as intermediate on the route from the reacting organo-nickel(II) complex to the organic carbonylation products. Previously isolated or postulated similar intermediates proved to be either very resistant to reductive elimination or so reactive that they could not be observed in solution and remain hypothetical [9,10,11].

(ii) A π-benzoyl cyanide(phosphino)metal(0) complex, of the type which generally has been only postulated as crucial intermediate in the template mechanism for the oxidative addition of RCOX to metal(0) complexes [10], has been detected spectroscopically.

Rather surprisingly, no accumulation of the species $Ni(CN)(COC_6H_5)(P)_n$ was observed in the conversion of the π-complexes $Ni(C_6H_5COCN)(P)_2$ to the $Ni(CN)(C_6H_5)(P)_2$ species. In this connection, however, it has been shown for the carbonylation of the $Ni(CN)(C_6H_5)(P)_2$ species that the existence of the $Ni(CN)(COC_6H_5)(P)_n$ complexes strongly depends (for thermodynamic reasons) on the free CO concentration. It is apparent that in the course of the oxidative addition of benzoyl cyanide (eqs. 4, 5) to nickel(0) the accumulation of cyanoacyl complexes is prevented by fast CO release followed by a fast and quantitative scavenging by $Ni(C_6H_5COCN)(P)_2$ (or other nickel(0) complexes) to give $Ni(CO)_2(P)_2$ (eq. 6) or $Ni(CO)(P)_3$ complexes depending on the bulk of the phosphine employed.

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