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THE COORDINATION CHEMISTRY OF HYDROGEN CYANIDE, CYANOGEN AND CYANOGEN HALIDES

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CONTENTS

A. INTRODUCTION

Of the reactive "small molecules" which have become increasingly popular over the last fifteen years as reagents towards numerous coordination

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* This review was initiated at the permanent address of the author (Padova) but largely written during a visit to T.U. Munich (Garching) as an A. von Humboldt fellow.

compounds [1], comparatively little attention has been given to the title compounds, particularly as oxidative addition reagents. This is rather surprising in view of the fact that there are reports dating from 1850 [2,3] on the first coordination chemistry experiments involving HCN and ClCN. Moreover, the intrinsically high "chemical quality" of the organic C≡N group, i.e. its ready transformation into such important functional groups as $C(O)NH_2$, C(O)OH, and CNH_2, makes it worthy of far more intense study. The activation, via metal coordination, of the readily available "small molecules" HCN, XCN and C_2N_2 with a view to, for example, nitrilic functionalization of organic substrates, requires consideration.

In spite of the relatively limited investigation into the coordination chemistry of HCN, a significant potentially economically viable application was discovered [4] a few years ago in the Ni^0 catalyzed synthesis of adiponitrile from HCN and butadiene. A comprehensive account covering the literature up to 1975 on the metal-catalyzed hydrocyanation of olefins is available [5a] and an up to date review is shortly to appear [5b]. As regards the chemistry of C_2N_2, a brief review of the aspects relevant to its metal coordination was published in 1979 [6] and an extensive account of its organic chemistry appeared twenty years previously [7].

The essential aim of this work is to review all reactions of the title compounds in which they interact with a Lewis acid or with an oxidizable metal center. Attention will be focused mainly on the following aspects: (i) the synthesis of acid–base adducts and a description of their physico-chemical properties; (ii) the synthesis of metal cyanide complexes resulting from oxidative addition processes, emphasizing the mechanistic implications; (iii) the physical and chemical modification of the X–C≡N (X = H, CN, halide) group upon coordination.

A further section of this work will be devoted to the recently discovered behavior of C_2N_2 with organic compounds bearing active hydrogens at carbon atoms which has led to a novel "one-pot" synthesis of highly functionalized pyrimidines.

Finally, a short section will be devoted to miscellaneous related topics.

B. SYNTHESIS, STRUCTURE, STABILITY AND PHYSICO-CHEMICAL PROPERTIES OF HCN, C_2N_2, XCN (X = F, Cl, Br, I)

All the compounds are colorless, volatile, and poisonous and should be stored and handled with extreme care. Details of their toxicity can be found in ref. 8. The compounds ClCN, BrCN and ICN are known to be thermodynamically unstable to dissociation into $\frac{1}{2}X_2$ and $\frac{1}{2}C_2N_2$ [9] but they can be prepared and stored due to their kinetic stability.

Table 1 lists the melting and boiling points of the title compounds and

TABLE 1

Melting and boiling points for HCN, C_2N_2, XCN (from refs. 11 and 12)

Compound	M.p. (°C)	B.p. (°C)
NCCN	−27.9	−21.17
HCN	−14	26
FCN	−82	−46.2
ClCN	−6.80	12.55
BrCN	51.3	61.3
ICN	148	

Table 2 summarizes their dissociation energies. It is evident that C_2N_2, ClCN and FCN are gases at ambient temperature but, in practice, FCN cannot be manipulated at room temperature due to its facile polymerization [10]. It can, however, be handled at −80°C.

C_2N_2 and HCN are characterized by an exceedingly high bond energy (C–C and C–H, respectively), which, as shall be seen, influences their reactivity as oxidative addition reagents, in the sense that they only react with the more electronically dense metal centers, thereby giving particularly strong metal (II)–cyanide bonds.

All the compounds can be prepared by a variety of procedures. Only the preparation of FCN appears to be limited to few routes. It is worthwhile to note that HCN is a chemical of great industrial importance (190000 tons were produced in the U.S.A. in 1965 [13]) and is formed in large quantities as a by-product in the ammono-oxidation process of propylene used in the large-scale synthesis of acrylonitrile [14].

A convenient method of preparing HCN on a laboratory scale is detailed

TABLE 2

Bond dissociation energies for C_2N_2, HCN, XCN (from refs. 11 and 12)

Compound	D (kcal mol^{-1})
NC–CN	132 ±6
H–CN	125.5
F–CN	111.0±0.8
ClCN	97 ±1
BrCN	83 ±1
ICN	73 ±1

in ref. 15. This compound is a mobile liquid, possessing a very strong "metallic" smell and can be stored in neutral glass vessels for long periods of time, if very pure and dry [16]. Traces of water tend to decrease its stability to polymerization. Less pure samples are stabilized by traces of H_2SO_4 (e.g. 0.001%) which prevent the possibility of polymerization (a base-catalyzed reaction). HCN is soluble in water and in most organic solvents.

C_2N_2 can be prepared on a laboratory scale by the method of ref. 17. Storage in steel cylinders is possible for long periods of time if the cyanogen is very pure and dry. It is soluble in most organic solvents as well as in water, where slow hydrolysis takes place. Stabilization of water solutions of C_2N_2 is achieved by addition of dilute acids [18]. C_2N_2 is highly combustible and burns in air generating temperatures as high as 4500–5000°C [19].

FCN can be prepared in high yields from the solids $C(CN)_4$ and CsF at room temperature [20], but it must be immediately trapped at -180°C. The physical and chemical properties of FCN are little known owing to its pronounced instability to polymerization.

ClCN, conveniently prepared from $Zn(CN)_4^{2-}$ in water by action of Cl_2 [21], is reported to be stable for at least six weeks if dry and pure, although traces of HCl catalyze polymerization. It exhibits complex hydrolytic behavior in water, although it can be used at a concentration of 7% (w/w) [22]. It is soluble and stable in dioxane and diethyl ether.

BrCN is a white solid which can be prepared from $Hg(CN)_2$ and Br_2 under anhydrous conditions, in the absence of solvent [23]. The solid, indefinitely stable at room temperature in the dark under dry conditions, is very slowly hydrolyzed by water [24] and is soluble in diethyl ether and dichloromethane.

ICN, a white solid prepared in the same way as BrCN, is stable in water and soluble in diethyl ether, dichloromethane and chloroform.

C_2N_2, HCN and XCN are all linear molecules which have been extensively studied by spectroscopic methods.

Considering the widespread use of IR spectroscopy in the physico-chemical characterization of the Lewis acid–base adducts of the title compounds, a summary of essential IR data is given (Table 3). References to electron diffraction and microwave studies of XCN may be found in ref. 25, while thermodynamic data are reported in refs. 7, 9.

The effect of solvent on the ν_{CN}*, $\nu_{\mathrm{C-I}}$ and δ_{ICN} bands of ICN, as well as on the molar absorbtivities, is reported in ref. 32. Similar data are available for HCN [29,33]. Data on the molar absorbtivities of the asymmetric ν_{CN} band of C_2N_2 in various solvents are reported in ref. 34.

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* In this review the symbol ν (e.g. ν_{CN}) is used to indicate a diatomic stretching vibration and $\bar{\nu}$ (e.g. $\bar{\nu}_{\mathrm{CN}}$) the relevant wavenumber.

TABLE 3

IR and Raman data for C_2N_2, HCN, XCN (and DCN)

Compound	Vibrational mode	Phase	$\bar{\nu}$ (cm^{-1})	Ref.
NCCN	ν_{CN} asymm.	Liquid	2158	26
	ν_{CN} symm.	Liquid	2336	26
	ν_{CN} asymm.	Gas	2147	27
HCN	ν_{CN}	Liquid	2096	28
	ν_{CH}	Liquid	3215	28
	δ_{HCN}	Liquid	794	28
	ν_{CN}	Gas	2096.7	29
	ν_{CH}	Gas	3311.4	29
	δ_{HCN}	Gas	711.9	29
	ν_{CN}	In HF	2138.9	30
DCN	ν_{CN}	Liquid	1909	28
	ν_{CD}	Liquid	2581	28
	δ_{DCN}	Liquid	615	28
	ν_{CN}	Gas	1925.3	29
	ν_{CD}	Gas	2630.3	29
	δ_{DCN}	Gas	569.1	29
FCN	ν_{CN}	Solid	2318.91	31
	ν_{CF}	Solid	1076.49	31
	δ_{FCN}	Solid	450.91	31
ClCN	ν_{CN}	Gas	2219	25
	ν_{CCl}	Gas	714	25
	δ_{ClCN}	Gas	380	25
ClCN	ν_{CN}	Solid	2212	25 [a]
	ν_{CCl}	Solid	734(?)	25
	δ_{ClCN}	Solid	398	25
BrCN	ν_{CN}	Gas	2200	25
	ν_{CBr}	Gas	575	25
	δ_{BrCN}	Gas	342.5	25
BrCN	ν_{CN}	Solid	2194	25
	ν_{CBr}	Solid	572.5	25
	δ_{BrCN}	Solid	363.5	25
ICN	ν_{CN}	In CCl_4	2168	32
	ν_{CI}		487	32
	δ_{ICN}	In $CHCl_3$	319	32
ICN	ν_{CN}	Solid	2176	25
	ν_{CI}	Solid	451.5	25
	δ_{ICN}	Solid	328.5	25

[a] Also gives Raman data.

TABLE 4

Geometric features of HCN, C_2N_2, ClCN, BrCN

Molecule	Symmetry	Bond distances (Å) [37]
HCN	$C_{\infty v}$	C–H = 1.064 ± 0.004; C≡N = 1.150 ± 0.001
NC–CN	$D_{\infty h}$	C–O = 1.37 ± 0.02; C≡N = 1.16 ± 0.02
Cl–CN	$C_{\infty v}$	C–Cl = 1.57 ± 0.018; C≡N = 1.16 ± 0.020
BrCN	$C_{\infty v}$	Br–C = 1.79 ± 0.02; C≡N = 1.13 ± 0.04

Concerning the electronic structure of C_2N_2, HCN and XCN, the ground state of C_2N_2 deserves some comment. While, HCN and XCN can be described satisfactorily by the canonical formula

$$\underset{\text{I}}{\text{X–C}\equiv\text{N:}}\quad (\text{X} = \text{H, F, Cl, Br, I})$$

some disagreement arises for the C_2N_2 molecule, thus either structure II alone [35] or an electronic ground state with partial C–C double bond character [36] have been proposed on theoretical bases. There is no doubt that a contribution from III would account for the particularly high dissociation energy of the C–C bond in C_2N_2, as well as the short C–C bond distance, 1.37 ± 0.02 Å [the sum of two C(*sp*) covalent bonds is 1.40 Å].

$$\underset{\text{II}}{\text{:N}\equiv\text{C–C}\equiv\text{N:}} \quad \leftrightarrow \quad \underset{\text{III}}{\text{:N=C=C=N:}}$$

Finally, Table 4 collects the essential geometric features of the title compounds.

C. PREPARATION OF LEWIS ACID–BASE ADDUCTS, THEIR CHEMISTRY AND SPECTROSCOPIC PROPERTIES

(i) Hydrogen cyanide

The known reaction products of HCN with a variety of Lewis acids are listed in Tables 5 and 6. The lists differ in that the compounds of Table 5 can be safely defined as coordination compounds (from IR and NMR data), while those of Table 6 are, in principle, simply reaction products between HCN and potential Lewis acids. The reaction conditions are various but

TABLE 5

Coordination compounds of HCN [a]

Compound	Color	Remarks	Ref.
$[TiCl_4(HCN)_2]$	Yellow	*trans* species	38, 39
$[TiBr_4(HCN)_2]$	Red	*trans* species	39, 40
$[VCl_4(HCN)_2]$	Black	unstable at 40°C	41
$[Cr(CO)_5(HCN)]$	Yellow		42
$[W(CO)_5(HCN)]$	Yellow		42
$[Ru(NH_3)_5(HCN)^+]$	Greenish white	stable in H_2O at $pH<1$	43
$[Rh(Cl)(H)(CN)(PPh_3)_2(HCN)]$			44
$[Ag(HCN)^+]$		characterized in HF	30
$[Ag(HCN)_2^+]$		characterized in HF	30
$[SbCl_5(HCN)]$	White		38, 45
$[Cu(HCN)^{2+}]$		characterized in HF	30
$[BCl_3(HCN)]$			38

[a] Compounds formulated as $[TiI_4(HCN)_x]$ and $[TiF_4(HCN)_x]$ have been reported [39] and proposed to contain N-coordinated HCN on the basis of IR data.

generally mild. Thus, acid–base interaction has been positively tested by treating the Lewis acid with liquid or gaseous pure HCN or with HCN in organic solutions and even in HF as solvent. It is quite possible that these

TABLE 6

Reaction products of HCN with potential Lewis acids

Compound	Color	Remarks	Ref.
$FeCl_3(HCN)_2$	Red		46
$FeCl_3(HCN)_3$	Red		47
$(CuCl)_2(H_2O)_2(HCN)$	White	thermally unstable at room temp.; readily oxidized by O_2	48
$ZnCl_2(HCN)_3$			49
$SbCl_5(HCN)_3$		sublimes at 70–100°C	46
$BeCl_2(HCN)_4$	White		50
$BF_3(HCN)$		gaseous and partially dissociated at room temp.	51
$BBr_3(HCN)$		gaseous and partially dissociated at room temp.	52

compounds are real adducts. The compounds $[BX_3(HCN)]$ (X = F, Br), for example, readily lose HCN at ambient temperature and are obviously related to the characterized $[BCl_3(HCN)]$ (Table 5). $[(CuCl)_2(H_2O)_2(HCN)]$ is also likely to be a real adduct owing to its thermal instability and ease of oxidation.

Some doubts arise as to the nature of the Fe^{III} compounds which could be cyano complexes [47], as well as to the existence of the compound $[SbCl_5(HCN)_3]$, which has an unusual stoichiometry.

There are also reports of some less well characterized coordination compounds containing HCN. A white compound, proposed to be $[SnCl_4(HCN)_2]$ and readily formed from $SnCl_4$ and liquid or gaseous HCN [53], is stable at room temperature but is immediately decomposed by moisture. The existence of the white boron compound $[B_2Cl_4(HCN)_2]$ has also been claimed [54] and an adduct formulated as $[Ni(CN)_2(PPh_3)_2 \cdot HCN]$, observed by IR and NMR in benzene [55], could neither be isolated nor sufficiently characterized in solution. For metals in normal oxidation states and non-metals, the compounds containing coordinated HCN are typically very sensitive to water which liberates HCN and hydrolytically attacks the acid residue. They are reasonably thermally stable at room temperature with the notable exceptions of $[BF_3(HCN)]$ and $[BBr_3(HCN)]$, in which cases, interestingly, the "acidic" core is a non-metal center.

The coordination mode of HCN appears to be a "nitrile end-on" type [57]. In contrast to the abundance of IR studies on acid–HCN adducts (Table 7), other physical data are scarce (Tables 8 and 9).

With two exceptions, the coordination of HCN to a metal (or non-metal) center is accompanied by an increase in $\bar{\nu}_{CN}$. For $[Ag(HCN)]^+$ (in solution) there is no accompanying spectral shift and for $[Ru(NH_3)_5\ HCN]^{2+}$ a quite substantial decrease in $\bar{\nu}_{CN}$ is observed.

Although X-ray based structural analyses on acid–base HCN adducts are not available, it is accepted that HCN coordinates through the nitrogen lone pair. The source of the predominantly observed hipsochromic shift of the ν_{CN} band has been discussed in detail in ref. 38 (see also ref. 56 for analogous acetonitrile complexes), and is recognized as being due to authentic electronic effects (i.e. strengthening of the C≡N bond upon coordination). It should be noted, however, that the predominance of electronic over kinematic effects in influencing the observed ν_{CN} band is not a general rule and, therefore, any correlation and interpretation of these data should be made with care.

The observed decrease in $\bar{\nu}_{CN}$ for $[Ru(NH_3)_5HCN]^{2+}$ has been attributed [43] to an important π-back-bonding effect from Ru^{II} to the π^* orbitals of the C≡N group, causing sufficient weakening of the C≡N force constant as to overwhelm any opposing effects of kinematic coupling or σ-electronic

TABLE 7

IR data for coordination compounds of HCN

Complex	$\nu_{C\equiv N}$ (cm^{-1})	ν_{C-H} (cm^{-1})	δ_{HCN} (cm^{-1})	Phase	Ref.
$[TiCl_4(HCN)_2]$	2135			Solid	39
$[TiCl_4(HCN)_2]$	2134 s	3173 m	764 s [a]	Solid	38
$[TiBr_4(HCN)_2]$	2127			Solid	39
$[VCl_4(HCN)_2]$	2140 s	3205 s [b]	769 s [b]	Solid	41
$[Cr(CO)_5(HCN)]$	2119 w	3267 w		C_6H_6 soln.	42
$[W(CO)_5(HCN)]$	2216 w	3261 w		C_6H_6 soln.	42
$[Rh(H)(Cl)(CN)(PPh_3)_2(HCN)]$	~2145 [c]			Solid	44
$[Ru(NH_3)_5(HCN)^{2+}]$	1960 vs			Solid	43
$[Ag(HCN)^+]$	2138			HF soln.	30
$[Ag(HCN)^+]$	2148	3225	770	Solid	30
$[Ag(HCN)_2^+]$	2147			HF soln.	
$[SbCl_5(HCN)]$	2152 vs	3167 vs	757		45
$[SbCl_5(HCN)]$	2135 s	3179 m	757	Solid	38
$[BCl_3(HCN)]$	2189 s	3156 s	750 s	Solid	38
free HCN	2096	3215	794	Liquid	28
free HCN	2138			HF soln.	30

[a] A second band at 741 s is reported.

[b] For the ν_{C-H} and δ_{HCN} modes two and three bands are observed, respectively, which are attributed to local symmetry effects.

[c] The assignment of this band to coordinated HCN is not clear in the reference cited.

TABLE 8

^{1}H NMR data for molecular adducts of HCN

Compound	δ (ppm)	Solvent	Reference proton	Ref.
$Cr(CO)_5(HCN)$	5.76	Hexadeuteroacetone	external TMS	42
$W(CO)_5(HCN)$	6.26	Hexadeuteroacetone	external TMS	42
Free HCN	4.46	Hexadeuteroacetone	external TMS	42
$Ag(HCN)^+$	1.66	HF	internal NMe_4^+	30
$Cu(HCN)^+$	2.02	HF	internal NMe_4^+	30
$Ag(HCN)_2^+$	1.71	HF	internal NMe_4^+	30
Free HCN	1.29	HF	internal NMe_4^+	30

factors. This view is indirectly supported by the marked change in $\bar{\nu}_{CN}$ which accompanies the coordination of CH_3–CN (2254 cm^{-1}) to Ru^{III} ($\bar{\nu}_{CN} = 2286$ cm^{-1}) and to Ru^{II} ($\bar{\nu}_{CN} = 2239$ cm^{-1}) [56], as well as by relevant data on cyanogen complexes (see later).

The invariance of $\bar{\nu}_{CN}$ for $[Ag(HCN)]^+$ in solution is curious and probably results from a combination of molecular and solvent effects as suggested by the value of 2148 cm^{-1} for the same compound in the solid state.

As regards the general problem of the geometry of HCN coordination to the metals, the possibility of "side-on" coordination [57] has to be considered, as indeed it should be for C_2N_2 and XCN as ligands. The pronounced bathochromic shift in $\bar{\nu}_{CN}$ upon nitrile "side-on" coordination [57] appears to be a good analytical tool for revealing this coordination mode for all the molecules.

The effect of HCN coordination on the $\bar{\nu}_{C-H}$ band is less well documented,

TABLE 9

Electronic spectra of molecular adducts of HCN

Compound	λ (nm)	Solvent	Ref.
$Cr(CO)_5(HCN)$	378	CH_2Cl_2	42
$W(CO)_5(HCN)$	367	CH_2Cl_2	42
$VCl_4(HCN)_2$	625	HCN	
	465		41
	265		
$[Ru(NH_3)_5(HCN)]^{2+}$	241	H_2O	43

the data being a little less clear-cut. This is shown by the cases of $[M(CO)_5(HCN)]$ (M = Cr, W) and $[Ag(HCN)]^+$ which display an increase in $\bar{\nu}_{C-H}$ upon coordination, in contrast to the decrease observed for the majority of other examples. Again, any interpretation of this $\bar{\nu}_{C-H}$ shift in terms of a weakening of the C–H bond has to be prudent, since it is known that the C≡N and C–H stretching modes in HCN are effectively coupled (cf. in Table 3 the significant effect on $\bar{\nu}_{CN}$ of deuterated free HCN). This means that any change in the observed position of $\bar{\nu}_{CN}$ may, in principle, affect the actual position of $\bar{\nu}_{C-H}$ (and vice versa). However, theoretical calculations support the statement [38] that the decreases in $\bar{\nu}_{C-H}$ observed in $[BCl_3 \cdot HCN]$, $[SbCl_5 \cdot HCN]$ and $[TiCl_4 \cdot (HCN)_2]$ are due to a real decrease in the force constant as a result of increased polarity upon complexation. In this connection it is notable that the few NMR data available support the proposal of an increase in the C–H bond polarity caused by coordination, as shown clearly by the downfield shift observed for the five complexes listed in Table 8. There is also chemical evidence to support a real weakening of the C–H bond as a consequence of coordination; this effect could be described as an activation process of HCN by metal coordination. The reaction of $[M(CO)_5(HCN)]$ (M = Cr, W) with a weak base (piperidine) in benzene causes the deprotonation of HCN [42] according to eqn. (1)

$$M(CO)_5(NCH) + pip \rightarrow M(CO)_5(CN)^- + pipH^+ \tag{1}$$

which gives a high product yield with no evidence for isocyanide complexes. Moreover, the complex $[Ru(NH_3)_5(HCN)]^{2+}$ is such a strong acid that it can only survive at $pH \leqslant 1$ [43]; at higher pH values the complex undergoes deprotonation and irreversible decomposition. An important utilization of the increase in HCN acidity upon coordination has been found in the essential role played by metal halides as cocatalysts in the catalytic addition of HCN to butadiene and other olefins [5] promoted by a variety of nickel(0) complexes. The catalytic hydrocyanation of 1-hexene has been thoroughly investigated in CH_3CN with $[Ni\{P(O\text{-}p\text{-tol})\}_4]$ as the catalyst and $ZnCl_2$ as cocatalyst. The proposed mechanism [58] can be summarized as follows

$$[NiL_4] + HCN + ZnCl_2 \rightarrow [L_3NiH]^+[ZnCl_2CN]^- + L \tag{2}$$

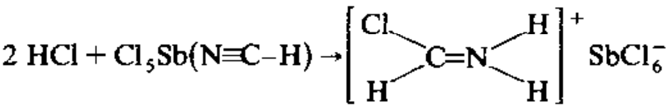
$$[L_3NiH]^+ + ene \rightarrow [NiL_3R]^+ \tag{3}$$

$$[L_3Ni(R)]^+ + [ZnCl_2CN]^- \rightarrow NiL_3 + R\text{–}CN + ZnCl_2 \tag{4}$$

The reaction step depicted in eqn. (2) is very likely preceded by another crucial stage, i.e.

$$ZnCl_2 + HCN \rightleftharpoons [ZnCl_2(HCN)] \tag{5}$$

whereby the molecular adduct can act as a stronger acid on nickel(0) thus rendering the protonation of NiL_4, eqn. (2), thermodynamically more effective. The species $ZnCl_2(NC)^-$ thus formed is expected to isomerize immediately [42] to $[ZnCl_2(CN)]^-$. This serves as an effective "reservoir" of CN^- ligands, ready for scavenging the nickel(II)-coordinated R ligand, which can be extracted formally as a cationic +1 species, thus critically inducing the reductive elimination process, eqn. (4), which stops the catalytic cycle. This section is concluded by mention of another interesting consequence of HCN coordination. It is known that HCl can react with HCN to give a compound analyzing as $(HCN)_2(HCl)_3$ [45]. When HCl is treated with $[SbCl_5 \cdot HCN]$, however, a clean reaction takes place according to eqn. (6)



$$2\,\mathrm{HCl} + \mathrm{Cl_5Sb(N{\equiv}C{-}H)} \rightarrow \left[\overset{\mathrm{Cl}}{\underset{\mathrm{H}}{>}}\mathrm{C{=}N}\overset{\mathrm{H}}{\underset{\mathrm{H}}{<}} \right]^+ \mathrm{SbCl_6^-} \qquad (6)$$

where the extra stability of the chloroimidinium hexachloroantimonate is attributed to the impossibility of H^+ abstraction by the anion (i.e. the expected decomposition route) owing to geometric factors.

(ii) Cyanogen

The coordination compounds of C_2N_2 known to date are listed in Table 10. Only those characterized by IR, VIS-UV or NMR techniques are given, together with some appropriate remarks. In addition several presumed coordination compounds, not spectroscopically investigated, should be mentioned. Thus gaseous BBr_3, BCl_3 and B_2Cl_4 react with cyanogen to give non-volatile compounds characterized by a tensometric procedure [66] (for data on the vapour pressure of C_2N_2, see ref. 67). BCl_3 reacts with C_2N_2 in a 1 : 1 ratio at room temperature to give a white solid, $[BCl_3 \cdot (C_2N_2)_2]$. When BCl_3 is in excess, the yellow-orange benzene-soluble compound $[(BCl_3)_2(C_2N_2)]$ is obtained. BBr_3 reacts much more rapidly with C_2N_2 (1 : 1) and at −22°C gives the dark brown solid $[(BBr_3) \cdot (C_2N_2)]$, sparingly soluble in benzene, but soluble in 1,2-dimethoxyethane; when in excess, BBr_3 gives $(BBr_3)_2(C_2N_2)$ at 130°C in 5 days. BF_3 does not react with C_2N_2 even at 100°C. Gaseous B_2Cl_4 reacts in a similar manner to BBr_3 with C_2N_2 to give the non-volatile compound $[B_2Cl(C_2N_2)_{1.5}]$.

The thermally unstable complex $[BeCl_2(C_2N_2)_4]$ has been claimed [50] to be formed from $BeCl_2$ and C_2N_2 in ether at −10°C. It is worthwhile mentioning that this species is much less stable than the analogous HCN adduct thus offering a rare chance of comparing the bonding abilities of

TABLE 10

Coordination compounds of C_2N_2

Compound	Color	Remarks	Ref.
$Cr_2(CO)_{10}(C_2N_2)$	Reddish violet	photochem. cond.	59
$Mo_2(CO)_{10}(C_2N_2)$	Dark brown	photochem. cond.	59
$W_2(CO)_{10}(C_2N_2)$	Violet	photochem. cond.	59
$Ru_2(NH_3)_{10}(C_2N_2)^{4+}$			60
$Ru_2(NH_3)_{10}(C_2N_2)^{5+}$		[a]	60
$Ru_2(NH_3)_{10}(C_2N_2)^{6+}$		[a]	60
$Ru(NH_3)_5(C_2N_2)^{2+}$		[a]	60
$RhCl(PPh_3)_2(C_2N_2)$	Yellow-brown	loses C_2N_2 at amb. cond.	61
$RhCl(PPh_3)_2I_2(C_2N_2)$	Brown	loses C_2N_2 in vacuo	62
$[RhCl(PPh_3)_2(CN)_2]_2(C_2N_2)$	Yellow	loses C_2N_2 in vacuo	62
$[RhBr(PPh_3)_2(CN)_2]_2(C_2N_2)$	White		62
$Ni(PEt_3)_3(C_2N_2)$		observed only in solution	63
$Ni(PMe_3)_3(C_2N_2)$		observed only in solution	63
$Ni\{P(O\text{-}p\text{-tol})_3\}_3(C_2N_2)$		observed only in solution	63
$Ni\{P(O\text{-}o\text{-tol})_3\}_3(C_2N_2)$		observed only in solution	63
$Ni\{P(OPh)_3\}_3(C_2N_2)$		observed only in solution	66
$Cu(CN)_2(C_2N_2)^-$	Brown		64
$Cu(CN)(H_2O)(C_2N_2)$	Brown		65

[a] These compounds are mentioned in ref. 60 with a remarkable lack of detail. In view of their importance at least with respect to their IR features (see later), in understanding the nature of metal–cyanogen bonding they deserve reconsideration and full characterization.

C_2N_2 and HCN towards the same metal center. However, the lack of information on the corresponding structures makes this fact scarcely useful.

The complexes listed in Table 10 are generally stable to thermal dissociation at ambient temperature, the only exception being $[RhCl(PPh_3)_2(C_2N_2)]$ which in the solid state slowly releases C_2N_2. These compounds are prepared in various solvents at ambient temperature without any particular difficulty. They are normally obtained by treating C_2N_2 dissolved in an inert solvent with a convenient metal complex which, upon ligand displacement, accommodates cyanogen in the coordination sphere. An interesting exception is the preparation of $[RhCl(PPh_3)_2I_2(C_2N_2)]$ which is achieved by oxidizing $[RhCl(PPh_3)_3]$ with I_2 in the presence of C_2N_2 in benzene. The complexes have been characterized mainly by IR spectroscopy (Table 11).

The compounds of Table 11 are listed in such a way as to embrace three

TABLE 11

IR data for coordination compounds of C_2N_2 [a]

Compound	Ref.	$\nu_{C\equiv N}$ (cm^{-1}) [b]	Phase
$Rh^{I}Cl(PPh_3)_2(C_2N_2)$	61	2240 2090	Solid
$Rh^{III}Cl(PPh_3)_2I_2(C_2N_2)$	62	2320 2170	Solid
$Ru^{II}(NH_3)_5(C_2N_2)^{2+}$ [c]	60	2220 2090	
$Ni^{0}(PEt_3)_3(C_2N_2)$	63	2232 2066	C_6H_5Me
$Ni^{0}(PMet)_3(C_2N_2)$	63	2232 2064	C_6H_5Me
$Ni^{0}\{P(O\text{-}p\text{-tol})_3\}_3(C_2N_2)$	63	2215 2088	C_6H_5Me
$Ni^{0}\{P(O\text{-}o\text{-tol})_3\}_3(C_2N_2)$	63	2215 2089	C_6H_5Me
$Ni^{0}\{P(OPh)_3\}_3(C_2N_2)$	66	2220 2085	C_6H_6
$Cu^{I}(CN)_2(C_2N_2)^-$	64	2225 (2325)	Solid
$Cr_2^{0}(CO)_{10}(C_2N_2)$	59	2118 (2263)	CCl_4
$Mo_2^{0}(CO)_{10}(C_2N_2)$	59	(2267)	CCl_4
$W_2^{0}(CO)_{10}(C_2N_2)$	59	2107 (2267)	CCl_4
$Ru_2^{III}(NH_3)_{10}(C_2N_2)^{6+}$	60	2330	Solid
$Ru_2^{II,III}(NH_3)_{10}(C_2N_2)^{5+}$	60	2210	
$Ru_2^{II}(NH_3)_{10}(C_2N_2)^{4+}$	60	1960	Solid
$[Rh^{III}Cl(PPh_3)_2(CN)_2]_2(C_2N_2)$	62	2115	Solid
$[Rh^{III}Br(PPh_3)_2(CN)_2]_2(C_2N_2)$	62	2115	Solid
$[Cu^{I}(CN)(H_2O)(C_2N_2)]_n$	65	2160	Solid

[a] Free liquid C_2N_2 exhibits bands at 2158 cm^{-1} (asymmetric) and 2336 cm^{-1} (symmetric) due to C≡N stretching modes.

[b] Data refer only to coordinated C_2N_2.

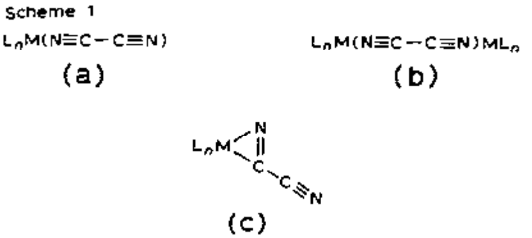
[c] For this compound, see the footnote to Table 10.

types of species: (i) those in which two well defined $\nu_{C\equiv N}$ bands are observed; (ii) those in which a single band can be detected; (iii) those $\{[M_2(CO)_{10}](C_2N_2)\}$ (M = Cr, Mo, W) complexes which exhibit a pattern of bands, some of which are given in parentheses.

On the basis of elementary symmetry considerations, the nitrile-like "end-on" [57] monohapto coordination of C_2N_2 (Scheme 1) to a metal center is expected to give two IR-active C≡N stretching bands, while an "end-on" bihapto bonding geometry is expected to lead to a single band. Hence the first eight complexes of Table 11 are thought to contain one monohapto C_2N_2 molecule while the last six complexes very likely contain one bridging C_2N_2 ligand per two metal atoms.

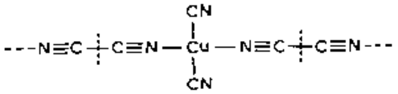
The case of the $[M_2(CO)_{10}(C_2N_2)]$ (M = Cr, Mo, W) complexes is intriguing. These have been proposed [59] to exhibit a dinuclear structure of type (b) as a consequence of the observed molecular weight and of their elementary composition, in which case only one C≡N band is expected. Unfor-

Scheme 1



tunately, the data for these compounds refer to solution spectra which exhibit bands defined by the author as "very weak" and to complicate the matter further, the Mo^0 species exhibits only one band. Considering the bands resulting from $[Cu^I(CN)(H_2O)(C_2N_2)]_n$ and the binuclear Ru^{II} complexes, it is likely that the bands at 2118 and 2107 cm^{-1} are attributable to the asymmetric C≡N stretch of the bridging C_2N_2 moiety and that those at 2263 and 2267 cm^{-1} are not related to this group. This implies that for the Mo^0 complex, the real C≡N band due to coordinated C_2N_2 is not detected owing to the unfavorable sampling system employed.

The spectrum of $[Cu(CN)_2(C_2N_2)]^-$ deserves separate comment. This species is proposed [64] to have a structure of the type



$$---N{\equiv}C\,\vdots\,C{\equiv}N-\underset{CN}{\overset{CN}{Cu}}-N{\equiv}C\,\vdots\,C{\equiv}N---$$

in which case the band at 2225 cm^{-1} may be attributed to the asymmetric C≡N stretch of the bridging C_2N_2 group; no other cyanogen band is expected and so the band at 2325 cm^{-1} must have some other origin.

In all cases of monohapto behavior, except that of Rh^{III}, both bands undergo a bathochromic shift with respect to free C_2N_2. For Rh^{III} there is essentially no effect of metal coordination on the stretching bands. It is well known that any observed $\bar{\nu}_{CN}$ shift caused by C_2N_2 coordination is influenced by both mechanical and electronic factors [68]. Furthermore, "end-on" coordination is expected to be intrinsically accompanied by opposite tendencies in the C≡N force constants (the σ component of the N → metal bond enhances the force constant, while the π component of the metal → N bond causes it to decrease, see above). The significant general decrease in both observed bands, particularly those referring to electronically "dense" centers like Ni^0 and, in a sense, Ru^{II}, strongly suggest the existence of a decisive π bonding component in the metal–cyanogen bond. For Rh^{III} it may well be that a balance of electronic and mechanical contributions is responsible for the small net effect on the $\bar{\nu}_{C{\equiv}N}$ frequencies. Some support for this reasoning is afforded by the cases of the bridged Ru^{II}, Ru^{II-III}, Ru^{III} cyanogen complexes [60]. It is tempting to state that when the metal possesses a relatively low oxidation state, important π-back-donation from

Ru to the π^* orbitals of the N≡C moiety dominates over the expected opposite σ effect on the observed wavenumber [68] and that an almost perfect balance of these factors is attained for intermediate formal valencies. It should be remembered, in this context, that in the case of CH_3CN coordination to Ru^{II}, oxidation of the metal gives rise to an inversion of the observed $\nu_{C\equiv N}$ shift of coordinated with respect to free ligand [56] [Section C(i)].

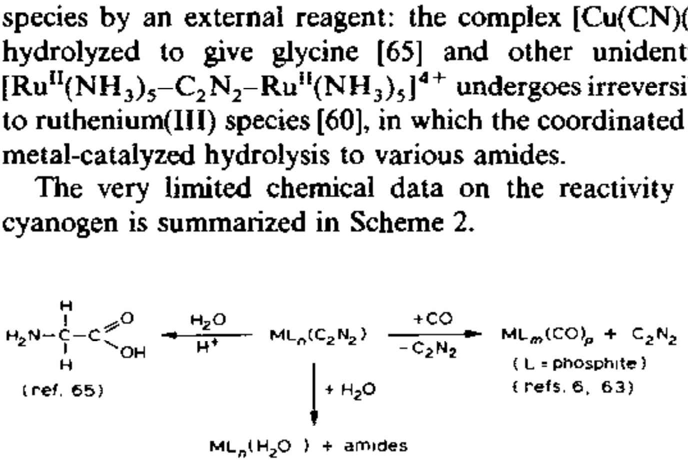
Although no "side-on" C_2N_2 coordination has been observed, in principle there is no reason why such a coordination mode should not exist.

The IR properties of the cyanogen complexes show that C_2N_2 behaves as a typical dinitrile [57], being capable of "end-on" monohapto and dihapto behavior in the coordination sphere of a Lewis acid. This flexibility is clearly exhibited in two rhodium(III) complexes (Table 11) which as well as having the metal in the same oxidation state also have similar ligand sets.

It is pertinent to anticipate here that an interesting feature of C_2N_2 is its ability not only to undergo metal coordination but also to undergo reduction by suitable low-valent metal centers (see Section D). The same feature recently became apparent for classical nitrile complexes [69].

It is worth underlining the ability of C_2N_2 to bind metal centers having quite different formal oxidation states (e.g. from 0 to +3), as well as its bonding properties which are similar to those of typical soft ligands such as phosphines, phosphites and carbon monoxide [6,63]. These two features could prove useful in pursuing metal coordination for the promotion of homogeneous organic syntheses involving cyanogen and simple organic substrates under mild conditions. There are, to date, two examples of the chemical transformation of coordinated cyanogen into another organic species by an external reagent: the complex $[Cu(CN)(C_2N_2)H_2O]^-$ can be hydrolyzed to give glycine [65] and other unidentified products while $[Ru^{II}(NH_3)_5–C_2N_2–Ru^{II}(NH_3)_5]^{4+}$ undergoes irreversible oxidation in water to ruthenium(III) species [60], in which the coordinated nitrile undergoes fast metal-catalyzed hydrolysis to various amides.

The very limited chemical data on the reactivity of metal-coordinated cyanogen is summarized in Scheme 2.



Scheme 2. Reactions of coordinated C_2N_2

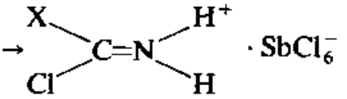
(iii) Cyanogen halides

All the reported complexes (or compounds probably containing molecular XCN) are listed in Tables 12 and 13. The systems have been divided, as in the case of HCN, into those sufficiently well characterized by chemical and physico-chemical data and those possessing a reasonably ascertained composition, although not characterized as actual Lewis acid–base adducts.

The syntheses of all these compounds involve the direct contact of XCN with the desired Lewis acid (mass conditions) at temperatures ranging from a few degrees to 120°C or the interaction of the reagents in an inert solvent. The compounds listed in Tables 12 and 13 are, as a rule, extremely water-sensitive species, which must be handled with great care.

The coordination compounds of Table 12 exhibit normal coordination numbers and geometries: $[TiCl_4(XCN)_2]$ are octahedral *trans* complexes [70b,71]. The majority of the compounds of Table 13, however, exhibit unusual coordination numbers and, therefore, structures which are not easy to predict. Of particular interest are the polynuclear complexes of iron and titanium, for which modern physico-chemical data would be highly desirable.

A very simple but elegant example of the reactivity of coordinated XCN (X = Cl, Br, I) is given by the reaction of XCN with HCl



$$XCN + 2\,HCl + SbCl_5 \rightarrow \left[(X)(Cl)C{=}NH(H^+)\right]\cdot SbCl_6^- \qquad (7)$$

This reaction gives a stable haloimidinium salt only in the presence of $SbCl_5$ [74]. This is due to the fact that the size of the $SbCl_6^-$ counter-anion prevents the interaction of a chloride ion with any of the hydrogen atoms in the haloimidinium cation, which is a recognized decomposition pathway. It appears that the attack of HCl at the C≡N group occurs according to the following equations

$$XCN + SbCl_5 \rightarrow SbCl_5(XCN) \qquad (8)$$

$$SbCl_5(XCN) + HCl \rightarrow SbCl_5(XCN \cdot HCl) \qquad (9)$$

$$SbCl_5(XCN \cdot HCl) + HCl \rightarrow [C(X)Cl{=}NH_2^+](SbCl_6^-) \qquad (10)$$

An analogous case has been observed [45] for X = H [see Section C(i)].

A significant role played by the coordination of XCN to Lewis acids in organic synthesis is exemplified by the ability of XCN adducts to cyanate aromatic rings in the presence of $AlCl_3$. It has long been known [78] that ClCN and BrCN, in the presence of $AlCl_3$, act as cyanating agents of aromatic nuclei (ICN produces iododerivatives). The direct use of

TABLE 12

Coordination compounds of XCN

Compound	Color	Remarks	Ref.
$TiCl_4(ClCN)_2$	Yellow		70a, b
$TiCl_4(BrCN)_2$	Yellow		70b
$TiCl_4(ICN)_2$	Yellow	from Ti/ICN (molar ratio 1:2)	71
$[TiCl_4(ICN)]_2$	Yellow	from metal/ICN (molar ratio 1:1)	71
$[ZrCl_4(ICN)]_2$	White	from metal/ICN (molar ratio 1:1)	71
$NbCl_5(ClCN)$			72
$TaCl_5(ClCN)$			72
$MoO_2Cl_2(ClCN)_2$	White	unstable above 20°C	73
$VO_2Cl_2(ClCN)_2$	Pale yellow	stable up to 240°C	73
$SbCl_5(ClCN)$	White		70a, b
$SbCl_5(BrCN)$	White		70b
$SbCl_5(ICN)$	White		74
$AlCl_3(ClCN)$	White		70a, b
$AlBr_3(BrCN)$			70b

TABLE 13

Reaction products of XCN with potential Lewis acids

Compound	Color	Remarks	Ref.
$(TiCl_4)_3(BrCN)_2$	Orange-red	Mass reaction [a]	75
$TiBr_4(BrCN)_2$	Red	Reaction in CS_2	76
$FeCl_3(ClCN)$	Yellow-brown	Mass reaction, unstable at room temp. and 1 atm	70a
$(FeBr_2)_2(BrCN)$		Mass reaction, at 60°C from $FeBr_2$ and BrCN	77
$Fe_3Br_8(BrCN)_3(CN)_2$	Dark brown	Mass reaction at 100°C from FeBr and excess BrCN	77
$Fe_3Br_8(BrCN)_4$	Dark brown	Mass reaction at 40°C from Fe_3Br_8 and BrCN	77
$(FeBr_3)_3(BrCN)_4$	Dark brown	From 1 $Fe_3Br_8(BrCN)$ $+0.5$ Br_2 at 90°C	77
$AuCl_3(ClCN)$	Yellow	Mass reaction	70a
$SnBr_4(BrCN)_2$	Yellow	Mass reaction at 120°C	75
$SbCl_3(BrCN)_2$	Yellow	Mass reaction	75
$(SbBr_3)_2(BrCN)_3$	Yellow	Mass reaction at 180°C	75
$AsCl_3(BrCN)_2$	Yellow	Mass reaction at 120°C	75
$AsBr_3(BrCN)_2$	Yellow	Mass reaction at 120°C	75

[a] No solvent.

[$AlCl_3$(ClCN)] and [$AlBr_3 \cdot$ (BrCN)] as reagents with benzene in nitromethane [78] gives benzonitrile in up to 50% yields even though the use of freshly prepared BrCN achieves similar yields [78b]. It is remarkable that [$TiCl_4 \cdot (ClCN)_2$] does not give benzonitrile on reaction with benzene under a variety of conditions. Since $TiCl_4$ is known to be a poor Friedel–Crafts promoter, this observation has been discussed in connection with the importance of CN^+ as a crucial cyanating agent [70a].

Like their HCN and C_2N_2 analogs, the XCN coordination compounds were characterized mainly by IR spectroscopy. The relevant data are given in Table 14. It can be seen from the figures that the coordination of XCN to any Lewis acid leads to an increase in the energy of the observed ν_{CN} and $\nu_{C\text{-}X}$ bands and a full discussion of this effect can be found in ref. 70b in specific connection with the proposed "end-on" coordination mode. The observed $\Delta\bar{\nu}$ values for the ClCN complexes of Table 14 are given in Table 15.

The significant increase in the wavenumber of the ν_{CN} band has been interpreted [70b] for [$AlCl_3$(ClCN)] and [$AlBr_3$(BrCN)] in terms of a small increase in the C≡N force constant with a predominant kinematic contribution arising from mechanical coupling of the C≡N and C–X stretching modes. Considering that the C–X stretch increases markedly and that this

TABLE 14

IR data for coordination compounds of XCN [a]

Complex	$\bar{\nu}_{CN}$ (cm^{-1}) [b]	$\bar{\nu}_{CX}$ (cm^{-1})	Ref.
$TiCl_4(ClCN)_2$	2255 s	788 m	70b
$NbCl_5(ClCN)$	2256 s	797 w	72
$TaCl_5(ClCN)$	2264 s	804 w	72
$MoO_2Cl_2(ClCN)_2$	2263 vs		73
$VO_2Cl_2(ClCN)_2$	2249 s		73
$AlCl_3(ClCN)$	2276 vs	822 s	70b
$SbCl_5(ClCN)$	2250 vs	784 s	70b
$TiCl_4(BrCN)_2$	2227 s	646 m	70b
$AlBr_3(BrCN)$	2236 vs	697 vs	70b
$SbCl_5(BrCN)$	2218 m	636 s	70b
$TiCl_4(ICN)_2$	2190 vs	530 w	71
$[TiCl_4(ICN)_2]_2$	2195 vs	538 vs	71
$[ZrCl_4(ICN)_2]_2$	2190 vs	550 m	71
$SbCl_5(ICN)$	2206 vs	822 s	74

[a] All data refer to solid phase spectra.

[b] Free ligands: ClCN, $\bar{\nu}_{CN} = 2212$ and $\bar{\nu}_{C\text{-}Cl} = 734$; BrCN, $\bar{\nu}_{CN} = 2194$ and $\bar{\nu}_{C\text{-}Br} = 572$; ICN, $\bar{\nu}_{CN} = 2176$ and $\bar{\nu}_{CI} = 451$ cm^{-1}.

TABLE 15

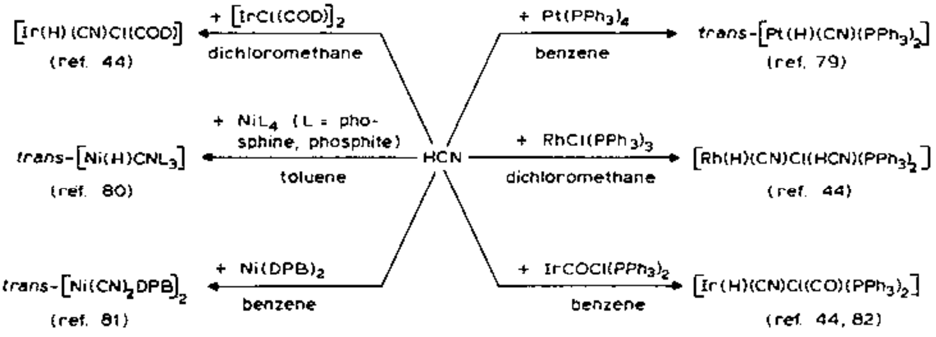
Observed wavenumber shifts for ClCN upon coordination

Complex	$\Delta\bar{\nu}_{CN}$ (cm^{-1})	$\Delta\bar{\nu}_{CCl}$ (cm^{-1})
$AlCl_3(ClCN)$	64	88
$TaCl_5(ClCN)$	52	70
$MoO_2Cl_2(ClCN)_2$	51	
$NbCl_5(ClCN)$	44	63
$TiCl_4(ClCN)_2$	43	54
$SbCl_5(ClCN)$	38	50
$VO_2Cl_2(ClCN)_2$	37	

shift is likely to be due to electronic factors [70b] (i.e. real strengthening of the C–X bond), the explanation for the hipsochromic shifts being largely due to kinematic effects is qualitatively acceptable in every case.

D. THE ACTION OF HCN, C_2N_2 AND XCN AS OXIDATIVE ADDITION REAGENTS

The majority of the chemical data available on this subject are collected in Schemes 3–5. Scheme 3, however, does not include those reactions observed for HCN which give rise to poorly identified products; these will be dealt with separately in the text.



Scheme 3. Known oxidative addition reactions of HCN

HCN reacts with typical electronically "dense" metal centers, i.e. Ni^0, Pt^0, Rh^I, Ir^I, to give generally stable species. A notable exception is that of the addition of HCN to [Ni(DPB)$_2$]* [80,81] in benzene. Depending on the

---

* DPB denotes $P(C_6H_5)_2-(CH_2)_4-P(C_6H_5)_2$; DPB-P denotes one DPB molecule acting as a monohapto ligand (see below).

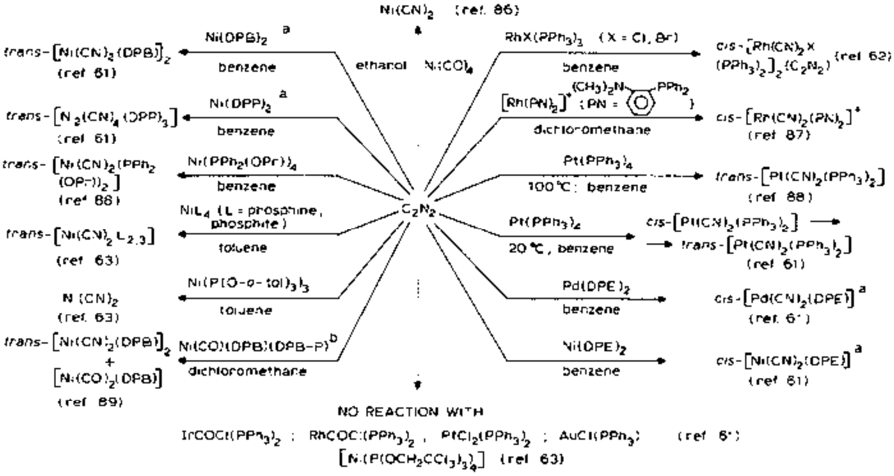
excess of HCN over Ni^0, either the pentacoordinate *trans* hydridocyanide species, $[Ni(H)(CN)(DPB)(DPB\text{-}P)]$ [80], or the tetracoordinate dimeric dicyanide *trans* species, $[Ni(CN)_2(DPB)]_2$ [81], is obtained. It is likely that a hydrido species is an important intermediate in dicyano complex synthesis and it is pertinent to remember that $[Ni(DPB)_2]$ is an excellent catalyst for the mono addition of hydrogen cyanide to butadiene under mild conditions [83], particularly as regards high selectivity in the synthesis of linear rather than branched mono-unsaturated nitriles. When in the presence of Lewis acids (metal halides) as cocatalysts, certain NiL_4 complexes act as active catalysts for the double addition of HCN to butadiene to give adiponitriles [5] or the hydrocyanation of terminal olefins [5] in mild conditions. The Pt^{II} and Ni^{II} complexes display a *trans* hydrido cyanide geometry, while Rh^{III} is proposed to have a *cis* arrangement as in the Ir^{III} triphenylphosphine product [44], although a *trans* geometry for the H^- and CN^- ligands has also been proposed for the iridium system [82]. No quantitative kinetic investigations have been undertaken, so far, on any of the reported reactions. Qualitative kinetic data [80] show that oxidative addition to NiL_4 complexes is fast for L a phosphine or sterically hindered phosphite and slow when L is $P(OEt)_3$ or $P(OCH_2CH_2Cl)_3$. On the basis of the known properties of tetrakis-phosphino and -phosphito Ni^0 complexes [84], these observations are in accord with a reaction mechanism largely dissociative in character.

A series of rhodium complexes, $[RhCl(CO)(PPh_3)_2]$, $[RhCl(COD)_2]$, $[RhCl(norbornadiene)_2]$, $[Rh(CO)_2(acac)]$, $[Rh(CO)_2Cl_2]$, $[RhCl(CO)_2(p\text{-}toluidine)]$ and $[Rh(H)(CO)(PPh_3)_3]$, [44] react with HCN at ambient temperature to give unidentified but possibly interesting compounds. The first three compounds produce high yields of very unreactive species while the two products of the olefinic precursor compounds do not undergo hydrogenation of the coordinated unsaturated ligand.

The reaction of cobalt(II) acetate with HCN in water gives $[Co_3^{II}\{Co^{III}(CN)_6\}_2]$ [85]. Unfortunately, no details of the mechanism of this reaction or even the fate of the hydrogen atom of HCN are given.

The contents of Scheme 4 reveal a considerably more extensive chemistry for C_2N_2. The first report of C_2N_2 acting as an oxidative addition reagent appeared in 1904 [86a]. It is somewhat surprising that C_2N_2 reacts smoothly and quantitatively with $Ni(CO)_4$ in ethanol while the same complex is totally unreactive towards HCN in tetrahydrofuran [86b].

This drastic difference in reactivity towards the same metal center contradicts the general trends exhibited in Scheme 4 where it can be seen that the metal complexes typically found to be reactive towards C_2N_2 generally also react with HCN. However, exactly the opposite trend is observed for $[IrCl(CO)(PPh_3)_2]$ and $[RhCl(CO)(PPh_3)_2]$ which react readily and quantitatively with HCN in benzene or dichloromethane at ambient temperature to



a) DPB = $PPh_2-(CH_2)_4-PPh_2$, DPP = $PPh_2-(CH_2)_3-PPh_2$; DPE = $PPh_2-(CH_2)_2-PPh_2$

b) DPB = indicates a monohapto DPB

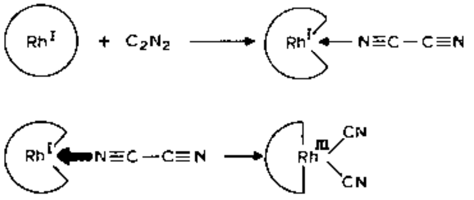
Scheme 4 Known oxidative addition reactions of C_2N_2

give the corresponding M^{III} complexes, whereas they are unreactive towards C_2N_2 under the same conditions [61].

In contrast to the behavior of HCN towards $[Pt(PPh_3)_4]$, C_2N_2 adds oxidatively to give primarily a *cis* Pt^{II} complex which slowly isomerizes to the more stable *trans* form [61]. This tendency for *cis* addition is also found for $[Pd(DPE)]_2$ and $[Ni(DPE)_2]$ but geometric requirements of these ligands prevent a *trans* configuration for the square-planar monomeric moiety $[M(CN)_2L_2]$.

All other oxidative addition products obtained from ML_n complexes exhibit *trans* geometries, which, of course, provides no information on the configuration of the primary oxidation product.

The oxidation of three Rh^I complexes again reveals the *cis* character of the addition of C_2N_2 to the reducing metal centers $[RhX(PPh_3)_3]$ (X = Cl, Br) [62] and $[Rh(PN)_2]^+$ [87] [PN = *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline] and, in addition, comparison of the two types of metal substrates emphasizes the importance of the electronic properties of the ligand sets in influencing the reversibility of the overall reaction



The set of ligands $\{Cl(PPh_3)_2\}$ facilitates the removal of C_2N_2 from the coordination sphere of rhodium(I) even at atmospheric pressure, while the $\{(PN)_2\}$ set induces irreversible electron transfer from Rh^I to C_2N_2 (giving Rh^{III}) thus preventing any appreciable formation of an $[Rh^I \cdot (C_2N_2)]$ adduct. This behavior is a consequence of the fact that the latter set of ligands is significantly more electron donating than the former. These findings suggest that it should be possible to arrange the electronic and steric features of the ligand set around Rh^I such that it is possible to control the activation of C_2N_2. It should be noted that in spite of the generally favorable electronic and steric situation in $[RhCl(PPh_3)_3]$, action of C_2N_2 on solutions obtained from this complex and *trans*-dicyanoethylene (known to be π coordinated to Rh^I under the conditions used [62]) did not lead to any dicyanation of the olefinic substrate. It would therefore seem that the reversible nature of the C_2N_2 coordination–addition reaction is more important in the coordination sphere of Rh^{III} than in that of Rh^I. Thus it should be possible, in principle, to initiate a set of elementary processes analogous to those known to occur in the Rh^I/Rh^{III} system for the catalytic hydrogenation of terminal olefins [90].

For the sake of clarity some important data on certain thermodynamic aspects of the oxidative addition of C_2N_2 to Ni^0 complexes are not shown in Scheme 4. The complexes $[Ni\{P(OCH_2CH_2Cl)_3\}_4]$ and $[Ni\{P(OCH_2)_3CPr\}_4]$ react to an almost negligible extent with C_2N_2 even after lengthy exposure and, as noted, the related $[Ni\{P(OCH_2CH_2CCl_3)_3\}_4]$ species is totally unreactive. Moreover, on heating the ligands $P(OEt)_3$ or $P(OCH_2)_3CPr$ with $Ni(CN)_2$ appreciable amounts of the corresponding NiL_4 complexes [63] were obtained. An obvious way of interpreting all these data is to describe the reaction of NiL_4 complexes with C_2N_2 according to the equilibrium

$$NiL_4 + C_2N_2 \overset{K}{\rightleftarrows} Ni(CN)_2L_3 + L \qquad (11)$$

Apparently, K is relatively large for good σ-donor ligands such as alkyl and aryl phosphines as well as for alkyl phosphites not bearing electronegative groups in the chain [e.g. $P(OEt)_3$ or $P(OMe)_3$]. In the case of the chlorine containing phosphites, the ability of the ligand to stabilize the zero oxidation state of the reacting metal center is so pronounced that the oxidative addition ability of C_2N_2 is no longer sufficient to provide the reaction with a convenient driving force.

There are two literature sources of information concerning the kinetics and mechanism of the oxidative addition of C_2N_2 to metal centers [63,89]. The first details the chemistry of NiL_4 complexes (L = phosphine, phosphite) (see Scheme 4), while the second reports the only kinetic work to date on the coordination chemistry of C_2N_2.

Analogous to the reactivity observed towards HCN, the NiL_4 complexes containing phosphines (known to be dissociated in solution and to rapidly exchange their coordinated ligands) [84] react much faster than the related NiL_4 phosphite complexes. This trend again stresses the predominantly dissociative character of this oxidative addition process. The same conclusion was reached in a quantitative way by a kinetic investigation of the unusual reaction [eqn. (12)]

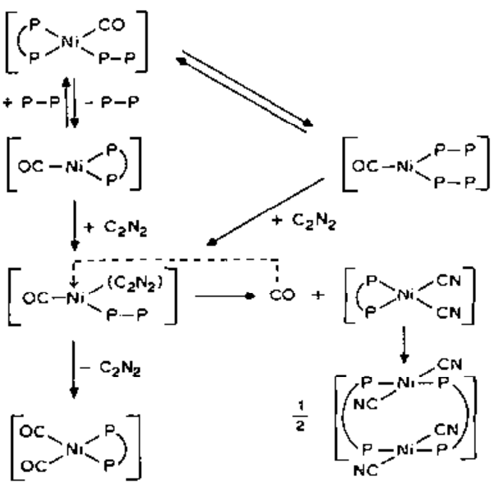
$$2\,Ni^0(CO)(DPB)(DPB\text{-}P) + C_2N_2 \rightarrow Ni^0(CO)_2(DPB) + \tfrac{1}{2}\,\textit{trans}\text{-}[Ni^{II}(CN)_2(DPB)]_2 \qquad (12)$$

after which follows the much slower conventional oxidative addition reaction [eqn. (13)]

$$Ni^0(CO)_2(DPB) + C_2N_2 \rightarrow \tfrac{1}{2}\,\textit{trans}\text{-}[Ni(CN)_2(DPB)]_2 + 2\,CO \qquad (13)$$

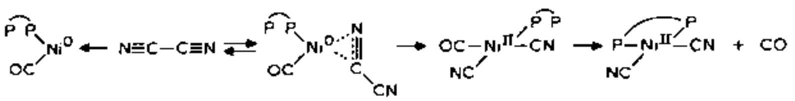
The first stage appears to be a combination of oxidative addition and internal ligand substitution for which the mechanism depicted in Scheme 5 was proposed

Scheme 5. Reaction mechanism for the cyanation of [Ni(CO)(DPB)$_2$] [89]



The kinetic importance of coordinatively unsaturated species is evident. The proposed mechanism indicates that the oxidation step is not rate-determining and therefore the kinetic data are little use in understanding the intimate mechanism of C_2N_2 reduction. The mechanism outlined in Scheme 6 appears to offer a reasonable proposal

Scheme 6. Proposed intimate mechanism for cyanogen activation by nickel (0)

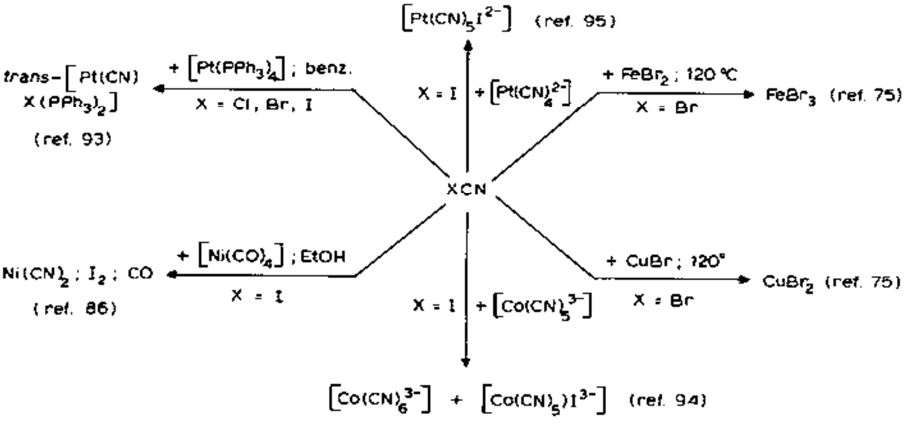


The "end-on" cyanogeno active intermediate complex accords with available data (see Table 10) and a successive isomerization to a kinetically significant amount of a "side-on" species is also conceivable (Scheme 1(c)]. Through this π complex, electron transfer to C_2N_2 and subsequent formation of a *cis*-dicyanonickel(II) species appears feasible. This mechanism closely resembles that proposed in ref. 91 for the oxidative addition of acyl halides to $[Ni(PEt)_3)_4]$ and the π "side-on" intermediate resembles a dihapto-$(\eta)^2$-iminoacylmolybdenum complex reported in the literature [92].

The feasibility of the preliminary "end-on" coordination of C_2N_2 to the metal in Scheme 6 is strongly supported by the data of Table 10 and ref. 63. When $[Ni(PEt_3)_4]$ and $[Ni(PMe_3)_4]$ are treated with C_2N_2 in toluene, the preliminary formation of the corresponding "end-on" $[NiL_3(C_2N_2)]$ species can be detected unambiguously prior to the rapid appearance of the corresponding *trans*-$[Ni(CN)_2L_3]$ final product; an analogous intermediate is formed when $[Ni\{P(O\text{-}o\text{-}tol)_3\}_3]$ reacts with C_2N_2, the final product in this case being $Ni(CN)_2$.

Scheme 7 summarizes the few data available on the oxidative addition of

Scheme 7. Oxidative addition reactions of XCN



cyanogen halides to metal centers. The earliest reference in the literature [86] reports on the reaction of $Ni(CO)_4$ with ICN in ethanol or chloroform. The reaction pattern resembles that exhibited by C_2N_2 and thus contrasts with that shown by HCN. It seems likely that the primary oxidation product is an unstable species $[Ni(CO)_2(I)(CN)]$ which converts to $Ni(CN)_2$ according to eqns. (14)–(16)

$$\mathrm{Ni^0(CO)_4 + ICN \rightarrow Ni^{II}(CO)_2(CN)I + 2\ CO} \quad (14)$$

$$\mathrm{Ni^{II}(CO)_2(CN)I \rightarrow Ni^{II}(CN)I + 2\ CO} \quad (15)$$

$$\mathrm{Ni^{II}(CN)I + ICN \rightarrow Ni^{II}(CN)_2 + I_2} \quad (16)$$

Two unusual oxidative addition reactions are shown by BrCN reacting in a molten mass with $FeBr_2$ and CuBr [75]. The reactions are said to give high yields of pure products. More recently [93], $[Pt(PPh_3)_4]$ was reported to give *trans*-$[Pt(CN)X(PPh_3)_2]$ upon reaction with XCN ($X = Cl$, Br, I) analogously to the reaction with HCN. Finally, ICN was found to react with $[Co(CN)_5]^{3-}$ [94] and $[Pt(CN)_4]^{2-}$ [95] in water at ambient temperature. The reactions have been studied kinetically and the following mechanisms proposed (the reaction of Pt^{II} is catalyzed by free CN^-)

$$\mathrm{Co(CN)_5^{3-} + ICN \rightarrow Co(CN)_5I^{3-} + CN\cdot} \quad (17)$$

$$\mathrm{CN\cdot + Co(CN)_5^{3-} \rightarrow Co(CN)_6^{3-}} \quad (18)$$

and

$$\mathrm{Pt(CN)_4^{2-} + CN^- \rightleftharpoons Pt(CN)_5^{3-}}\ \text{fast} \quad (19)$$

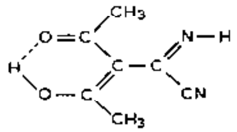
$$\mathrm{Pt(CN)_5^{3-} + ICN \rightarrow Pt(CN)_5(ICN)^{3-}}\ \text{fast} \quad (20)$$

$$\mathrm{Pt(CN)_5(ICN)^{3-} \rightarrow Pt(CN)_5I^{2-} + CN^-}\ \text{slow} \quad (21)$$

E. CYANOGEN AS AN ELECTROPHILE TOWARDS METAL-COORDINATED LIGANDS. CATALYTIC IMPLICATIONS

(i) Reactivity with $[M(acac)_n]$ complexes ($M = Mn$, Co, Fe, Ni, Cu, Zn for $n = 2$; $M = Mn$, Fe, Cr for $n = 3$)

The metal–β-diketonate ring is known to undergo various substitution reactions of the hydrogen methino group under electrophilic conditions [96]. In 1977 a novel insertion, rather than substitution, reaction was reported of three electrophiles (alkylisocyanates, dimethyl acetylenedicarboxylate, diethyl azodicarboxylate) into the methino C–H bond [97]. At about the same time it was noted [98] that cyanogen also reacted in this manner with the β-diketonate ring of $[Ni(acac)_2]$. Moreover, this new reaction mode for cyanogen was found to form the basis of a new catalytic process in which C_2N_2 could be added to Hacac, the reaction product being not the simple [99] 3-cyanoiminomethyl acetylacetone

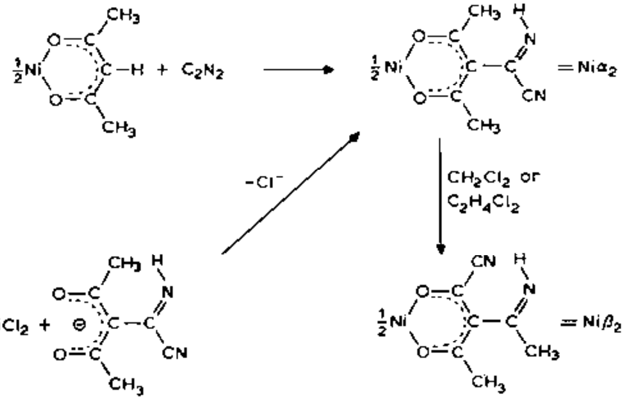


= αH

but a more complex highly functionalized compound (Scheme 10).

The reaction of C_2N_2 with $[Ni(acac)_2]$ and the subsequent evolution of the primary reaction product are illustrated in Scheme 8 [100].

Scheme 8. Behaviour of C_2N_2 towards $[Ni(acac)_2]$



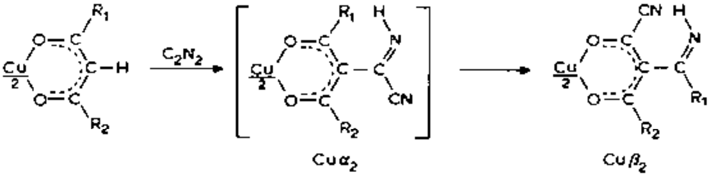
It should be noted that the trimeric structure of $[Ni(acac)_2]$, in which each nickel ion is surrounded by an octahedral shell of oxygen atoms, is completely broken down in favor of the monomeric square planar form by the insertion of C_2N_2 into the C–H methino bond. The reasons for this behavior are not yet clear. Also, quite remarkable is the isomerization reaction $Ni\alpha_2 \rightarrow Ni\beta_2$, for which a plausible mechanism is given in ref. 100.

A single crystal X-ray structure of $Ni\beta_2$ is depicted in Fig. 1. X-ray structure of bis[2-(1-imminoethyl)-1-cyano-1,3-butenedionato]nickel II.

This new β-diketoenolate ligand, 2-(1-iminoethyl)-1-cyano-1,3-butanedionato, causes appreciable distortion in the symmetry of the Ni(0) square moiety by lengthening the two NiO(1) bonds with respect to NiO(2) as a consequence of the inductive effect of the two CN groups on the appropriate oxygen-donor sites.

Copper(II) β-carbonylenolate complexes also react with C_2N_2 according to this new coordination mode (vide infra) to give solid complexes of the α or β type. In the case of $Cu(acac)_2$, a $Cu\beta_2$ species is isolated [101] (Scheme 9).

Scheme 9. Behaviour of C_2N_2 towards β-carbonylenolate copper(II) complexes



$R_1 = R_2 = CH_3$
$R_1 = CH_3$, $R_2 = C_6H_5$
$R_1 = CH_3$, $R_2 = OC_2H_5$
$R_1 = R_2 = C_6H_5$

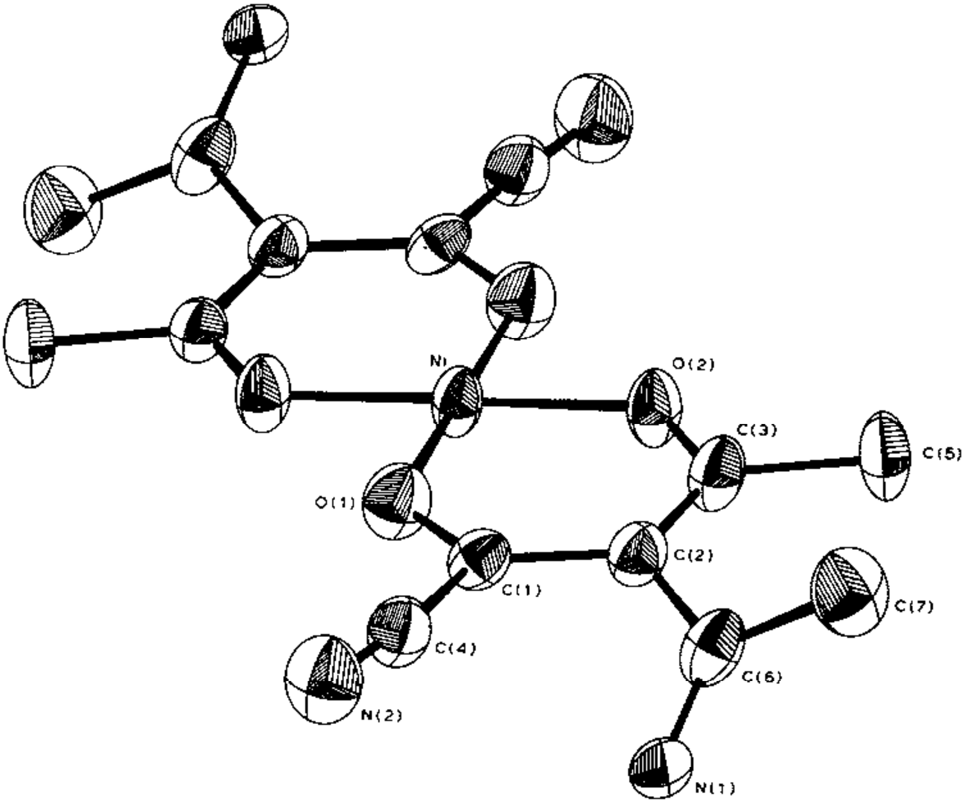


Fig. 1. X-ray structure of bis[2-(1-imminoethyl)-1-cyano-1,3-butenedionato]nickel(II).

The yields are good and the reaction conditions are mild. No reaction is observed with bis(trifluoroacetyl-acetonate)copper(II).

A complex and still obscure reaction mechanism is shown by other M(acac)$_2$ and M(acac)$_3$ complexes [102]. [Mn(acac)$_2$], [Fe(acac)$_2$] and [Co(acac)$_2$] react with C_2N_2 in dichloroethane to give high yields of, as yet, unidentified compounds which all contain bridging CN^- ligands. [Pd(acac)$_2$] and [Cr(acac)$_3$] are unreactive towards C_2N_2 even under forcing thermal conditions. [Fe(acac)$_3$] exhibits modest reactivity with C_2N_2 in dichloroethane with reaction times of the order of several days at room temperature, while [Mn(acac)$_3$] exhibits a similar reactivity to that of [Cu(acac)$_2$] (i.e. hours). Nevertheless, the reaction products from [Fe(acac)$_3$] and [Mn(acac)$_3$] are much more like those obtained from [Mn(acac)$_2$], Fe(acac)$_2$] and [Co(acac)$_2$] than those from [Cu(acac)$_2$]. Quite recently [103], [Zn(acac)$_2$] was also found to react with cyanogen in dichloroethane according to a mechanism analogous to that exhibited by the complexes of Mn^{II}, Fe^{II} and Co^{II}.

Scheme 10. The cyanation of β-dicarbonylic compounds catalyzed by $[Ni(acac)_2]$

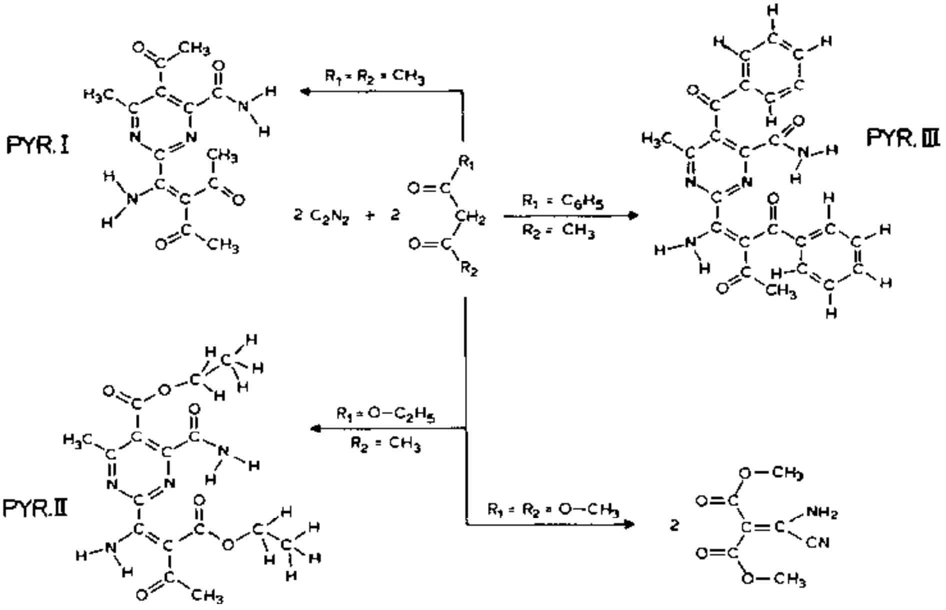


TABLE 16

Some analytical and catalytic data on the addition reaction of C_2N_2 to Hacac in the presence of various $[M(acac)_n]$ ($n = 2.3$) complexes

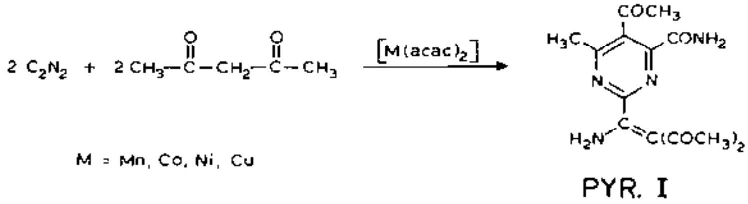
Catalyst	Anal. of organic products (crude samples)			No. of cycles (TN)	
$Ni(acac)_2$	54.07	5.29	17.97	370	[catalyst] = 4×10^{-4} M
$Cu(acac)_2$	55.42	5.63	18.18	332	$[C_2N_2] = 0.45$ M
$Cu\beta_2$	54.67	5.69	17.93	316	[Hacac] = 0.25 M
$Mn(acac)_2$	55.64	5.79	18.19	136	
$Co(acac)_2$				231	
$Mn(acac)_3$				93	reaction time 24 h
$C_7H_8N_2O_2$ [a]	55.26	5.26	18.42		$t = 26°C$
$Cr(acac)_3$				0	
$Fe(acac)_3$				0	
$Pd(acac)_2$				0	

[a] Theoretical.

(ii) Metal-catalyzed addition of C_2N_2 to β-dicarbonyl organic compounds

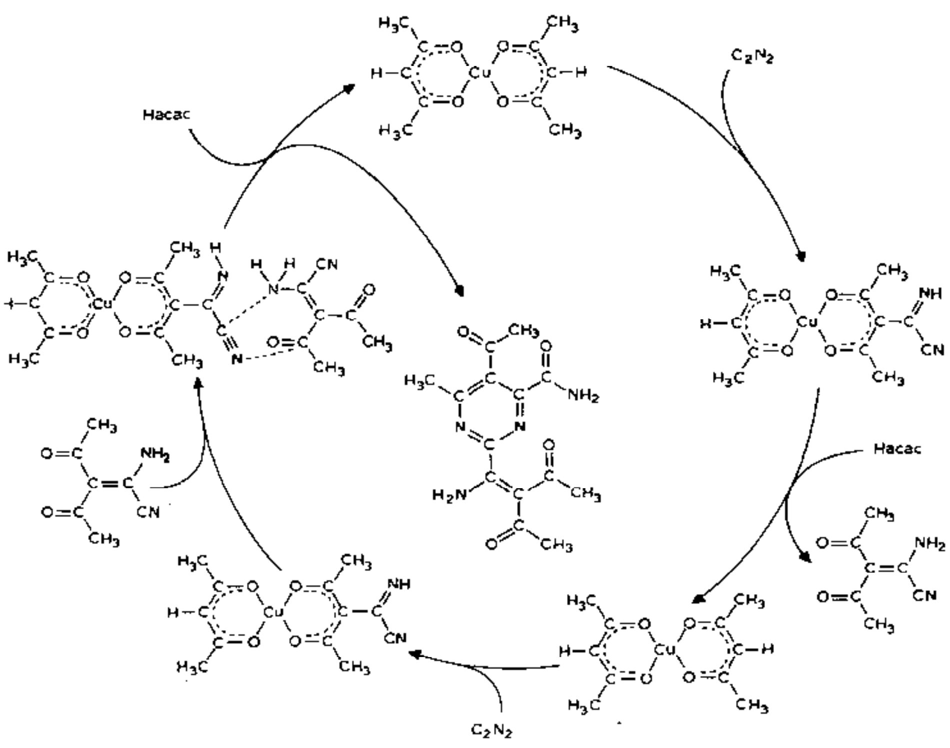
The complexes $M(acac)_2$ (M = Cu, Mn, Co, Mn, Zn) [102,103] are efficient catalysts in the same type of reaction mentioned above for $[Ni(acac)_2]$; some relevant data are reported in Table 16. In each case the reaction product of the organic synthesis is 2-(1′-amino-2′-acetyl-but-1′-enonyl)-4-carboxamido-5-acetyl-6-methyl-1,3-diazyne (Schemes 10 and 11) for which a complete single-crystal X-ray structure has been determined [102].

Scheme 11. Catalytic reaction of C_2N_2 with Hacac



A kinetic investigation of the synthesis of pyr(I) catalyzed by $[Cu(acac)_2]$ has been carried out [104] and the proposed catalytic cycle is reported in Scheme 12.

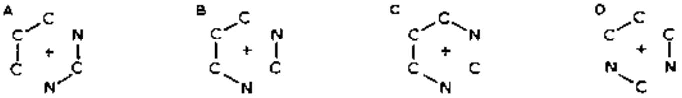
Scheme 12 Proposed catalytic cycle for the synthesis of PYR I catalyzed by $[Cu(acac)_2]$



An obvious implication of this catalytic cycle is that in the cases of [Mn(acac)$_2$], [Co(acac)$_2$] and [Zn(acac)$_2$], species analogous to Niα_2 and Cuα_2 must be formed in the reaction with C_2N_2 and must have an appreciable thermodynamic stability in order to facilitate the catalysis. Apparently the Mn, Co and Zn intermediates are relatively unstable (note the relatively low TN values for these complexes compared to those of [Cu(acac)$_2$] and [Ni(acac)$_2$]) and transform to different catalytically inactive species (i.e. the cyanometal species mentioned above). The new pyrimidine synthesis discovered for Hacac has recently been extended to a typical aliphatic β-ketoester as well as to a paradigmatic arylalkyl β-diketone, but not to β-dialiphatic esters or β-diarylketones [105], at least not at ambient temperature (see Scheme 10).

It is convenient to conclude this section by underlining the fact that a classic inorganic (or organometallic in a wider sense) investigation of the coordination chemistry of cyanogen has led to a fourth general synthesis (method D, Scheme 13) of the pyrimidine ring. This method displays some notable advantages with respect to the other three procedures presently known.

Scheme 13. Known and new syntheses of the pyrimidinic ring



F. MISCELLANEOUS ASPECTS OF THE COORDINATION AND GENERAL CHEMISTRY OF HCN, C_2N_2, XCN

(i) Metal-promoted stoichiometric hydrocyanation of organic substrates

Several organic polycyclic compounds of interest in the chemistry of naturally occurring substances can be effectively hydrocyanated (in stoichiometric processes) by a combination of alkylaluminium compounds and HCN in aprotic media (ether, tetrahydrofuran, benzene) at room temperature [106a]. The yields are high and the stereoselectivity is appreciably different to that of the conventional hydrocyanation method previously employed, i.e. KCN–NH_4Cl in dimethylformamide [106b].

The relevance of these data to this review is that in the formation of an acid–base Lewis adduct [$AlCl_3$(HCN)]* should play an important role in

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* The complex [$AlCl_3$(HCN)] has not been isolated. A compound of stoichiometry [$AlCl_3$(HCN)$_2$] was found not to contain individual HCN moieties [107].

the success of the promoted synthesis. The relevant authors, however, seem not to be aware of this possibility and tend to explain the effectiveness of their synthesis in terms of the presence of a "complex acid", [106a] $H[R_3AlCN]$, and of the species R_2AlCN.

(ii) Interaction of HCN, C_2N_2 and BrCN with solid surfaces

There are few data available on the ability of various solid materials to act as coordinating centers for HCN, C_2N_2 and BrCN. However, facile chemisorption of all these molecules occurs at room temperature onto nickel and iridium finely dispersed on SiO_2 [108]. The nature of the so obtained "sui generis" coordination compounds (fixed to the solid surface) was investigated by IR spectroscopy. For HCN strong bands at 2195 cm^{-1} (with shoulders at ~2160 and ~2110 cm^{-1}) in the case of Ni and at 2100 cm^{-1} (with a shoulder at ~2060 cm^{-1}) for Ir were observed. In the case of C_2N_2 a pair of strong bands is observed at 2200 and 2310 cm^{-1} for Ni and at 2180 and 2320 cm^{-1} for Ir. A spectral pattern similar to that of C_2N_2 was observed for BrCN. Although the authors interpret their data in terms of fission of the molecules on the metal surface, the data for HCN and C_2N_2 might indicate (see Tables 7 and 11) the presence of strongly bonded HCN and C_2N_2 molecules at the metal centers.

Another interesting report of a gas–solid state chemical interaction of C_2N_2 [109] states that the C_2N_2 ends up on a single crystal of metallic nickel. The suggestion is that C_2N_2 undergoes metal coordination by lying "more or less parallel to the surface with both the carbon and nitrogen atoms bonded to the surface".

(iii) The analytical determination of cyanogen in solution and in the gas phase

The need for fast straightforward methods of determining the concentration of C_2N_2 in water or organic solvents has led to a recent very simple method based on a combination of aqueous titration and spectrophotometric measurements in the IR region [34]. The quantitative estimation of cyanogen in cyclohexane has also been carried out by UV measurements at 222 nm (molar absorbance = 13) [65].

For a qualitative determination of cyanogen (and HCN) in the gas phase a method based on photoelectron spectroscopy was recently published [110] and used for the monitoring of the cyanation reaction of benzene by C_2N_2 at 600 K in the presence of Cu supported on Al_2O_3 [111].

G. CONCLUSION

In spite of a fairly extensive preparative chemistry of the title compounds very little is yet known about (i) the mechanisms of their reactions with metal centers, (ii) the physico-chemical (and the chemical) consequences of metal coordination. Exploitation of the potential synthetic utility of these CN-bearing small molecules will only be possible when these two topics are fully investigated.

In general, preparative work involving important metal centers such as Co, Fe, Ti, V, Mn etc., is required, as well as studies on the reactivity of all the title compounds with organometallic rings. It has been shown here how such studies can lead to unpredictable but practical organic syntheses (Schemes 10 and 13) and it is hoped that the reactions of C_2N_2 with the β-ketoenolate metal rings summarized here will stimulate further work in this field.

To Pia, Laura and Livio.

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