Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

HYDROGEN CYANIDE AS A LIGAND IN PHOSPHINO COMPLEXES OF NICKEL(II)

B. CORAIN

Centro di Stabilità e Reattività dei Composti di Coordinazione, C N.R., Istituto di Chimica Generale Università di Padova, Padua (Italy)

Hydrogen cyanide appears as a versatile reagent in the chemistry of the coordination compounds, behaving either as an oxidising or a coordinating reagent.

All the HCN complexes hitherto reported are thought to contain nitrogen-bonded HCN and no example of coordination of HCN through the C≡N triple bond has been reported.

When HCN behaves as an oxidising agent, the reaction leads to the breaking off of the HCN molecule, to the oxidation of the metal and to the formation of hydride complexes[1]

We reported recently[2] that $Ni^{I}(CN)(DPB)_{1.5}$ and $Ni^{I}(CN)(DPB)_{1.5}(HCN)$ were found to be intermediates in the oxidation of $Ni(DPB)_2$ to $Ni(CN)_2(DPB)$ by HCN dissolved in benzene (DPB = 1,4-bis(diphenylphosphino)butane). In order to investigate further the nature of the Ni–HCN bond, we have studied reactions between HCN and some Ni^{II} complexes. The reaction products contain HCN as a ligand and apparently no oxidation of the metal takes place.

The selected substrates were the square planar complex *trans*-$Ni(CN)_2(PPr_3)_2$ [PPr_3 tri(*n*-propyl)phosphine], the pentacoordinate species[3] $Ni_2(CN)_4(DPP)_3$ (DPP = 1,3-bis(diphenylphosphino)propane) and a solution of *trans*-$[Ni(CN)_2(DPB)]_2$ in benzene containing free diphosphine. In the DPP complex two diphosphines act as chelating ligands, and one bridges the two nickel atoms[3], while, under the experimental conditions employed, a benzene solution of $[Ni(CN)_2(DPB)]_2$ contains this complex in equilibrium with a pentacoordinate compound containing the moiety[3] $Ni(CN)_2(DPB)_2$.

The choice of these complexes was governed by their close similarity to $Ni(CN)(DPB)_{1.5}$, their known physical and chemical properties and their resistance to oxidation.

A. EXPERIMENTAL SECTION

The reactions were carried out at 20–22°C, in closed vessels under air. The complexes $[Ni(CN)_2(DPB)]_2$, $Ni(CN)_2(DPP)_{1.5}$ and $Ni(CN)_2(PPr_3)_2$ were prepared by published methods[3,4].

DCN was prepared from DCl and dry HCN in D_2O. HCN (Montedison) was purified by room temperature distillation under reduced pressure and degassing with argon. Benzene (C. Erba) was purified and dried by standard methods. A glass syringe equipped with a filtering attachment was used to obtain perfectly clear solutions for IR analysis even from reaction mixtures where a precipitate was present

The action of HCN on $Ni(CN)_2(DPB)$ was studied by adding 0 3 mmole complex, 0.15 mmole DPB (to increase the concentration of Ni^{II} in solution) and ca 4 mmole HCN to 5 ml benzene

The reaction of $Ni(CN)_2(DPP)_{1.5}$ with HCN was carried out by mixing 0 3 m mole complex and 3 mmole HCN in 5 ml benzene A significant increase of solubility was immediately observed About 50 ml ethyl ether was added three hours after the addition of HCN and the resulting red precipitate was filtered off and washed immediately with small portions of ether (total 30 ml). The mother liquor appeared practically colourless.

The reaction of $Ni(CN)_2(PPr_3)_2$ with HCN was followed mainly by IR spectroscopy Solutions containing 0.1 M complex and variable molar ratios of HCN/Ni^{II} from 1 to 10 were normally used. The general reaction pattern does not change appreciably in this molar ratio range

A solution 0 8 x 10^{-2} M in Ni^{II} and ca 15 x 10^{-2} M in HCN was found suitable for the simultaneous IR and visible analysis. The concentration of the HCN solutions used was determined by means of their IR spectra and a calibration graph.

IR spectra were recorded on a Perkin Elmer 257 spectrophotometer and visible absorption on an Optica CF4R NMR spectra were recorded on a Perkin Elmer R12 spectrometer (temp. 37°C).

B. RESULTS AND DISCUSSION

The complex *trans*-$[Ni(CN)_2(DPB)]_2$, in the presence of diphosphine, shows some tendency to react with HCN. Thus, when HCN is added to a benzene suspension of the complex, the IR spectrum of the supernatant solution displays a very weak shoulder and weak bands at 2115 and 2100 cm^{-1}, attributable respectively to the CN stretching frequencies of the square planar complex and to the pentacoordinate moiety $Ni(CN)_2(DPB)_2$. Near to the band at 2085 cm^{-1} attributable to free HCN, a weak but well defined shoulder appears at ca. 2075 cm^{-1} Filtration of the suspension enables the complex $[Ni(CN)_2(DPB)]_2$ to be recovered unchanged in high yield

A band at 2065 cm^{-1} has been previously assigned[2] to the $\nu_{(C\equiv N)}$ of HCN coordinated to the complex $Ni(CN)(DPB)_{1.5}$ and this suggests that either $[Ni(CN)_2(DPB)]_2$ or the moiety $Ni(CN)_2(DPB)_2$ forms an unstable product containing HCN and that the weak shoulder observed at ca 2075 cm^{-1} can be attributed to the coordinated HCN.

On the other hand, the pentacoordinate complex $Ni(CN)_2(DPP)_{1.5}$ shows a very pronounced tendency to react with HCN When HCN is added to a red suspension of this complex in benzene, the IR spectrum of the solution shows the following pattern of bands a medium intensity band at 2100 cm^{-1} ($\nu_{C\equiv N}$ of the reacting complex), a band at 2085 cm^{-1} (free HCN) and a weak, but well defined, band at 2065 cm^{-1} This pattern is stable for at least 60 h.

On addition of ethyl ether to the benzene suspension, a crystalline product is obtained whose colour, visible and IR spectra in methylene chloride are practically identical with those of the starting compound. In contrast, the IR spectrum in Nujol displays, near to a strong band at 2100 cm^{-1} (which is coincident with the $\nu_{C\equiv N}$ of the complex $Ni(CN)_2(DPP)_{1.5}$) a sharp medium-intensity band at 2065 cm^{-1}. When the solid sample is left for some hours in the atmosphere at room temperature, the band loses intensity and gradually disappears.

The results reported so far suggest that these complexes are able to interact with HCN in mild conditions to give unstable reaction products, in which an IR band at 2075–2065 cm^{-1} suggests that HCN is coordinated to the metal.

The crude reaction product obtained from the reaction of $Ni(CN)_2(DPP)_{1.5}$ with HCN was not a convenient sample for a physico-chemical analysis of the interaction of HCN and Ni^{II}, because both the substrate and the reaction product are sparingly soluble in the common organic solvents, and the absorption due to the ν_{C-H} of the coordinated HCN would be masked by the strong band due to the C–H stretching of the aromatic rings of the diphosphine.

We have found the complex *trans*-$Ni(CN)_2(PPr_3)_2$, I, to be a more convenient substrate. This compound is perfectly stable in solution and very soluble in the common solvents. Its IR spectra in Nujol and in benzene solution display a single sharp, strong band, due to the asymmetric CN stretching vibration, at 2105 and 2115 cm^{-1} respectively. The visible spectrum shows a single band at 340 nm

When a 0 1 *M* benzene solution of I is made 0.1 *M* in HCN, the IR spectrum of the solution changes instantaneously and remains unaltered for at least three days This behaviour is illustrated in Fig. 1. The band at 2115 cm^{-1} does not change appreciably either in position or intensity, the 2085 cm^{-1} band due to unreacted HCN appears decreased in intensity, and a medium to strong band appears at 2070 cm^{-1}, as well as a weak shoulder at ca 2120 cm^{-1}. The change in the intensity of the bands caused by HCN reveals that about 30% of the HCN has reacted with the Ni^{II} complex.

When the solution is pumped off under vacuum, I is recovered unchanged When this reaction is followed by IR and visible spectra, it is found that no appreciable variation in position and intensity of the band at 340 nm parallels the changes observed in the IR spectrum.

When the reaction is followed in C_6D_6, it is observed that, while the band at 3220 cm^{-1}, due to the C–H stretching of free HCN, decreases in intensity, a new

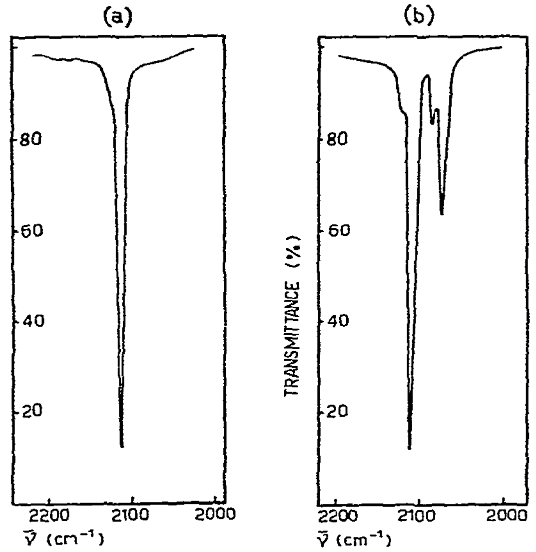

Fig 1 IR spectrum of a benzene solution containing (a) $Ni(CN)_2(PPr_3)_2$, 0.1 *M*; (b) $Ni(CN)_2(PPr_3)_{2\,tot}$, 0.1 *M* and $HCN_{tot.}$, 0.1 *M*. Cell thickness 0.45 mm.

band, apparently due to the reaction product, appears at ca. 3050 cm^{-1} (Fig. 2). When DCN is reacted with I in C_6D_6 (molar ratio ca. 1:1) a band at 2500 cm^{-1} appears (ν_{C-D} of free DCN at 2590 cm^{-1}) and, at lower wave numbers, a band appears at 1860 cm^{-1} ($\nu_{C\equiv N}$ of free DCN at 1910 cm^{-1}) (Fig. 3)

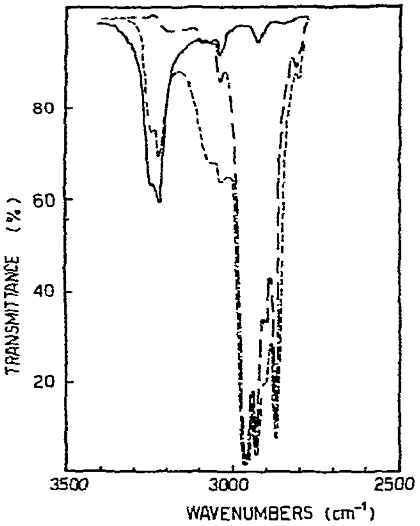

Fig. 2. ——, [HCN] = 0.1 *M*, – – – – –, $[Ni(CN)_2(PPr_3)_2]_{tot.}$ = 0.1 *M*, $[HCN]_{tot}$ = 0.1 *M*, – – – – –, $[Ni(CN)_2(PPr_3)_2]$ = 0.1 *M* Solvent C_6D_6, cell thickness = 0.45 mm

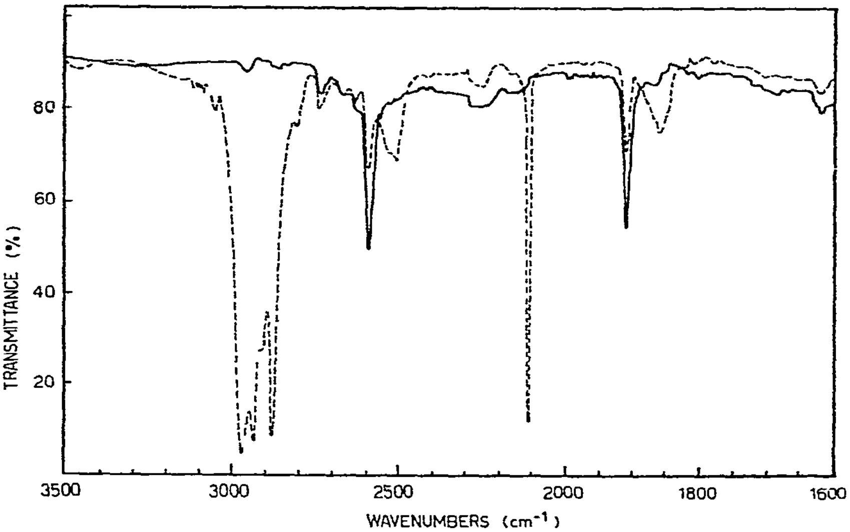

Fig. 3. IR spectrum of a C_6D_6 solution containing ———, DCN ca. 0.1 *M*, – – – – – –, [$Ni(CN)_2(PPr_3)_2$]$_{tot.}$ 0.1 *M*, $DCN_{tot.}$ 0.1 *M* Cell thickness 0.45 mm.

Combination of the data obtained in benzene and deuterated benzene, by employing both HCN and DCN, suggests that the bands at ca. 3050 and 2070 cm^{-1} (for HCN) and at 2500 and 1860 cm^{-1} (for DCN) can be attributed to the $\nu_{C-H}(\nu_{C-D})$ and $\nu_{C\equiv N}$ of HCN and DCN coordinated to the metal to give a molecular adduct, whose simplest formula can be written as $Ni(CN)_2(PPr_3)_2$ (HCN)

The appearance of the weak shoulder at 2120 cm^{-1} (Fig. 1) can be explained by the coordination of HCN to the square unit *trans*-$Ni(CN)_2(PPr_3)_2$, which forces a symmetric motion in the reacting complex (the symmetric stretch) to become IR active in the reaction product.

A fairly large number of examples of the coordination of nitriles and, to a lesser extent, of HCN in metal complexes is known. In a large majority of cases, the C≡N stretching frequency of the coordinated nitriles increases upon coordination through the nitrogen atom[5] and this fact is accompanied by a marked increase in the band intensity[6]

When HCN forms molecular adducts with typical Lewis acids or with metal complexes, the $\nu_{C\equiv N}$ increases[7,8], but in one case it remains constant[9] and in another case it decreases[10]. The C–H stretching frequency normally decreases[7–9] The variations of the $\nu_{C\equiv N}$ upon coordination of HCN through the nitrogen atom have been discussed in terms of combination of electronic and mechanical effects[7].

We believe that the IR data reported in this paper are sufficient to demonstrate that a molecular adduct is formed between HCN and I and we think that the decrease of the $\nu_{C\equiv N}$ observed in this investigation is consistent with coordination through the nitrogen atom.

However, the occurrence[7] of coupling between the C≡N and C–H stretching vibrations in HCN, together with the existence of electronic effects on the CN bond upon coordination[6,7], makes it difficult to determine their individual contributions to the net variation of the $\nu_{C\equiv N}$ of coordinated HCN. Moreover, the apparent increase of the intensity of the band assigned to $\nu_{C\equiv N}$ of coordinated HCN is in agreement with observations on N-bonded nitriles[6]. Finally, coordination through the triple bond C≡N does not seem likely to occur, because a more pronounced decrease of the C≡N stretching frequency would be expected[11].

Some NMR results confirm the formation of an adduct between I and HCN and could possibly shed more light on the type of HCN–metal interaction. The variation of the single hydrogen resonance band observed in solutions, in which the concentration of I is constant and that of HCN changes, are reported in Table 1. The δ value (vs. TMS) increases, in absolute value, with decrease of the ratio (total moles HCN)/(total moles Ni^{II}). These results may be accounted for on the basis of an equilibrium of the type

TABLE I

Dependence of the hydrogen resonance band on the ratio $[HCN]_{tot.}/[Ni^{II}]_{tot.}$, in the system[a] Ni^{II}/HCN

Ni^{II} (mmole)	HCN (mmole)	δ (vs. TMS)	$R = \frac{[HCN]_{tot.}}{[Ni^{II}]_{tot}}$
0.25	2.5	−3.4	10
0.25	0.75	−3.6	3
0.25	0.25	−4.2	1
	2.5	−2.5	
	0.25	−1.6	

[a] Temp. = 37° C, vol. = 0.5 ml, solvent C_6D_6.

$$Ni(CN)_2(PPr_3)_2 + HCN \rightleftharpoons Ni(CN)_2(PPr_3)_2(HCN)$$

and a rapid exchange between free and coordinated HCN. Moreover, the type of dependence of the single resonance band on the relative concentration of the reagents leaves little doubt of the fact that the resonance band of the hydrogen atom of coordinated HCN appears at δ values more negative than those observed for free HCN at the same total concentration. This observation is in qualitative agreement with data reported by Guttemberger[8], who has prepared and characterised the complexes $(CO)_5Me(N\equiv C\text{–}H)$(Me=Cr,Mo)

REFERENCES

1 F. Cariati, R Ugo and G Bonati *Inorg. Chem* , 5 (1966) 1128, H Singer and G Wilkinson, *J Chem Soc. A* (1968) 2516, L. Benzoni, C. Zanzottera, M. Tacchi Venturi and M. De Innocentis, *Chim Ind. (Milan)* 50 (1968) 1222.
2 B. Corain, P. Rigo and G. Favero, *Inorg. Chem.* 10 (1971) 2329
3 P. Rigo B. Corain and A. Turco, *Inorg Chem.*, 7 (1968) 1623.
4 P. Rigo, G. Guastalla and A Turco, *Inorg Chem* , 8 (1969) 375
5 B D. Catsikis and M.L. Good, *Inorg. Chem.* 8 (1969) 1095, R.E. Clarke and P.G Ford, *Inorg. Chem.*, 9 (1970) 227.
6 K.F. Purcell and R.S Drago, *J Amer. Chem Soc.*, 88 (1966) 919.
7 K Kawai and J Kanesaka, *Spectrochim. Acta Part A*, 25 (1969) 1265
8 J.F. Guttemberger, *Chem. Ber* , 101 (1968) 403.
9 M.F.A. Dove and J.G. Hallet, *Chem. Commun.* (1967) 571, *J. Chem. Soc. A* (1969) 2781
10 P.C. Ford, *Chem. Commun.*, (1971) 7
11 W J. Bland, R D W Kemmit, I W Nowell and D R Russel, *Chem Commun* , (1968) 1065