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CYANIDE PHOSPHINE COMPLEXES OF TRANSITION METALS

P. RIGO and A. TURCO

Centro di Studio sulla Stabilita' e Reattivita' dei Composti di Coordinazione, C.N.R., Istituto Chimica Analitica, Universita' di Padova, Padova (Italy)

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CONTENTS

ABBREVIATIONS

Me = methyl
Et = ethyl
Pr = n-propyl
Bu = n-butyl
Cy = cyclohexyl
Ph = phenyl
P = donor phosphorus atom of a ligand molecule
dpm = 1,2-bis (diphenylphosphino) methane
dme = 1,2-bis (dimethylphosphino) ethane
dee = 1,2-bis (diethylphosphino) ethane
dpe = 1,2-bis (diphenylphosphino) ethane
dmp = 1,3-bis (dimethylphosphino) propane
dpp = 1,3-bis (diphenylphosphino) propane
dpb = 1,4-bis (diphenylphosphino) butane
deb = 1,4-bis (diethylphosphino) butane
VDP = *cis*-1,2-bis (diphenylphosphino) ethylene
PPP = bis (2-diphenylphosphinoethyl) phenylphosphine
DAP = bis (3-dimethylarsinopropyl) phenylphosphine
TDPME = 1,1,1, tris-(diphenylphosphinomethyl) ethane
TAP = tris (3-dimethylarsinopropyl) phosphine
N_3P = bis (2-diethylaminoethyl)-(2-diphenylphosphinoethyl) amine
DH = dimethylglyoxime
QP = tris-(*o*-diphenylphosphinophenyl) phosphine

A. INTRODUCTION

The general importance of the phosphine complexes with transition metals is reflected by the large number of papers on this subject which have been published in recent years. The interest in this field is stimulated by the useful chemical properties displayed by such complexes. Thus the phosphine ligands can give compounds with transition metals in low or unusual oxidation states and are among the few ligands which promote the formation of otherwise generally unstable transition metal compounds, e.g. organometallics, hydrides, dinitrogen complexes, etc.

Moreover, the fact that the phosphines may form complexes with a metal in different oxidation states and coordination numbers makes this class of compound important for many catalytic processes in solution.

Discussions covering the features common to these topics, occasionally containing information on cyanide complexes, can be found in other recent reviews[1-3]. The chemistry of simple and complex metal cyanides has also been reviewed[4-6]. One of the aims of the present review is to focus attention on the mixed cyanide phosphine complexes and on their most peculiar properties. In fact, in the context of the intense current interest in the properties of cyanide complexes, directed in part at the roles of such compounds in homogeneous catalysis, the phosphine cyanide complexes have been the object of considerable recent attention and study.

The nature of the phosphorus–metal bond, including the controversial aspects on the degree of σ- and π-bonding, will not be discussed here, since a detailed analysis of these arguments has recently been published[7].

B. BONDING CHARACTERISTICS OF THE CYANIDE ION

The cyanide ion is a 14-electron group which may be represented as having unshared pairs of electrons on the carbon and nitrogen atoms, and a triple bond (one σ- and two π-bonds) between them.

The MO energy level ordering and occupations are $(1\sigma)^2$ $(2\sigma)^2$ $(3\sigma)^2$ $(4\sigma)^2$ $(1\pi)^4$ $(5\sigma)^2$ 2π (refs. 8–13). Examination of the overlap populations shows that the formal triple bond is the result mainly of the 3σ and 1π orbitals. The 4σ orbital corresponds virtually to the lone pair on nitrogen whereas the 5σ orbital is predominantly localized on the carbon atom.

Energy level considerations show that the 5σ pair is much more easily involved in bond formation than the 4σ pair. Thus for terminal cyanide groups the carbon-bonded structure appears decidedly preferred, although nitrogen-bonded cyanides are known in a few cases. The effect of coordination of the carbon lone pair of CN^- appears to be such as to increase the bonding ability of the nitrogen lone pair. The ambident nature of the cyanide group appears manifest in a number of bridged cyanides . . . M–CN–M . . . , several examples of which will be encountered also in complexes with the phosphines.

In addition to σ bonds, the cyanide group can form M–CN bonds by occupation of the 2π (antibonding) orbitals via interaction with metal d_π orbitals. Although the π-accepting tendency of CN^- does not seem to be as high as for CO, NO^+ or RNC, the bonding appears to be a function of both σ-donor and π-acceptor abilities, which vary according to the formal oxidation state of the metal, charge of the complex and total intramolecular environment.

Semi-empirical SCF calculations performed for a series of XCN and, for comparison, XCO molecules show that cyanide is a better σ donor and poorer π acceptor than carbon monoxide[14]. The greater σ donation by CN^- is due to less nuclear charge in this ligand and is manifest in a greater carbon charge density for CN^- than for CO.

The relative σ-donor and π-acceptor abilities of cyanide and carbonyl have been examined via molecular orbital calculations on a series of cyanide–carbonyl complexes of manganese[11]. The results of this study show again that carbonyl is a better π-acceptor than cyanide.

Support for the general importance of π-bonding in complex cyanides is provided by the Mössbauer spectra of a series of ions $[Fe(CN)_5L]^{n-}$ (ref. 15). Information about the π-bonding ability of the ligands L has been obtained from the value of the isomer shift δ. The order of increasing π-bond strength of the ligands was found to be

$$NH_3 < NO_2^- < PPh_3 < SO_3^{2-} < CN^- < CO < NO^+$$

The values of the ^{19}F NMR shielding parameters in the series of fluorophenyl complexes *trans*-$[Pt(FC_6H_4)(L)(PEt_3)_2]$ provide further evidence for the good π-bonding ability of the CN^- group[16].

The CN^- group is one of the best *trans*-activators. In the context of the present theories the strong *trans* effect of the cyanide ion is to be attributed more to π- than to σ-bonding properties[17].

It may also be noted that the very high position in the spectrochemical series and the large nephelauxetic effect of the cyanide group are accounted for most easily in terms of M–CN π-bonding[18].

C. CN STRETCHING FREQUENCIES

In addition to the C$\equiv$N stretching bands in the region 2000–2250 cm^{-1}, the cyano complexes exhibit M–C stretching, M–C≡N and C–M–C bending bands in the lower frequency region. Assignments of the lower frequency bands are not easy to make in the vibrational spectra of mixed cyanide phosphine complexes and these bands appear to have been neglected. The ν_{CN} infrared stretching frequency is currently used as a valuable tool for diagnostic purposes, since it gives rise to intense sharp bands generally well separated from other vibrational modes in the complex.

For the mixed cyanide phosphine complexes the infrared CN stretching frequency appears to depend upon factors similar to those already observed for unsubstituted cyano complexes[19].

For a given metal, other things being equal, the ν_{CN} frequency is expected to increase with increasing oxidation state. This effect is seen in the frequency order 2045 cm^{-1} in $[Co(CN)(dpe)_2]$, 2080 cm^{-1} in $[Co(CN)(dpe)_2]^+$ (ref. 20).

For a given metal in a particular oxidation state ν_{CN} should decrease with increase in coordination number (e.g. 2112 cm^{-1} in *trans*-$[Ni(CN)_2(PEt_2Ph)_2]$, 2100 cm^{-1} in $[Ni(CN)_2(PEt_2Ph)_3]$ (ref. 21); 2120 cm^{-1} in *trans*-$[Rh(CN)(CO)(PPh_3)_2]$, 2110 cm^{-1} in $[Rh(CN)(CO)(PPh_3)_3]$) (ref. 22).

The effect of changing the metal atom is seen in the frequency order 2105 cm^{-1} in *trans*-$[Pd(CN)_2(PEt_3)_2]$, 2124 cm^{-1} in *trans*-$[Pt(CN)_2(PEt_3)_2]$ (ref. 23). An analogous increase of ν_{CN} can be observed going from $[Co(CN)(dpe)_2]$ (2045 cm^{-1}) (ref. 20) to $[Rh(CN)(dpe)_2]$ (2080 cm^{-1}) (ref. 22).

Finally, as can be seen in Table 1, substitution of cyanide or phosphine ligands

TABLE 1
C≡N stretching frequencies for some cyanide phosphine complexes

Compound	ν_{CN} (cm^{-1})[a]	Ref.
$[Co(CN)_2(CO)(PPh_3)_2]^-$	2081, 2065	24
$[Co(CN)(CO)_2(PPh_3)_2]$	2100	24
$[Co(CN)_2(CO)(PEt_3)_2]^-$	2062, 2045	24
$[Co(CN)(CO)_2(PEt_3)_2]$	2095	24
$[Co(CN)(dpe)_2]$	2045	20
$[Co(CN)_2(CO)(dpe)]^-$	2085, 2080	24
$[Co(CN)(CO)_2(dpe)]$	2105	20
$[Rh(CN)(PPh_3)_3]$	2085	22
$[Rh(CN)(CO)(PPh_3)_3]$	2100	22
$[Rh(CN)(CO)(PPh_3)_2]$	2120	22

[a] Nujol mulls.

by carbon monoxide invariably results in an increase in the ν_{CN} frequency. A shift to a higher frequency is also observed, in spite of the increase in the coordination number, even in going from $[Rh(CN)(PPh_3)_3]$ to $[Rh(CN)(PPh_3)_3(CO)]$.

The infrared cyanide stretching frequencies observed in the spectra of the cyanide phosphine complexes are reported in the appropriate tables.

D. THE CYANIDE PHOSPHINE COMPLEXES

The chemistry of the cyanide phosphine complexes is entirely restricted to the *d* block transition metals. The discussion will follow the periodic chart by sub-group beginning with iron. In fact the sole cyanide phosphine complexes reported in the literature are those given by the elements of Group VIII (with the exception of osmium) and those of the copper sub-group, although it may be anticipated that at least for some of the other transition elements the preparation of the complexes should not present particular problems. The discussion within each sub-group will begin with the lower oxidation states of the metal involved and will progress to the more positive oxidation states.

Complexes containing bridging cyanide groups will be discussed in a separate section at the end of the paper.

Complexes containing the NO ligand will not be treated here since they have been discussed in a recent review on transition metal nitrosyl chemistry[25].

E. IRON AND RUTHENIUM

(i) Iron

It is known that one CN^- group in hexacyanoferrates may be replaced by different ligands, L, giving a variety of substituted ions $[Fe(CN)_5L]^{n-1}$.

The reaction of tertiary phosphines with $Na_3[Fe(CN)_5(NH_3)]$ suspended in methanol yields the series of diamagnetic yellow complex ions $[Fe(CN)_5(PR_3)]^{3-}$ (Pr_3 = PBu_3, PCy_3, PPh_3)[26,27]. The corresponding low-spin paramagnetic derivatives of iron(III) can be readily obtained by oxidation of the iron(II) complex with bromine in methanol. Treatment of aqueous solutions of the iron(II) complex $[Fe(CN)_5(PR_3)]^{3-}$ with hydrogen chloride yields the fairly strong acid $H_3[Fe(CN)_5(PR_3)]$ (ref. 27). This protonation reaction is similar to that of $[Fe(CN)_6]^{4-}$ leading to $H_4[Fe(CN)_6]$.

Information about the π-acid character of a series of ligands, L, has been obtained from the values of the isomer shift, δ, in the Mössbauer spectra measured for the ions $[Fe(CN)_5L]^{n-}$. The π-acidity was found to follow the order $NO^+ > CO > CN^- > SO_3^{2-} > PPh_3 > NO_2^- \approx NH_3$ (ref. 28).

Iron(II) gives 5-coordinate complexes of the type $[FeX(QP)]^+$ when X = Cl, Br, I, and 6-coordinate complexes of the type $[FeX(QP)]$ when X = NCS and CN (ref. 29). The influence of the anionic ligand on coordination number and geometry of these complexes has been discussed[30].

The Mössbauer spectra of these iron(II) complexes have also been reported and discussed[31].

(ii) Ruthenium

The dicyanide complexes $[Ru(CN)_2(dme)_2]$ (ref. 32) and $[Ru(CN)_2(QP)]$ (ref. 33) have been prepared from the corresponding dichlorocomplexes by metathetical reaction with cyanide ions. Similar preparative methods have been used for the preparation of the hydridocyano-complexes *trans*-$[Ru(CN)(H)(diphosph)_2]$ (diphosph = dme, dee) (ref. 34).

The values of the metal–hydrogen stretching frequencies in the region 1800–2000 cm^{-1} for the $[Ru(X)(H)(diphosph)_2]$ series (X = mononegative ion) have been correlated with the position of the ligand X in the *trans*-effect series. The data confirm the high *trans*-effect of the cyanide group.

F. COBALT, RHODIUM, IRIDIUM

(i) Cobalt

A considerable number of mixed cyanide phosphine complexes have been reported in the literature for the oxidation states I, II and III (Table 3). They can be related to

TABLE 2
Iron and Ruthenium complexes

Compound	Colour	Dec.p. (°C)	$\nu_{C\equiv N}$ (cm^{-1})	Ref.
$Na_3[Fe(CN)_5(PPh_3)]\cdot 2H_2O$	Yellow		2095, 2052, 2070 [a]	26, 27
$Na_3[Fe(CN)_5(PBu_3)]$			2093, 2049, 2065 [a]	27
$Na_3[Fe(CN)_5(PCy_3)]$			2089, 2042, 2060 [a]	27
$H_3[Fe(CN)_5(PPh_3)]\cdot H_2O$	Green		2033, 2060, 2082, 2130, 2146 [a]	27
$H_3[Fe(CN)_5(PBu_3)]$	Green		2080, 2108 [a]	27
$H_3[Fe(CN)_5(PCy_3)]\cdot H_2O$	Green		2101 [a]	27
$[Fe(CN)_2(QP)]$	Yellow	364–368		29
$Na_2[Fe(CN)_5(PPh_3)]\cdot 2H_2O$	Green		2117, 2044 [a]	25
trans-$[Ru(CN)_2(dme)_2]\cdot H_2O$	Colourless	> 350	2064 [b]	32
$[Ru(CN)_2(QP)]$	White	387–393		33
trans-$[Ru(CN)(H)(dme)_2]$	Yellow	230	2062 [b]	34
trans-$[Ru(CN)(H)(dee)_2]$ [c]	Colourless		2069 [b]	34

[a] In KBr pellet.
[b] In Nujol mull.
[c] Not pure.

the simple cyanide complexes $[Co(CN)_5]^{4-}$ (ref. 35), $[Co(CN)_5]^{3-}$ (ref. 36), $[Co(CN)_6]^{3-}$ (ref. 4).

1. Cobalt(I) complexes

The complexes with phosphines and cyanides as the sole ligands are known only with chelating diphosphines. They have been prepared by reduction from cobalt(II) complexes or by metathetical reaction of cobalt(I) complexes with cyanide ions. Thus the complex $[Co(CN)(dpe)_2]$ (ref. 20) has been obtained by reduction of $[Co(CN)_2(dpe)_2]$ and the complex $[Co(CN)(VDP)_2]$ has been prepared by anionic exchange using $[Co(VDP)_2]ClO_4$ and an anionic resin in the CN^- form[37]. Attempts to prepare the complexes with tertiary phosphines (PPh_3, $PPhEt_2$, PPh_2Et) have failed.

Solutions of $[Co(CN)(dpe)_2]$ react with molecular oxygen[20]. There are indications that the adduct is a bridged Co–O–O–Co binuclear complex, which by further reaction yields the cobalt(II) complex $[Co(CN)(dpe)_2]^+$. The same cationic complex is formed by treating $[Co(CN)(dpe)_2]$ with perchloric acid in ethanol solution.

The cobalt(I) complex $[Co(CN)(dpe)_2]$ is five-coordinate in solvents where the corresponding bromide complex $[CoBr(dpe)_2]$ undergoes dissociation into $[Co(dpe)_2]^+$ and Br^- (ref. 38). The cyanide complex reacts with carbon monoxide giving $[Co(CN)(dpe)(CO)_2]$. By contrast the bromide complex yields the ionic $[Co(dpe)_2(CO)]Br$. This different behaviour is a consequence of the different bonding abilities of CN^- relative to Br^- in the cobalt(I) complex.

TABLE 3
Cobalt complexes

Compound	Colour	Dec.p. (°C)	$\nu_{C\equiv N}$ (cm^{-1})	μ (B.M.)	Ref.
$[Co(CN)(dpe)_2]$	Red	140	2045		20
$[Co(CN)(VDP)_2]$	Red	246	2050		37
$[Co(CN)(CO)_2(dpe)_2]$	Yellow	184	2105		20
$Et_4N[Co(CN)_2(CO)_2(PCy_3)] \cdot H_2O$			2105, 2085		24
$Et_4N[Co(CN)_2(CO)(PPh_3)_2] \cdot H_2O$			2081, 2065		24
$K[Co(CN)_2(CO)(PMePh_2)_2] \cdot 3H_2O$			2065, 2050		24
$K[Co(CN)_2(CO)(PMe_2Ph)_2] \cdot 3H_2O$			2070, 2060		24
$K[Co(CN)_2(CO)(PEt_3)_2] \cdot CH_3COCH_3 \cdot H_2O$	Yellow		2062, 2045		24
$K[Co(CN)_2(CO)(dpe)] \cdot H_2O$			2085, 2080		24
$[Co(CN)(CO)_2(PPh_3)_2]$	Yellow		2100		24, 42
$[Co(CN)(CO)_2(PEt_3)_2]$	Yellow		2095		24
$[Co(CN)(CO)_2(PEt_2Ph)_2]$	Yellow		2100		42
$[Co(CN)(CO)_2(PCy_3)_2]$	Yellow		2092		24
$K[Co(CN)_2(PEt_3)_2(CH_2CHCN)]$					43
$[Co(CN)_2(PPh_2Et)_3]$	Red	108–110	2080, 2098	2.0	44
$[Co(CN)_2(PPhEt_2)_3]$	Red	110–113	2080, 2098	2.0	44
$[Co(CN)_2(PPh_2Me)_3]$	Red	161–163	2075, 2095	2.1	45
$[Co(CN)_2(PPhMe_2)_3]$	Red	177–179	2070, 2090	2.0	45
$[Co(CN)_2(HPCy_2)_3]$	Orange–red	92–94	2080	2.0	45
$[Co(CN)_2(HPPh_2)_3]$	Red	88–92	2075	1.9	45
$[Co(CN)_2(dpe)_2]$	Red		2080	2.4	20
$[Co(CN)(dpe)_2]ClO_4$	Red–brown	257	2090	2.2	20
$[Co(CN)_2(dpp)_{1.5}]_2$	Pink–red		2080, 2090	2.3	44

TABLE 3 (continued)

Compound	Colour	Dec.p (°C)	$\nu_{C\equiv N}$ (cm^{-1})	μ (B.M)	Ref.
$[Co(CN)_2(dpb)_{1.5}]_2$	Pink–red		2080, 2090	2.4	44
trans-$[Co(CN)_2(dpe)_2]ClO_4$	Yellow		2113		49
trans-$[Co(CN)_2(VDP)_2]ClO_4$	Yellow		2115		37
$K_2[Co(CN)_5(PPh_3)] \cdot 3H_2O$	Yellow		2118, 2140		51
$K[Co(CN)_4(PPh_3)_2] \cdot 2H_2O$	Yellow		2110, 2150		51
$[Co(CN)_2(acac)(PPh_3)_2]$	Orange		2100		53
$[Co(CN)(DH)_2(PPh_3)] \cdot 3.5H_2O$	Brown		2155		55
$[(\eta^5\text{-}C_5H_5)Co(CN)_2(PPh_3)]$	Yellow		2120, 2110		54
$K_3[Co(CN)_2(Y)(PEt_3)_2(H_2O)]$[b]	Dark-orange		2125, 2065, 2040		41, 43
$[(\eta^3\text{-}C_3H_5)Co(CN)_2(PEt_3)_2]$					43

[a] In Nujol mull.

[b] $Y = (NC)_5Fe^{II}CN-$.

The compound $[\mathrm{Co\,(CN)\,(dpe)\,(CO)_2}]$ has also been prepared by the disproportionation reaction[39]

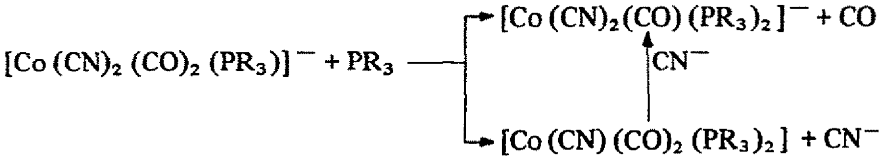
$$2\,[\mathrm{Co\,(CN)_2\,(dpe)_2}] + 2\,\mathrm{CO} \rightarrow [\mathrm{Co\,(CN)\,(dpe)\,(CO)_2}] + [\mathrm{Co\,(CN)_2\,(dpe)_2}]^{+} + \mathrm{dpe} + \mathrm{CN}^{-}$$

which is similar to the disproportionation of $[\mathrm{Co\,(CN)_5}]^{3-}$ (ref. 40).

$$2\,[\mathrm{Co\,(CN)_5}]^{3-} + 2\,\mathrm{CO} \rightarrow [\mathrm{Co\,(CN)_3\,(CO)_2}]^{2-} + [\mathrm{Co\,(CN)_6}]^{3-} + \mathrm{CN}^{-}$$

The compound $[\mathrm{Co\,(CN)_3(CO)_2}]^{2-}$ can easily undergo substitution reactions with tertiary phosphines[24] to yield complexes of the types $[\mathrm{Co\,(CN)_2(CO)_2\,(PR_3)}]^{-}$, $[\mathrm{Co\,(CN)_2\,(CO)\,(PR_3)_2}]^{-}$ and $[\mathrm{Co\,(CN)\,(CO)_2\,(PR)_2}]$ in accord with the schemes depicted by the equations

$$[\mathrm{Co\,(CN)_3\,(CO)_2}]^{2-} + \mathrm{PR_3} \rightarrow [\mathrm{Co\,(CN)_2\,(CO)_2\,(PR_3)}]^{-} + \mathrm{CN}^{-}$$



$$\begin{tikzcd}
 & {[\mathrm{Co\,(CN)_2(CO)\,(PR_3)_2}]^{-} + \mathrm{CO}} \\
{[\mathrm{Co\,(CN)_2\,(CO)_2\,(PR_3)}]^{-} + \mathrm{PR_3}} \arrow[ur] \arrow[dr] & \\
 & {[\mathrm{Co\,(CN)\,(CO)_2\,(PR_3)_2}] + \mathrm{CN}^{-}} \arrow[uu, "\mathrm{CN}^{-}"']
\end{tikzcd}$$

The neutral complexes $[\mathrm{Co\,(CN)\,(PR_3)_2\,(CO)_2}]$ are also formed in the reaction of the cobalt(II) complex $[\mathrm{Co\,(CN)_2\,(PR_3)_3}]$ with carbon monoxide, leading by disproportionation to cobalt(III), and have also been obtained by treating solutions of $[\mathrm{CoX_2\,(PR_3)_2}]$ complexes (X = halide) with an anionic resin in the CN^{-} form in the presence of carbon monoxide[42].

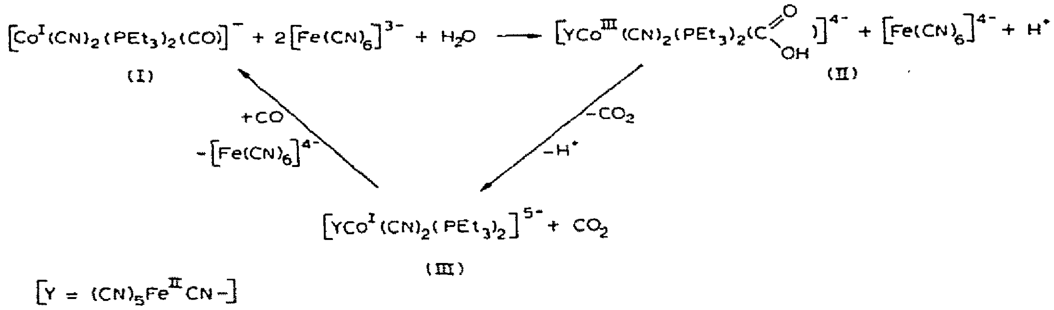
The chemistry of the anionic complex $[\mathrm{Co\,(CN)_2\,(CO)\,(PEt_3)_2}]^{-}$ (I) has been thoroughly investigated, revealing the following characteristic features[24,41]. In contrast to other cobalt(I) anionic complexes this complex exhibits only weak nucleophilicity towards organic halides and also shows a relatively weak basicity towards protonation. In slightly acidic aqueous solutions the hydrido complex $[\mathrm{HCo\,(CN)_2\,(CO)\,(PEt_3)_2}]$, which is a weak acid ($\mathrm{p}K_a$ of ca. 5) is presumably formed.

Complex (I) reacts rapidly with excess $[\mathrm{Fe\,(CN)_6}]^{3-}$ in alkaline solution according to the reaction

$$[\mathrm{Co\,(CN)_2\,(CO)\,(PEt_3)_2}]^{-} + 4\,[\mathrm{Fe\,(CN)_6}]^{3-} + 4\,\mathrm{OH}^{-} \rightarrow 3\,[\mathrm{Fe\,(CN)_6}]^{4-} + \mathrm{CO}_3^{2-} + [\mathrm{(CN)_5Fe{-}CN{-}Co\,(CN)_2\,(PEt_3)_2\,(H_2O)}]^{3-} + \mathrm{H_2O}$$

which involves oxidation of the CO ligand. A detailed study of this reaction has shown that carbon monoxide can be oxidized to carbon dioxide by $[Fe(CN)_6]^{3-}$ under the catalytic influence of (I) (ref. 43). The corresponding catalytic cycle is depicted by the following simplified scheme

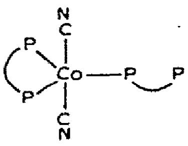
SCHEME

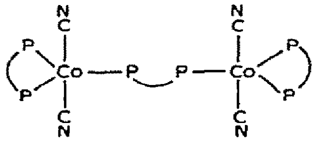


Addition of (I) to an aqueous solution of $[Fe(CN)_6]^{3-}$ results in the formation of the relatively unstable compound (II) which by elimination of CO_2, in the presence of excess CO returns to (I) through (III). The intermediate (III) can also be trapped by adding other ligands which are effective in displacing $[Fe(CN)_6]^{4-}$ from cobalt(I). Thus the reaction of (I) with $[Fe(CN)_6]^{3-}$ in the presence of acrylonitrile yields the stable anionic complex $[Co^I(CN)_2(PEt_3)_2(CH_2=CH-CN)]^-$. In the presence of allyl alcohol the π-allyl cobalt (III) compound $[(h^3-C_3H_5)Co^{III}(CN)(PEt_3)_2]$ was obtained and isolated in pure form[43].

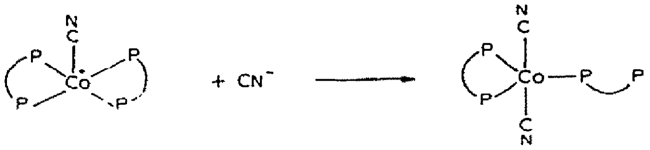
2. Cobalt(II) complexes

The mixed phosphino cyanide complexes so far prepared are all 5-coordinate, the cobalt atom being bound to two cyanide groups and three phosphorus atoms of a tertiary or ditertiary phosphine. These complexes have been prepared by halide–cyanide exchange on anionic resins in CN^- form starting from halide–phosphine complexes. With the tertiary phosphines PEt_2Ph, $PEtPh_2$, PMe_2Ph and $PMePh_2$, complexes corresponding to the formulation $[Co(CN)_2(PR_3)_3]$ have been isolated in the solid state[44,45]. Complexes of the same composition have also been prepared with the secondary phosphines $HPCy_2$ and $HPPh_2$ (ref. 45). These 5-coordinate complexes are also formed in solution using the phosphines PEt_3, PPr^n_3 and PBu^n_3, $HPEt_2$, HPEtPh, HPPhCy but are difficult to isolate owing to their high solubility. The remarkable stability of the $[Co(CN)_2(P)_3]$ moiety is evidenced by the structure of the complexes with ditertiary phosphines[44]. The structures are apparently governed by the requirement of binding three phosphorus atoms and two cyanide groups to the cobalt atom. Thus the phosphine dpe gives the 5-coordinate complex $[Co(CN)_2(dpe)_2]$ (I) in which one of the two diphosphine molecules acts as a monodentate ligand. The diphosphines dpp and dpb yield the binuclear complexes $[Co(CN)_2(diphosph)_{1.5}]_2$ (II), in which one diphosphine molecule acts as a bridge between two different cobalt atoms


(I)


(II)

Oxidation of the cobalt(I) 5-coordinate complex [Co(CN)(dpe)$_2$] gives the corresponding cobalt(II) complex [Co(CN)(dpe)$_2$]$^+$ (ref. 20). This compound, which is the sole example reported of a complex of the type [Co(CN)(P)$_4$]$^+$, easily gives the 5-coordinate derivative of the common [Co(CN)$_2$(P)$_3$] type in the presence of stoichiometric cyanide ions[39]



By contrast, in the case of the halide complexes the ionic structure [CoX(dpe)$_2$]$^+$X appears to be preferred[46,47].

The magnetic moments of the complexes are in the range 1.9 – 2.4 B.M. in accord with a low-spin d^7 configuration. The infrared spectra of most of the [Co(CN)$_2$(P)$_3$] complexes display two infrared absorptions attributable to ν_{CN} stretching, suggesting structures distorted from idealized geometries.

Similarly to the pentacyanocobaltate(II) ion[36], the cobalt(II) phosphino–cyanide complexes display a remarkable activity towards several reagents. The most extensively studied reactions are those of the complex [Co(CN)$_2$(dpe)$_2$].

The complex in methanol forms a bridged peroxo complex by absorption of molecular oxygen and this then reacts with the solvent to give formaldehyde and the 6-coordinate cobalt(III) ion [Co(CN)$_2$(dpe)$_2$]$^+$ (ref. 48). Reaction with 1,2-dichloroethane and oxygen in the presence of [Co(CN)$_2$(dpe)$_2$] leads to carbon dioxide[48,49]. By contrast, the binuclear complexes [Co(CN)$_2$(diphosph)$_{1.5}$]$_2$ (diphosph = dpp, dpb) were found not to react with oxygen in alcohol or dichloroethane. This striking difference has been attributed to the bridged structure of the binuclear complexes (II) which prevents the formation of the "peroxo" bridges. The lack of reactivity of the latter two complexes is confirmed by their behaviour in other "insertion" reactions. Thus, whereas the mononuclear complex [Co(CN)$_2$(dpe)$_2$] has been found to react readily with sulphur dioxide in benzene or with tin(II) chloride in ethanol, the binuclear complexes did not show any reactivity towards the same reagents[39]. The reaction of the complex $[Co(CN)_2(dpe)_2]$ with organic halides, R–X, has also been investigated. The products found in the reactions with C_2H_5X were ethylene and ethane with the reactivity order $C_2H_5I > C_2H_5Br > C_2H_5Cl$. The yellow cobalt(III) complex $[Co(CN)_2(dpe)_2]X$ was isolated from the reaction solutions[39,48]. The reactions with dichloroethane, dibromoethane and diiodoethane produced the same cobalt(III) cationic complex and ethylene, with the reactivity order $I > Br > Cl$. The reaction patterns with the organic halides are similar to those observed for the pentacyanocobaltate ion and the suggested mechanism involves an halogen abstraction step from the organic halide by the metal atom[50].

The reactions of the diphosphine complexes with diluted solutions of protonic acids have also been studied. The mononuclear $[Co(CN)_2(dpe)_2]$ has been found to react in ethanol with hydrogen halides or perchloric acid to give the cobalt(III) complex $[Co(CN)_2(dpe)_2]X$ (X = halide, ClO_4^-). By contrast, the binuclear complexes were found to react with the hydrogen halides but not with perchloric acid. The overall patterns of these reactions are rather complicated and the destiny of the reduced proton has not been ascertained. Only trace amounts of hydrogen were evolved during the reaction[39].

An interesting difference from the pentacyanocobaltate ion is the lack of reactivity of these complexes towards the hydrogen molecule. In contrast to the easy activation of hydrogen by $[Co(CN)_5]^{3-}$ leading to $[CoH(CN)_5]^{3-}$ and to hydrogenation of activated olefins[36], one finds that the mixed tertiary or ditertiary phosphino–cyanide complexes do not appreciably react with hydrogen nor do they hydrogenate activated olefins[39].

The complexes with tertiary phosphines $[Co(CN)_2(PR_3)_3]$ react in solution with carbon monoxide giving first the substitution products $[Co(CN)_2(PR_3)_2(CO)]$. The latter compounds give by disproportionation the cobalt(I) complexes $[Co(CN)(PR_3)_2(CO)_2]$ and uncharacterized cobalt(III) complexes, following a reaction similar to that discussed above for the complex $[Co(CN)_2(dpe)_2]$ (ref. 42).

3. *Cobalt(III) complexes*

The reactions of the tertiary phosphine PPh_3 with $K_3[Co(CN)_5X]$ (X = Br, I) in aqueous acetic acid gives the complexes $K_2[Co(CN)_5(PPh_3)] \cdot 3H_2O$ and $K[Co(CN)_4(PPh_3)_2] \cdot 2H_2O$ (ref. 51). The latter compound can also be obtained by reaction of the sulfito–cyanide complex ion $[Co(SO_3)_2(CN)_4]^{5-}$ with PPh_3 in acetic acid[52]. The polarographic behaviour suggests a *trans*-configuration for the tetracyanocomplex.

The acetylacetonato complex $[Co(CN)_2(acac)(PPh_3)_2]$ (ref. 53) and the cyclopentadienyl complex $[(h^5\text{–}C_5H_5)Co(CN)_2(PPh_3)]$ (ref. 54) are examples of mixed dicyanide derivatives.

The monocyano complex $[Co(CN)(DH)_2(PPh_3)]$ completes the series of the few known mixed tertiary phosphine–cyanide complexes of cobalt(III) (ref. 55).

As mentioned above, the oxidation of the 5-coordinate $[Co(CN)_2(dpe)_2]$ by several reagents readily leads to the cobalt(III) 6-coordinate $[Co(CN)_2(dpe)_2]^+$ ion. The oxidation reaction is undoubtedly favoured by the availability of one uncoordinated phosphorus atom in the $[Co(CN)_2(dpe)_2]$ complex. The loss of one electron is, in fact, accompanied by further coordination of this free phosphorus end of the diphosphine.

A single absorption attributable to the ν_{CN} stretching is present in the infrared spectrum of the compound and this suggests that the two CN^- groups are in a *trans* position in the octahedral complex[48,49].

(ii) Rhodium

1. Rhodium(I) complexes

The complexes so far prepared are reported in Table 4. The dimeric $[Rh(CN)(PPh_3)_2]_2$ has been obtained by heating the polymeric $[Rh(CO)_2(CN)]_n$ in fused phosphine[56]. The infrared spectrum of the compound is consistent with cyano-bridges. The compound does not form a hydride with molecular hydrogen although it acts as a homogeneous hydrogenation catalyst for olefins.

The monomeric $[Rh(CN)(PPh_3)_3]$ has been prepared by chloride–cyanide exchange starting from $[Rh(Cl)(PPh_3)_3]$ (ref. 22). Determination of the molecular weight shows that the compound is not dissociated in benzene. In contrast with the behaviour of the chloride $[Rh(Cl)(PPh_3)_3]$, the cyanide complex appears to react reversibly with excess PPh_3 in solution, to give the 5-coordinate $[Rh(CN)(PPh_3)_4]$. The reactivity of $[Rh(CN)(PPh_3)_3]$ towards carbon monoxide is also different from that of the corresponding halide complexes[57] in so far that in the presence of excess phosphine only the cyanide can yield 5-coordinate complexes of the type $[Rh(X)(CO)(PPh_3)_3]$. In the absence of added phosphine both complexes give the 4-coordinate *trans*-$[Rh(X)(CO)(PPh_3)_2]$ derivatives. The compound *trans*-$[Rh(CN)(CO)(PPh_3)_2]$ has also been obtained by substitution from the fluoro-analogue $[Rh(F)(CO)(PPh_3)_2]$ (ref. 58).

The complex $[Rh(CN)(PPh_3)_3]$ in solution reversibly adds molecular hydrogen. The 5-coordinate $[Rh(CN)(H)_2(PPh_3)_2]$ has been isolated from the reacted solutions. The reaction of $[Rh(CN)(PPh_3)_3]$ with molecular oxygen occurs in the solid and in solution yielding $[Rh(CN)(O_2)(PPh_3)_2]$ (ref. 22).

Mixed complexes $[Rh(CN)(HPR_2)_3]$ with the secondary phosphines $HPPh_2$ and $HPCy_2$ are also known. They have been obtained by ion exchange treating dichloromethane solutions of the complexes $[Rh(HPR_2)_4]ClO_4$ with an ionic resin in the CN^- form[59].

A similar method has been used for the preparation of $[Rh(CN)(dpe)_2]$. The complex is 5-coordinate in the solid and in freshly prepared solutions. In non-polar solvents it slowly transforms into the binuclear complex $[Rh(CN)(dpe)_{1.5}]_2$ in

TABLE 4
Rhodium complexes

Compound	Colour	Dec.p. (°C)	$\nu_{C\equiv N}$ (cm^{-1})[a]	Ref.
$[Rh(CN)(PPh_3)_2]_2$	Yellow	174–175	2119, 2113	56
$[Rh(CN)(PPh_3)_3]$	Orange–yellow		2085	22
$[Rh(CN)(HPPh_2)_3]$	Yellow	104	2090	59
$[Rh(CN)(HPCy_2)_3]$	Yellow	199–200	2080	59
$[Rh(CN)(O_2)(PPh_3)_2]$	Green		2105	22
trans-$[Rh(CN)(CO)(PPh_3)_2]$	Yellow		2120	22, 58
$[Rh(CN)(CO)(PPh_3)_3]$	Orange		2110	22
$[Rh(CN)(H)_2(PPh_3)_2]$	Yellow		2110	22
$[Rh(CN)(dpe)_2]$	Red	124–125	2080	22
$[Rh(CN)(dpe)_{1.5}]_2$	Yellow	225–228	2085	22
$[Rh(CN)(CO)(dpe)]$	Yellow		2095	22
$[Rh(Cl)(H)(CN)(HCN)(PPh_3)_2]$	Yellow	180–190	2128, 2145, 2163	60
$[Rh(Cl)(CN)_2(PPh_3)_2]_2(C_2N_2)$	Yellow		2115, 2135, 2145	61
$[Rh(Cl)(CN)_2(PPh_3)_2(CH_3CN)]$	Yellow		2130, 2140	61
$[Rh(Cl)(CN)_2(PPh_3)_2(CH_3CHCHCN)]$	Yellow		2130, 2140	61
$[Rh(Cl)(CN)_2(PPh_3)_2(C_6H_5CHCHCN)]$	Yellow		2130, 2140	61
$[Rh(Cl)(CN)_2(PPh_3)_2(C_6H_5CN)]$	Yellow		2130, 2140	61
$[Rh(Br)(CN)_2(PPh_3)_2(CH_3CN)]$	Yellow		2130, 2140	61
$[Rh(Br)(CN)_2(PPh_3)_2(CH_3CHCHCN)]$	Yellow		2130, 2140	61
$[Rh(Br)(CN)_2(PPh_3)_2(C_6H_5CHCHCN)]$	Yellow		2130, 2140	61
$[Rh(Br)(CN)_2(PPh_3)_2(C_6H_5CN)]$	Yellow		2130, 2140	61

[a] In Nujol mull.

which one diphosphine acts as a bridge between two rhodium atoms. In polar solvents [Rh (CN) (dpe)$_2$] undergoes a slow dissociation into the ions [Rh (dpe)$_2$]$^+$ and CN$^-$. The complex reacts with carbon monoxide giving [Rh (CN) (CO) (dpe)] (ref. 22).

2. Rhodium(III) complexes

All the complexes have been obtained by oxidation of rhodium(I) phosphine complexes. The reaction of [Rh (Cl) (PPh$_3$)$_3$] with HCN in dichloromethane yields a crystalline compound of the stoichiometry RhCl (HCN)$_2$ (PPh$_3$)$_2$ (ref. 60). Available information, based upon IR and NMR spectra, suggests the formulation [Rh (Cl) (H) (CN) (PPh$_3$)$_2$ (HCN)] for this rhodium(III) complex. The compound reacts with carbon monoxide to give [Rh (Cl) (CO) (PPh$_3$)$_2$] presumably through the intermediate [Rh (Cl) (H) (CN) (CO) (PPh$_3$)$_2$].

The reaction of [Rh (Cl) (PPh$_3$)$_3$] with cyanogen gives the dicyanide complex [Rh (Cl) (CN)$_2$ (PPh$_3$)$_2$]$_2$ (C_2N_2) where one C_2N_2 cyanogen molecule acts as a bridge between the rhodium atoms of two Rh (Cl) (CN)$_2$ (PPh$_3$)$_2$ moieties[61].

A series of complexes of composition [Rh (X) (CN)$_2$ (PPh$_3$)$_2$ (NC–R)] (X = Cl, Br; R = CH_3, CH_3–CH = CH, C_6H_5–CH = CH, C_6H_5) was obtained by the reaction of cyanogen with solutions containing [Rh (X) (PPh$_3$)$_3$] and the nitriles R–CN. The complex [Rh (X) (CN)$_2$ (PPh$_3$)$_2$ (NC–CH$_3$)] was also obtained by treating the binuclear [Rh (X) (CN)$_2$ (PPh$_3$)$_2$]$_2$ (C_2N_2) with methyl cyanide[61].

(iii) Iridium

1. Iridium(I) complexes

The iridium(I) complex [Ir (CN) (CO) (PPh$_3$)$_3$] has been obtained by the reaction of [Ir (CO) (MeCN) (PPh$_3$)$_2$]$^+$ with cyanide[62], or by chloride–cyanide exchange treating [Ir (Cl) (CO) (PPh$_3$)$_2$] in a chloroform solution of PPh$_3$ with an anionic resin in CN$^-$ form[59]. It is remarkable that the 5-coordinate tris-phosphine complexes of the type [Ir(X) (CO) (PPh$_3$)$_3$] are stable when X = CN$^-$ and cannot be obtained when X is a halogen atom. The effect of the cyanide group in promoting 5-coordination may be compared with that of the hydride and acetylide ligands in the complexes [Ir (H) (CO) (PPh$_3$)$_3$] (ref. 63) and [Ir (C ≡ CR) (CO) (PPh$_3$)$_3$] (ref. 64). It is also worth noting that the 5-coordinate [Ir (CN) (CO) (PPh$_3$)$_3$] does not react with oxygen[59], in contrast to the 4-coordinate complexes [Rh (X) (CO) (PPh$_3$)$_2$] (X = Cl, Br, I) (ref. 69).

2. Iridium(III) complexes

Mixed cyanide complexes of iridium(III) (Table 5) have been obtained by oxidative addition of cyanide derivatives on iridium(I) complexes of the type [Ir (Cl) (CO) (PR$_3$)$_2$]. The derivatives used have been hydrogen cyanide, sulphur dicyanide and mercury(II) cyanide. Hydrogen cyanide reacts with [Ir (Cl) (CO) (PR$_3$)$_2$] (PR$_3$ = PPh$_3$)

TABLE 5
Iridium complexes

Compound	Colour	Dec.p. (°C)	$\nu_{C\equiv N}$ (cm^{-1})[a]	Ref.
$[Ir(CN)(CO)(PPh_3)_3]$	Yellow		2120	62
$[Ir(CN)(H)(Cl)(CO)(PPh_3)_2]$	White	275–280	2160	66, 60
$[Ir(CN)(Cl)(SCN)(CO)(PPh_3)_2]$	Colourless	> 300	2155	67
$[Ir(CN)(Cl)(NCS)(CO)(PPh_3)_2]$	Colourless		2153	67
$[Ir(CN)(Cl)(SCN)(CO)(PMePh_2)_2]$		135–138	2145	67
$[Ir(CN)(Cl)(NCS)(CO)(PMePh_2)_2]$		95–98	2147	67
$[Ir(CN)(Cl)_2(PMe_2Ph)_3]$	Yellow	204–207		69
$[Ir(CN)(Cl)(CO)(PPh_3)_2{-}HgCN]$	White	248	2128, 2150	68

[a] In Nujol mull.

in benzene at room temperature to yield the hydrido complex [Ir (Cl) (H) (CN) (CO) $(PPh_3)_2$] (ref. 60, 66). Sulphur dicyanide, S $(CN)_2$, reacts as a pseudohalogen with the complex (PR_3 = PPh_3, $PMePh_2$) to form the cyano–S–thiocyanato complexes [Ir (Cl) (CN) (SCN) (CO) $(PR_3)_2$]. Recrystallization of these compounds from methanol–dichloromethane mixtures is accompanied by isomerization to the N-bonded form[67]. Finally, oxidation of [Ir (Cl) (CO) $(PPh_3)_2$] with Hg $(CN)_2$ in benzene–ethanol yields the complex [Ir (Cl) (CN) (CO) $(PPh_3)_2$ Hg (CN)] containing iridium–mercury bonds[68].

G. NICKEL, PALLADIUM, PLATINUM

(i) Nickel

The mixed cyanide phosphine complexes of nickel are listed in Table 6. A very extensive series of complexes is formed by the metal in oxidation state II. Oxidation state I is also represented but the nickel(I) complexes are rare.

1. Nickel(I) complexes

The reduction of the nickel(II) complexes $[Ni(CN)_2(diphosph)_{1.5}]_2$ (diphosph = dpp, dpb) with sodium borohydride in ethanol yields the nickel(I) compounds $[Ni(CN)(diphosph)_{1.5}]_2$ which are fairly stable in the solid state in an inert gas atmosphere[70]. The magnetic moments of the compounds are in the range 2.0–2.2 B.M. as expected for a d^9 configuration. The complexes have been formulated as binuclear species [(CN) (diphosph) Ni (diphosph) Ni (diphosph) (CN)] with a planar arrangement of three phosphorus atoms and one cyanide group around the nickel atom.

In dichloroethane the complexes take up molecular oxygen in 1 : 1 mole ratio giving diphosphine dioxide, the nickel(II) complexes [Ni $(CN)_2$ (diphosph)] and nickel metal[71]. In the presence of excess diphosphine catalytic oxidation to diphosphine dioxide has been observed. The overall reaction (disproportionation and catalytic oxidation) has been interpreted according to the following scheme for the complex with dpb.

$$[Ni(CN)(dpb)_{1.5}]_2 + dpb + O_2 \rightarrow [Ni(dpb)_2] + dpbO_2 + [Ni(CN)_2(dpb)]$$

$$dpb + O_2 \xrightarrow{[Ni(dpb)_2]} dpbO_2$$

$$[Ni(dpb)_2] + 2\,O_2 \rightarrow Ni + 2\,dpbO_2$$

2. Nickel(II) complexes

The following preparative methods were employed: (i) reaction of nickel(II) cyanide with phosphine; (ii) metathetic exchange of halide by cyanide in $[NiX_2(P)_2]$

TABLE 6
Nickel complexes

Compound	Colour	M.P. (°C)	$\nu_{C\equiv N}$ (cm^{-1})^a	Ref.
$[Ni(CN)(dpp)_{1.5}]_2$	Golden–yellow		2100	70
$[Ni(CN)(dpb)_{1.5}]_2$	Golden–yellow		2100	70
trans-$[Ni(CN)_2(PMe_3)_2]$	Yellow	231–235 (d)		73
$[Ni(CN)_2(PMe_3)_3]$	Orange–red	165–168		73
$[Ni(CN)_2(PMe_2Ph)_3]$	Dark–red		2100	72
$[Ni(CN)_2(PMe_2(C_6F_5))_3]$	Orange–red		2110	72
$[Ni(CN)_2(PMePh_2)_3]$	Red			72
trans-$[Ni(CN)_2(PEt_3)_2]$	Yellow	156–157	2108	113, 114
trans-$[Ni(CN)_2(PEt_2Ph)_2]$	Yellow	169–170	2112	21
$[Ni(CN)_2(PEt_2Ph)_3]$	Red	126–128	2100	21
trans-$[Ni(CN)_2(PEtPh_2)_2]$	Yellow	215–217	2105	21
trans-$[Ni(CN)_2(PPh_3)_2]$	Yellow	212 (d)		112, 77
$[Ni_2(CN)_4(PPh_3)_2]$	Grey–green			111
$[Ni(CN)_2]_3(PPh_3)$				110
trans-$[Ni(CN)_2(P(p\text{-tol})_3)_2]$				116
trans-$[Ni(CN)_2(PPr_3)_2]$	Yellow	75–77	2105	74
trans-$[Ni(CN)_2(PBu_3)_2]$	Yellow	70	2110	74
$[Ni(CN)_2(PBu_3)_3]$	Yellow	81		112
trans-$[Ni(CN)_2(PEtCy_2)_2]$	Yellow	202–203	2095	74
$[Ni(CN)_2$(9-methyl-9-phosphafluorene)$_3]$	Purple	> 300 (d)	2118, 2108, 2102	115
$[Ni(CN)_2$(9-ethyl-9-phosphafluorene)$_3]$	Red-purple	212–214 (d)	2118	115
trans-$[Ni(CN)_2(HPCy_2)_2]$	Yellow	185–188	2120	76
$[Ni(CN)_2(HPEt_2)_3]$	Red	(oil)	2100	76
$[Ni(CN)_2(HPEtPh)_3]$	Red	(oil)	2100	76

TABLE 6 (continued)

Compound	Colour	M.p. (°C)	$\nu_{C\equiv N}(cm^{-1})$ [a]	Ref.
$[Ni(CN)_2(HPPh_2)_3]$	Red	152–156	2100	76
$[Ni(CN)_2(dee)]$	Yellow			85
$[Ni(CN)_2(dpe)]$	Yellow		2125	86
$[Ni(CN)_2(dpp)_{1.5}]_2$	Red		2100	86
$[Ni(CN)_2(dpp)(PBu_3)]$	Red	143	2095, 2110	86
$[Ni(CN)_2(dpb)_{1.5}]_2$	Red		2100	86
$[Ni(CN)_2(dpb)]_2$	Yellow		2120	86
$[Ni(CN)_2(dmp)]$	Yellow		2112, 2114	87
$[Ni(CN)_2(dmp)_{1.5}]_2$	Red		2090, 2100	87
$[Ni(CN)_2(PPP)]$	Red		2110, 2100	88
$[Ni(CN)_2(TDPME)]$	Red		2105, 2165	89
$[Ni(CN)_2(DAP)]$				90
$[Ni(CN)_2(TAP)]$	Deep-red			92
$[Ni(CN)_2(N_3P)]$	Yellow	215–218 (d)		91
trans-$[Ni(CN)(H)(PCy_3)_2]$	Yellow	150 (d)		95
trans-$[Ni(CN)(Ph)(PEt_3)_2]$				98
trans-$[Ni(CN)(mesityl)(PMe_2Ph)]$	Pale–yellow	131–132	2105	96
trans-$[Ni(CN)(o\text{-styryl})(PEt_3)_2]$	Yellow	119–120	2095	97
$[(h^5\text{-}C_5H_5)Ni(CN)(PBu_3)]$	Green	94–95	2125	100
$[(h^5\text{-}C_5H_5)Ni(CN)(dpm)]$	Green	140		101
$[(h^5\text{-}C_5H_5)_2Ni_2(CN)_2(dpe)]$	Green	123		101
$[(h^5\text{-}C_5H_5)_2Ni_2(CN)_2(dpp)]$	Green	162		101
$[(h^5\text{-}C_5H_5)_2Ni_2(CN)_2(dpb)]$	Green	190.5		101

[a] In Nujol mull.

complexes (using potassium or silver cyanide); (iii) additive oxidation with cyanogen or hydrocyanic acid on $[Ni(P)_4]$ complexes; (iv) reaction of $[Ni(CN)_4]^{2-}$ with phosphine.

(a) The tertiary and secondary phosphine complexes. Nickel dicyanide forms diamagnetic 4-coordinate $[Ni(CN)_2(P)_2]$ or 5-coordinate $[Ni(CN)_2(P)_3]$ complexes with tertiary phosphines depending on the nature of the phosphines. The 4- and 5-coordinate complexes which have been isolated in the solid state are listed in Table 6. It may be noted that with some tertiary phosphines (e.g. PMe_2Ph, $PMe_2(C_6F_5)$ and $PMePh_2$) attempts to isolate 4-coordinate complexes were unsuccessful owing to the stability of the corresponding 5-coordinate complex[72]. With a few tertiary phosphines (PMe_3 (ref. 73), PEt_2Ph (ref. 21), PBu_3 (ref. 74, 75) it has been possible to obtain both 4- and 5- coordinate compounds.

Thermodynamic studies on the equilibrium

$$[Ni(CN)_2(PR_3)_3] \rightleftharpoons [Ni(CN)_2(PR_3)_2] + PR_3 \qquad (1)$$

show that the stability of the 5-coordinate complexes depends on the nature of the substituent R and follows the order $PEt_2Ph > PEt_3 \sim PEtPh_2 > PPr^n_3 \sim PBu^n_3 \gg PPh_3 \sim PCy_3$. Five-coordinate complexes with PCy_2Et, PCy_3, PPh_3 could not be obtained or detected even in solutions containing large excess of the phosphines[74].

Going to the secondary phosphines, HPR_2, spectrophotometric evaluation of the stability of the $[Ni(CN)_2(P)_3]$ complexes revealed the sequence $HPEt_2 \sim HPEtPh > HPPh_2 > HPPhCy \gg HPCy_2$. The trisphosphine complexes have been isolated with all these phosphines with the exception of $HPCy_2$ (ref. 76).

The relative importance of the electronic and steric effects on the stability of the $[Ni(CN)_2(P)_3]$ complexes in equilibrium (1) has received considerable attention (ref. 21, 72, 74, 77, 78). It has been proposed that the electronic factors which depend on the nature of the substituent R are of minor importance compared with the steric effects depending upon the bulkiness of the phosphines[39].

As expected, the 4-coordinate diamagnetic complexes are all *trans*-planar as shown by infrared and visible spectra.

Trigonal bipyramidal structures have been suggested for the low-spin $[Ni(CN)_2(P)_3]$ complexes on the basis of the visible ligand field spectra.

The presence of one single ν_{CN} absorption in the infrared spectra of these complexes would suggest coordination with two CN^- groups in the *trans*-position. However it has been noted that the infrared spectrum of $[Ni(CN)_2\{PPh(OEt)_2\}_3]$ in the solid exhibits one single C—N stretching frequency although the symmetry of the coordination sphere is halfway between the D_3h of a trigonal bipyramid and C_{2v} of a tetragonal pyramid (see below)[79].

A self consistent charge and configuration molecular orbital calculation has been reported for a model trigonal–bipyramidal system of the type *trans*-$[Ni(CN)_2(PR_3)_3]$ (ref. 77). Based upon this model, electronic spectral assignments have been made for *trans*-$[Ni(CN)_2\{PPh(OMe_3)_2\}_3]$.

The temperature dependence of the ligand field spectra for some of the 5-coordinate complexes[80] and the pressure effects on the ligand field spectra of $[Ni(CN)_2(PPh_2Me)_3]$ have also been investigated[81].

The crystal structure of the 5-coordinate complexes $[Ni(CN)_2(PPhMe_2)_3]$ (I)[82], $[Ni(CN_2\{PPh(OEt)_2\}_3]$ (II) (ref. 79) and $[Ni(CN)_2$ (9-alkyl-9-phosphafluorene)$_3]$ (III) (ref. 82, 83) has been determined by X-ray crystallography.

The coordination about the nickel atom in (I) is basically trigonal bipyramidal with the two cyanides at the apices and the three phosphines in the basal plane. There is, however, a slight distortion toward a tetragonal–pyramidal geometry. The same type of structure is exhibited by (II) but all the distortions are increased in magnitude. The methyl derivative of (III) may be isolated as two allogon isomers by crystallization from different solvents[84]. One form has tetragonal–pyramidal structure with one phosphafluorene ligand at the apex of the pyramid. Another form has a trigonal–bipyramidal structure with axial cyanide groups. The ethyl derivative has a similar trigonal–bipyramidal structure. All the structures become identical in solution when released from crystal lattice restraints, as shown by the visible spectra.

(b) The ditertiary phosphine complexes. The difunctional ligands $R_2P–(CH_2)_n–PR_2$ (= diphosph) have been found to act as chelating, bridging, or as monodentate ligands in complexes with nickel(II) cyanide. The occurrence of all possible modes of coordination is the result of the combined effects of the alkyl chain length in the diphosphine and of the possibility of nickel(II) to give four as well as five-coordination.

The 4-coordinate complexes $[Ni(CN)_2(diphosph)]$ (diphosph = dee[35], dpe[86], dmp[87]) have planar structures with one chelated diphosphine and two CN groups in the *cis*-position as shown by the presence of two sharp infrared bands in the cyanide stretching region. By contrast, the visible and infrared spectra of the 4-coordinate compound $[Ni(CN)_2(dpb)]_2$ are consistent with a *trans*-planar structure[86]. This complex is binuclear with two nickel atoms joined by two bridging diphosphines. In this complex a *cis* configuration is unfavoured by the length of the alkyl chain. The tendency of nickel(II) to give a *trans* configuration is attained by joining two *trans*-$Ni(CN)_2(P)_2$ moieties through two diphosphine bridges.

In the presence of added phosphine the 4-coordinate complexes readily give 5-coordinate $[Ni(CN)_2(P)_3]$ species. Addition of $PPhMe_2$ to solutions of $[Ni(CN)_2(dee)]$ gives the 5-coordinate $[Ni(CN)_2(dee)(PPhMe_2)]$ (ref. 85). The complex $[Ni(CN)_2(dpe)]$ can add one dpe molecule to give the 5-coordinate $[Ni(CN)_2(dpe)_2]$ which has a dangling phosphino group[86].

The complexes $[Ni(CN)_2(diphosph)_{1.5}]_2$, (diphosph = dmp[87], dpp[86], dpb[86]) and $[Ni(CN)_2(dpp)(PBu_3)]$ (ref. 86) have been obtained in the solid state. The binuclear 5-coordinate structure $[(CN)_2(diphosph)Ni–diphosph–Ni(diphosph)(CN)_2]$ has been suggested for the complexes of the first type in which one diphosph molecule bridges two different nickel atoms.

(c) Complexes with terdentate and quadridentate ligands. Neutral 5-coordinate complexes of the formulation [Ni (CN)$_2$ L] have been prepared with terdentate ligands with three phosphorus donors. The electronic spectra of the complex with the triphosphine ligand [(C$_6$H$_5$)$_2$ PCH$_2$–CH$_2$]$_2$ P(C$_6$H$_5$) (PPP), are indicative of square pyramidal nickel(II) (ref. 88). In the CN stretching region the infrared spectrum of the complex shows two sharp absorptions consistent with a square pyramidal structure with an apical cyanide. In contrast with the [Ni(X)$_2$ (PPP)] halide complexes which are 5-coordinate only in the solid state, the complex [Ni (CN)$_2$ (PPP)] remains 5-coordinate in acetonitrile solution, confirming the strong tendency of cyanide to promote five-coordination in the nickel–phosphine complexes. A square pyramidal structure has also been attributed to the complex [Ni (CN)$_2$(TDPME)] (TDPME = 1,1,1,tris-(diphenylphosphinomethyl) ethane) (ref. 89). The 5-coordinate complex [Ni (CN)$_2$ (DAP)] (DAP = (C$_6$H$_5$)P [CH$_2$CH$_2$CH$_2$As (CH$_3$)$_2$]$_2$) with the PAs$_2$ donor set, has a somewhat distorted square pyramidal structure[90].

Complexes with quadridentate tripod-like ligands, L, with donor sets nitrogen–phosphorus[91] and arsenic–phosphorus[93] are reported. The general formula of these complexes is [Ni (CN)L] X (X = BPh$_4^-$, ClO$_4^-$; L = (Et$_2$N–CH$_2$–CH$_2$)$_2$NCH$_2$CH$_2$–PPh$_2$ (N$_3$P), (Me$_2$AsCH$_2$CH$_2$CH$_2$)$_3$P (TAP)). X-Ray structural studies show that the cation [Ni (CN) TAP]$^+$ has a trigonal bipyramidal configuration with three arsenic atoms at equatorial sites and a phosphorus atom and a cyanide group in apical positions[93]. However, the potentially tetradentate ligand N$_3$P apparently behaves as a terdentate ligand in the corresponding complex, [Ni (CN) (N$_3$P)]$^+$. Indeed a square planar 4-coordinate structure can be assigned to the complex on the basis of the ligand field spectra[91].

(d) Hydride and organometallic complexes. Hydride and organonickel complexes including the cyanide derivatives *trans*-[Ni (CN) (H) (PCy$_3$)$_2$] (ref. 95, *trans*-[Ni(CN) (mesityl) (PPhMe$_2$)$_2$] (ref. 96) and *trans*-[Ni (CN) (*o*-styryl) (PEt$_3$)$_2$] (ref. 97) have been discussed in a recent review[94]. Other organonickel cyanide complexes of the σ-aryl or π-cyclopentadienyl type have recently been reported. Thus the complex [Ni (PEt$_3$)$_3$] has been reported to react with chlorobenzene and with benzonitrile at room temperature to give the corresponding *trans*-[Ni (X) (C$_6$H$_5$) (PEt$_3$)$_2$] compounds (X = Cl, CN) (ref. 98).

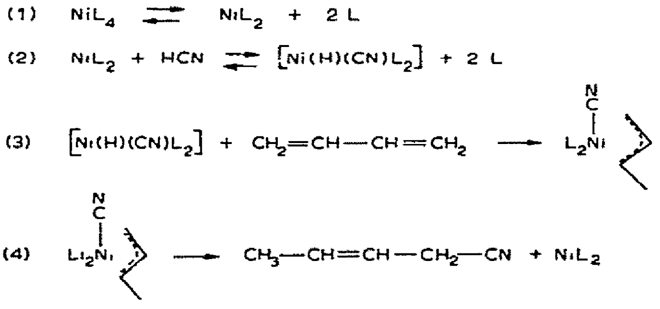
Correspondingly, the reaction of Ni (deb)$_2$ (deb = Et$_2$P(CH$_2$)$_4$PEt$_2$) with benzonitrile at 60°C gives [Ni(CN) (C$_6$H$_5$) (deb)] (ref. 99) which has been isolated and characterized in the solid state. π-Cyclopentadienyl complexes with general composition [(h^5–C$_5$H$_5$)Ni(CN)P] (P = phosphorus atom of a tertiary or ditertiary phosphine bound to the metal) have recently been reported. The complex [(h^5–C$_5$H$_5$)Ni(CN) (PBu$_3$)] (ref. 100) has been obtained by treatment of [(h^5–C$_5$H$_5$)Ni(PBu$_3$)$_2$]Cl with sodium cyanide in aqueous solution. The complexes with the diphosphines Ph$_2$P(CH$_2$)$_n$ PPh$_2$ (diphosph; n = 1–4) have been prepared by a similar method starting from [(h^5–C$_5$H$_5$)Ni(Ph$_2$P(CH$_2$)$_n$PPh$_2$)]Cl (ref. 101). The reaction of

$[(h^5-C_5H_5)Ni(Ph_2PCH_2)]Cl$ with sodium cyanide gives a mononuclear complex of formula $[(h^5-C_5H_5)Ni(CN)(Ph_2PCH_2PPh_2)]$ in which the diphosphine molecule acts as a monodentate ligands. The analogous reactions with the diphosphines where $n = 2$–4, on the other hand, gave the binuclear compounds $[(h^5-C_5H_5)(CNO)Ni(diphosph)_{0.5}]_2$ where one diphosphine molecule acts as a bridge between two nickel atoms.

3. Homogeneous catalytic reactions

One of the most peculiar reactions catalyzed by nickel compounds is the formation of organonitriles from olefins and hydrocyanic acid, involving cyanide–phosphine–organonickel complexes.

Several patents on the synthesis of nitriles describe the use of nickel(0) complexes with phosphites or phosphines for the homogeneous catalytic addition of hydrogen cyanide to butadiene[102–105]. The first step of the addition process leads to pentene nitriles. The complex $[Ni(dpb)_2]$ appears to be a particularly efficient catalyst for the homogeneous reaction in benzene. The following reaction scheme (possibly involving also a σ-allyl–metal system) may tentatively account for the observed results.



(L = dpb)

The formation of pentene nitriles is an example of reductive elimination of unsaturated nitriles via π-allyl phosphine cyanide complexes, which, in combination with the oxidative addition step of hydrogen cyanide to the nickel complex makes the overall process become catalytic. Reductive elimination of organic nitriles has also been observed for σ-aryl organonickel–cyanide complexes. Thus the compound $[Ni(CN)(C_6H_5)(deb)]$ eliminates benzonitrile by simple heating at 60°C in benzene if diphosphine or carbon monoxide are added to the solution[99].

The oxidative addition of aromatic halides to nickel(0) complexes, followed by metathetic exchange of the halide by the cyanide ion and by the reductive elimination of benzonitrile has recently afforded the way for a new synthesis of aromatic nitriles catalyzed by $Ni(PR_3)_4$ complexes in solution[106]. The overall process is depicted by the equation

$$\mathrm{ArX + NaCN \xrightarrow{Ni(PPh_3)_4} ArCN + NaX}$$

where X = Cl, Br, I and the main steps are

$$\mathrm{[Ni(PR_3)_4] + ArX \rightarrow [Ni(Ar)(X)(PR_3)_2] + 2\,PR_3}$$

$$\mathrm{[Ni(Ar)(X)(PR_3)_2] + NaCN \rightarrow [Ni(Ar)(CN)(PR_3)_2] + NaX}$$

$$\mathrm{[Ni(Ar)(CN)(PR_3)_2] \xrightarrow{PR_3} ArCN + [Ni(PR_3)_4]}$$

$$\mathrm{R = C_6H_5, C_6H_{11}}$$

It is interesting to note that with *ortho*-substituted aromatic halides, e.g. *o*-dichlorobenzene, no elimination of *o*-chlorobenzonitrile occurs unless a chelating diphosphine such as $Ph_2P(CH_2)_3PPh_2$ (= dpp) is added to the solution. The result has been interpreted in terms of replacement of two PPh_3 molecules in *trans*-Ni(*o*-ClC_6H_4)(CN)$(PPh_3)_2$] by one diphosphine to give a nickel(II) complex containing the aryl and cyanide groups in mutually *cis* positions.

The nickel(I) complex [Ni(CN)(dpb)$_{1.5}$]$_2$ in dichloromethane at 20°C has proved to be a very efficient catalyst for the isomerisation of pentene-1, *cis*-pentene-2, *trans*-pentene-2, allyl alcohol and allylbenzene[107]. Similar results have been obtained with benzene solutions of the complex [Ni(dpb)$_2$] in the presence of free hydrocyanic acid[108,112]. It is likely that the nickel(0) complex acts simply as a precursor of the effective catalyst which is probably the nickel(I) complex [Ni(CN)(dpb)$_{1.5}$]$_2$. This interpretation is supported by studies on the reactions of hydrogen cyanide with the complex Ni(dpb)$_2$ (ref. 109). The results show that hydrogen cyanide reacts with Ni(dpb)$_2$ via a very reactive hydride intermediate to give [Ni(CN)(dpb)$_{1.5}$]$_2$. The latter compound can further react with hydrogen cyanide to give an adduct of the type [Ni(CN)(dpb)$_{1.5}$ · HCN] which finally gives the nickel(II) complex [Ni(CN)$_2$(dpb)]$_2$.

Patents describe the use of the complexes [Ni(CN)$_2$]$_3$(PPh_3) (ref. 110) and [Ni_2(CN)$_4$(PPh_3)$_2$] (ref. 111) as catalysts for the cyclic oligomerisation of acetylenes. The use of the complex [Ni(CN)$_2$(PPh_3)$_2$] as a catalyst for a number of oligomerisation and copolymerisation reactions has also been described[75].

(ii) Palladium

Tertiary phosphines form the square planar white derivatives *trans*-[Pd(CN)$_2$(P)$_2$] with palladium(II) cyanide. The *trans* structure has been attributed on the basis of the single ν_{CN} absorption found for these complexes in the ν_{CN} stretching region. The ditertiary phosphine complex [Pd(CN)$_2$(diphosph)] (diphosph = dee[85], dpe[117],

TABLE 7
Palladium complexes

Compound	Colour	M.P. (°C)	$\nu_{C\equiv N}$ (cm^{-1})[a]	Ref.
trans-[Pd $(CN)_2$ $(PMe_3)_2$]				124
trans-[Pd $(CN)_2$ $(PEt_3)_2$]	White	117	2105 (2128[b])	23, 118
trans-[Pd $(CN)_2$ $(PBu_3)_2$]	White	66–68	2126	122
trans-[Pd $(CN)_2$ $(PPh_3)_2$]	White	> 300 (d)	2150	123
trans-[Pd $(CN)_2$ (9-methyl-9-phosphafluorene)$_2$]	Colourless	300 (d)	2136	115
trans-[Pd $(CN)_2$ (9-ethyl-9-phosphafluorene)$_2$]	Colourless	272–275 (d)	2130	115
[Pd $(CN)_2$ (dee)]	White		2130, 2135	85
[Pd $(CN)_2$ (dpe)]	White		2135, 2139	117
[Pd $(CN)_2$ (dpp)]	White		2137, 2140	117
[Pd (CN) (SMe) $(PEt_3)_2$]	Yellow		2125[b]	118
[Pd (CN) (C_4H_7) (PPh_3)]	Colourless	139–143 (d)	2117	119
[Pd (CN) (C_4H_7) (PMe_2Ph)]	Colourless	175–180	2123	119

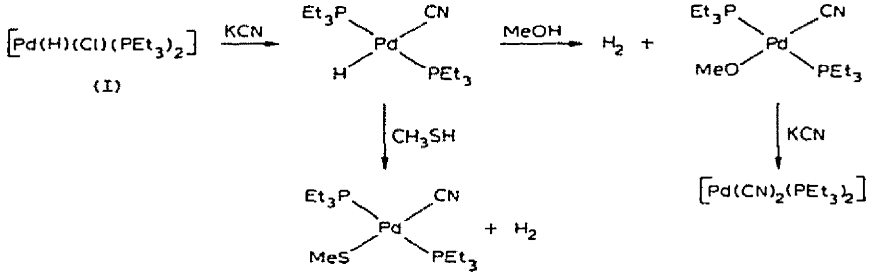
[a] In Nujol mull unless otherwise indicated.
[b] Benzene solution.

dpp[117]) has two sharp infrared bands in the CN stretching region indicative of *cis*-cyanide groups (Table 7).

Attempts to obtain 5-coordinate complexes of the type [Pd $(CN)_2$ $(P)_3$] have failed even using the phosphine 9-alkyl-9-phosphafluorene[115] which has proved particularly efficient in promoting 5-coordination in the corresponding nickel(II) complexes. These results are in accordance with the decreasing tendency to assume the 5-coordinate state in a given group of elements with increasing atomic number.

The complexes so far obtained have been prepared by one of the following methods: (i) reaction of palladium cyanide with the phosphine in ethanol; (ii) oxidation of [Pd (P_4)] complexes by cyanogen; (iii) substitution of chloride by cyanide in the complexes [Pd $(Cl)_2$ $(P)_2$].

It is interesting to note that the reaction of [Pd (H) (Cl) $(PEt_3)_2$] with potassium cyanide in ethanol does not give the expected [Pd (H) (CN) $(PEt_3)_2$] but instead produces [Pd $(CN)_2$ $(PEt_3)_2$] and hydrogen. The reaction gives [Pd (CN) (MeS)-$(PEt_3)_2$] when carried out in methanethiol[118]. The following scheme accounts for these results.



The formation of the labile intermediate *trans*-cyanohydride complex has been suggested in order to explain the reaction products in methanol and the fact that complex (I) does not liberate hydrogen in methanol in the absence of cyanide. The methylthiopalladium–cyanide complex, prepared by the reaction route in methanethiol, is a stable compound in contrast to the corresponding methoxy compound, sulphur being a much stronger ligand to palladium than oxygen.

Cyano-bridged π-allylic palladium complexes of the type [Pd (CN) (2-methylallyl)$]_n$ react with tertiary phosphines to give mononuclear complexes [Pd (CN) (2-methylallyl) (PR_3)] (ref. 119).

It is pertinent here to remember that mixed triphenylphosphite–cyanide complexes of palladium are important intermediates in the catalytic addition of hydrogen cyanide to olefins[120] and olefinic silanes[121], promoted by the palladium [0] complex, Pd $[P(OPh)_3]_4$. The reaction scheme suggested for the addition to olefins involves oxidative addition of hydrogen cyanide to palladium (0), followed by insertion of the olefin and reductive elimination of nitrile with concomitant regeneration of the catalyst (L = P $(OPh)_3$)

$$PdL_4 + HCN \rightarrow Pd(H)(CN)L_2 + 2\,L$$

$$Pd(H)(CN)L_2 + \text{olefin} \rightarrow Pd(\text{alkyl})(CN)L_2$$

$$Pd(\text{alkyl})(CN)L_2 \rightarrow \text{alkyl}-CN$$

(iii) Platinum

Several 4-coordinate planar complexes of the type $[Pt(CN)_2(PR_3)_2]$ have been prepared (Table 8). They generally have a *trans* configuration although an example of *cis* complex has also been reported (see below). The complexes are generally obtained by metathesis, from the halide complexes $[Pt(X)_2(PR_3)_2]$ with sodium or silver cyanide. Special preparative methods include the reduction of fulminato complexes by phosphine or phosphite[125] as depicted in the equation

$$[Pt(CNO)_2(PPh_3)_2] + 2\,PR_3 \xrightarrow[CHCl_3]{} [Pt(CN)_2(PPh_3)_2] + 2\,R_3PO$$

(R = Ph, OEt) and the oxidative addition of cyanogen to the platinum(0) complex[117]

$$[Pt(PPh_3)_4] + C_2N_2 \rightarrow [Pt(CN)_2(PPh_3)_2] + 2\,PPh_3$$

The infrared spectrum of the solid complex which is immediately formed on addition of cyanogen to a benzene solution of the platinum(0) complex, shows two bands at 2141 and 2148 cm^{-1} which have been assigned to the ν_{CN} stretching of two cyanide groups coordinated in *cis* position. The *cis* complex slowly isomerises in dichloromethane solution giving the *trans* compound the infrared spectrum of which displays one single ν_{CN} absorption at 2133 cm^{-1} (ref. 117).

The dealkylation of the methylisocyanide complexes $[Pt(Cl)(CNMe)(PEt_3)_2]^+Cl^-$ or $[Pt(X)(CNMe)(PPh_3)_2]^+X^-$ (X = Cl, Br) carried out by heating in refluxing benzene, yields the complexes $[Pt(CN)(Cl)(PEt_3)_2]$ and $[Pt(CN)(X)(PPh_3)_2]$ respectively.

The suggested mechanism involves initial halide attack at the metal, formation of a 5-coordinate intermediate (in equilibrium with $Pt(X)_2(PPh_3)(CNMe)$) from which the observed complexes are formed by elimination of methyl halide[126]. This dealkylation reaction is very interesting being the reverse of the well known alkylation of metal cyanides which leads to the isocyanide complexes.

A closely related compound is the 5-coordinate $[Pt(CN)(I)(PPh_3)_2(CNMe)]$ which has been obtained by elimination of one mole of methyl iodide from the 5-coordinate iodide derivative $[Pt(I)(PPh_3)_2(CNMe)_2]^+I^-$ in refluxing benzene[126].

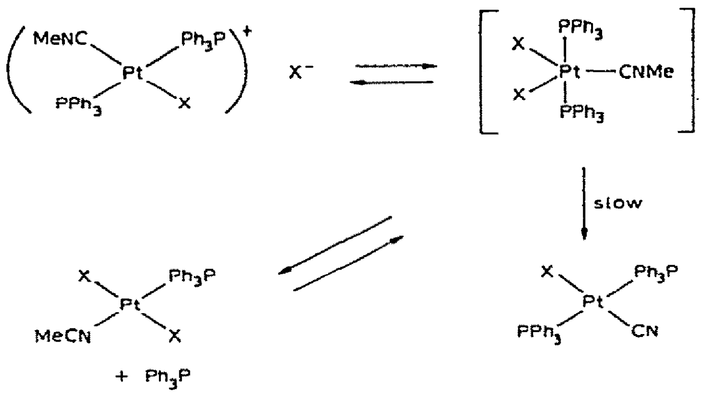
TABLE 8
Platinum complexes

Compound	Colour	M.p. (° C)	$\nu_{C\equiv N}$ (cm^{-1})^{a}	Ref.
$[Pt(CN)_2(PMe_3)_2]$				124
trans-$[Pt(CN)_2(PMe_2Ph)_2]$	White	198–199		128
trans-$[Pt(CN)_2(PMePh_2)_2]$	White	248–249		128
trans-$[Pt(CN)_2(PPh_3)_2]$	White	> 325 (d)	2133	117, 137, 123
cis-$[Pt(CN)_2(PPh_3)_2]$	White		2141, 2148	117
trans-$[Pt(CN)_2(PEt_3)_2]$	White	177	2124	23, 130
trans-$[Pt(CN)_2$(9-methyl-9-phosphafluorene)$_2]$	White	> 300 (d)	2136	115
trans-$[Pt(CN)_2$(9-ethyl-9-phosphafluorene)$_2]$	White	> 295 (d)	2140	115
$[Pt(CN)(Cl)(PEt_3)_2]$	White	146–149		126
$[Pt(CN)(Br)(PPh_3)_2]$	White	> 340		126
$[Pt(CN)(Cl)(PPh_3)_2]$	White	325–330		126
$[Pt(CN)(I)(PPh_3)_2(CNMe)]$	Yellow	328–332		126
$[Pt(CN)(PPh_3)_2(CNMe)]BF_4$	White	240–242		127
trans-$[Pt(CN)(H)(PEt_3)_2]$	White	106–107	2135	138
trans-$[Pt(CN)(H)(PEtPh_2)_2]$	White		2135	140
trans-$[Pt(CN)(H)(PPh_3)_2]$	White	224–227	2142	139
trans-$[Pt(CN)(H)(PMePh_2)_2]$	White	133–135 (d)	2138	128
trans-$[Pt(CN)(H)(PMe_2Ph)_2]$	White	116–118 (d)	2130	128
trans-$[Pt(CN)(Me)(PEt_3)_2]$	White	118–120		141
trans-$[Pt(CN)(Pr^n)(PMe_3)_2]$	White	150–152		141
trans-$[Pt(CN)(Ph)(PEt_3)_2]$	White			98
trans-$[Pt(CN)(p\text{-}FC_6H_4)(PEt_3)_2]$	White	134–135	2130^{b}	16
cis-$[Pt(CN)(p\text{-}FC_6H_4)(PEt_3)_2]$	White	144–145	2125^{b}	16
trans-$[Pt(CN)(m\text{-}FC_6H_4)(PEt_3)_2]$	White	97–99	2130^{b}	16

TABLE 8 (continued)

Compound	Colour	M.P. (° C)	$\nu_{C\equiv N}$ (cm^{-1})[a]	Ref.
cis-[Pt (CN) (*m*–FC_6H_4) $(PEt_3)_2$]	White	129–130		16
trans-[Pt (CN) (C_6F_5) $(PEt_3)_2$]	White	305–308	2135[b]	136
cis-[Pt (CN) (C ≡ C – CN) $(PPh_3)_2$]	White		2140	135
trans-[Pt (CN) $(GeMe_3)$ $(PEt_3)_2$]	Colourless	(Liquid)	2119[c]	132
cis-[Pt (CN) $(GeMe_3)$ $(PEt_3)_2$]	Colourless	102–103	2125[c]	132
[Pt (CN) $(C(CN)_2–CH_3)$ $(PPh_3)_2$]	White	> 300	2141	133
[Pt (CN) $(C(CF_3) = C(CN)CF_3)$ $(PPh_3)_2$]	Buff	278–280	2120	134
[Pt (CN) {$NHSO_2C_6H_4CH_3$–(*p*)} $(PEt_3)_2$]	Colourless	138	2128	131
[Pt (CN) (H) (TCNE) $(PEt_3)_2$]	Yellow		2135	129

[a] In Nujol mull except where otherwise indicated.
[b] In carbon tetrachloride solution.
[c] In benzene solution.



Finally, the nucleophilic substitution of methylcyanide by CN^- on $[Pt(PPh_3)_2(NCMe)_2]^{2+}$ yields the complex $[Pt(CN)(PPh_3)_2(NCMe)]^+$ (ref. 127).

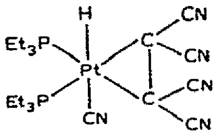
Hydride complexes of the general type *trans*-$[Pt(H)(CN)(PR_3)_2]$ are well known. They can generally be obtained by substitution of halide by cyanide in the complexes *trans*-$[Pt(H)(X)(PR_3)_2]$ or by oxidative addition of hydrogen cyanide to the platinum(0) complexes $[Pt(PR_3)_n]$ ($n = 3, 4$).

The reaction of *trans*-$[Pt(CN)_2(PPh_2Me)_2]$ with sodium borohydride in methanol leads to *trans*-$[Pt(H)(CN)(PPh_2Me)_2]$, although the dimethylphosphine analogue could not be prepared this way. The latter was prepared by reduction with sodium borohydride of a 1 : 1 mixture of *trans*-$[Pt(CN)_2(PMe_2Ph)_2]$ and *cis*-$[Pt(Cl)_2(PMe_3Ph)_2]$ in methanol[128].

An interesting difference between the halide derivatives $[Pt(H)(X)(PEt_3)_2]$ ($X = Cl, Br$) and the cyanide analogue is evidenced by the reaction with tetracyanoethylene (TCNE) in solution[129]. The halide complexes react according to the scheme

$$trans\text{-}[Pt(H)(X)(PEt_3)_2] + TCNE \rightarrow [Pt(TCNE)(PEt_3)_2] + HX$$

The reaction of the analogous cyanide complex with TCNE, however, yields



The *trans* arrangement of H and CN has been deduced from a comparison of the infrared spectra of the complex with its deuterio analogue. The instability of Pt (H) (X) $(PEt_3)_2$ TCNE has been explained in terms of the smaller strength of the Pt–X bonds compared with the Pt–CN bonds.

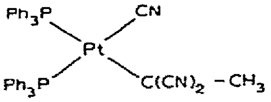
The reaction of ethylene with hydride platinum(II) complexes has also been studied[130]. Ethylene was shown to react with *trans*-[Pt(H) (Cl) $(PEt_3)_2$] to give a quantitative yield of *trans*-[Pt (C_2H_5) (Cl) $(PEt_3)_2$]. By contrast, the same reaction with *trans*-[Pt (H) (CN) $(PEt_3)_2$] gives a mixture of the expected [Pt (C_2H_5) (CN) $(PEt_3)_2$] and [Pt $(CN)_2$ $(PEt_3)_2$].

The reaction of *trans*-[Pt (H) (CN) $(PEt_3)_2$] with the organic azide $R{-}N_3$, ($R = p{-}H_3C{-}C_6H_4SO_2$) has been found to yield the amido complex [Pt (CN) (NHR) $(PEt_3)_2$] (ref. 131).

The preparation of trimethylgermyl complexes of platinum(II) of the type [Pt (CN) $(GeMe_3)$ $(PEt_3)_2$] has been described. They have been obtained by reacting *trans*-[Pt(Cl) $(GeMe_3)$ $(PPh_3)_2$] with potassium cyanide in methanol. The reaction yields a solid and a liquid product; on the basis of the ^1H NMR spectra the solid has been assigned a *cis* and the liquid a *trans* configuration[132].

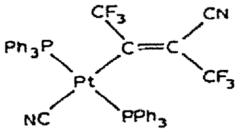
The organometallic complexes of general formula [Pt (CN) (R′) $(PR_3)_2$] (R′ = alkyl, aryl) are most easily obtained from the corresponding halide derivatives by reaction with alkali metal cyanides. However, oxidative addition methods appear to be a promising preparative procedure for the generation of particular organometallic cyanides. Thus addition of benzonitrile to a refluxing toluene solution of $[Pt(PEt_3)_3]$ readily yields *trans*-[Pt(CN) (C_6H_5) $(PEt_3)_2$] (ref. 98).

Carbon–carbon bond cleavage via oxidative addition also occurs in the reaction of $[Pt(PPh_3)_4]$ with 1,1,1,-tricyanoethane[133]. Heating of the reagents in refluxing benzene yields the organometal cyanide derivative (I)



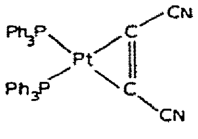
(I)

Another example of rupture of a carbon–CN bond is afforded by the reaction of *trans*-1,2-dicyano-1,2-bis(trifluoro methyl) ethylene with stilbenebis(triphenylphosphine) platinum[134] leading to

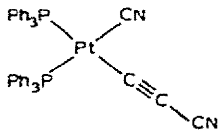


It is likely that the observed compound is not formed directly, but that an initially formed olefin complex rapidly undergoes a "vinyl-rearrangement" with rupture of a carbon–CN bond and formal migration of a CN group from carbon to platinum.

The photochemical isomerisation of the dicyanoethylene complex (II) to the cyanide (cyanoacetylido) derivative (III) also belongs to the class of reactions leading to formation of a new metal–CN bond[135].



(II)



(III)

Reaction of $[Pt(C_6F_5)Br(PPh_3)_2]$ with refluxing methylisocyanide produces the complex $[Pt(CN)(C_6F_5)(PPh_3)_2]$. The reaction is related to the dealkylation of the methyl isocyanide complexes of platinum mentioned above[136].

H. COPPER, SILVER, GOLD

(i) Copper

The reaction of solid copper(I) cyanide with molten triphenylphosphine[142], or with the phosphine dissolved in chloroform[143,144] leads to the white compound $[Cu(CN)(PPh_3)_2]$. Unlike the halide complexes of Cu(I) with triphenyl phosphine which are known to have metal-to-ligand ratios of 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 2 : 3 (ref. 1) with CN^- ions (as in the case of N_3^- and NCS^- (ref. 145)) only the 1 : 2-type complex has been observed in the solid state. The complex shows a lowering of the ν_{CN} stretching band from 2105 cm^{-1} to 2080 cm^{-1} on going from the solid to solution. This result suggests that copper is 4-coordinate in the solid by bridging of the nitrogen atom with an adjacent copper atom[142]. The compound apparently behaves as an approximately monometic species in dilute chloroform solution, where the metal is probably tricoordinated.

It is worth remembering here that trialkylphosphites $P(OR)_3$ react with copper cyanide to give $[Cu(CN)\{P(OR)_3\}]$ and $[Cu(CN)\{P(OR)_3\}_2]$ complexes. The molecular weights of the compounds were found to depend on solvent, temperature and the nature of R. The highest association degree observed corresponded to that of tetrameric species[146].

(ii) Silver

Silver cyanide in toluene reacts with tri-*p*-tolylphosphine giving $[Ag(CN)(PR_3)_2]$ and $[Ag(CN)(PR_3)_3]$ complexes[147] which can be readily isolated. The structure of the complexes in solution has been elucidated primarily through analysis of ^{31}P NMR data. A trigonal and a tetrahedral structure has been proposed for the bis- and tris-phosphine complex, respectively. The structural patterns of these cyanide complexes are not different from those shown by the analogous halide complexes. Lability of the phosphine ligands in the $[AgX(PR_3)_2]$ and $[AgX(PR_3)_3]$ series (X = halide, pseudohalide), evidenced by NMR results, is sensitive to the binding power of the X ligand, the cyanide complex being most labile.

(iii) Gold

The most thoroughly investigated cyanide phosphine gold complex appears to be $[Au(CN)(PPh_3)]$, obtained by reaction of gold cyanide with triphenylphosphine in ethanol[148], or by reaction of acetatotriphenylphosphinegold(I) with hydrogen cyanide according to the reaction

$$[Au(OAc)(PPh_3)] + HX \rightarrow [AuX(PPh_3)] + AcOH$$

An X-ray structural investigation shows that the complex is 2-coordinate and consists of an essentially linear P–Au–CN atomic arrangement[150].

The compound reacts with excess of triphenylphosphine in ethanol to give $[Au(PPh_3)_3][Au(CN)_2]$. Analysis of the infrared spectra reveals that the following equilibrium occurs in chloroform solution

$$[Au(PPh_3)_3]^+[Au(CN)_2]^- \rightleftharpoons 2[Au(CN)(PPh_3)] + PPh_3$$

TABLE 9
Copper, silver and gold complexes

Compound	Colour	M.P. (°C)	$\nu_{C\equiv N}$ (cm^{-1})^a	Ref.
$[Cu(CN)(PPh_3)_2]$	White	182.5–183.5	2105	142, 143, 144
$[Ag(CN)\{P(p\text{-}MeC_6H_4)_3\}_2]$	Colourless	154–156	~ 2110	147
$[Ag(CN)\{P(p\text{-}MeC_6H_4)_3\}_3]$	Colourless	128–133	~ 2110	147
$[Au(CN)(PPh_3)]$	White	204	2146	148, 149
$[Au(PPh_3)_3][Au(CN)_2]$	White	150	2140	148
$[Au(CN)\{P(p\text{-}ClC_6H_4)_3\}]$	White	123	2150	148
$[Au(CN)(PMe_3)]$				124

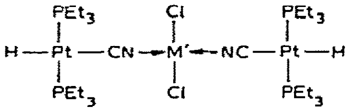
^{a} In Nujol mull.

The trimethylphosphine complex [Au (CN) (PMe_3)] (ref. 124) and the tri-(*p*-chlorophenyl) phosphine complex [Au (CN) { P(*p*-$ClC_6H_4)_3$}] (ref. 148) are briefly reported in the literature.

Finally, reaction of potassium cyanide with the metal atom cluster compound $Au_5Cl(PPh_3)_4 \cdot 3.5H_2O$ is reported to give $Au_3(CN)(PPh_3)_2$, a very insoluble red crystalline substance[151].

I. COMPLEXES WITH BRIDGING CYANIDE GROUPS

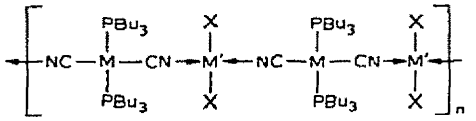
The CN group has been shown to act as a bidentate ligand in a number of cyanide phosphine transition metal complexes. In this class of compound the nitrogen end of a CN group bound to the transition metal atom M coordinates a divalent metal ion M′ giving M–CN→M′ bridges which, in principle, are analogous to those of the well-known polymeric simple or complex cyanides. The bridged compounds are readily obtained by adding $M'X_2$ (X = Cl, Br, NCS) to a solution of the cyanide phosphine complex. The complexes so far obtained belong to one of the following categories, in which the M′ ion is in a pseudo-tetrahedral environment and the coordination of the "donor" complex may be 4, 5 or 6 (ref. 49, 122).



$$\mathrm{H{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}CN{\rightarrow}\underset{Cl}{\overset{Cl}{M'}}{\leftarrow}NC{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}H}$$

(i)

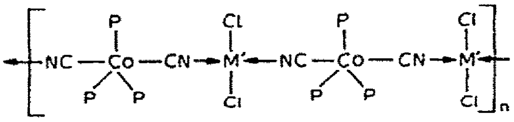
M′ = Mn^{II}, Fe^{II}, Co^{II}, Zn^{II}.



$$\left[\leftarrow \mathrm{NC{-}\underset{PBu_3}{\overset{PBu_3}{M}}{-}CN{\rightarrow}\underset{X}{\overset{X}{M'}}{\leftarrow}NC{-}\underset{PBu_3}{\overset{PBu_3}{M}}{-}CN{\rightarrow}\underset{X}{\overset{X}{M'}}}\leftarrow\right]_n$$

(ii)

M = Pd^{II}, Ni^{II}; M′ = Mn^{II}, Fe^{II}, Zn^{II}; X = Cl; M′ = Co^{II}; X = Cl, Br, NCS.



$$\left[\leftarrow \mathrm{NC{-}\underset{P\quad P}{\overset{P}{Co}}{-}CN{\rightarrow}\underset{Cl}{\overset{Cl}{M'}}{\leftarrow}NC{-}\underset{P\quad P}{\overset{P}{Co}}{-}CN{\rightarrow}\underset{Cl}{\overset{Cl}{M'}}}\leftarrow\right]_n$$

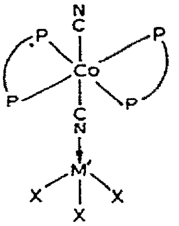
(iii)

P = PMe_2Ph; M′ = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}.

TABLE 10
Complexes with bridging cyanide groups

Compound	Colour	$\nu_{C\equiv N}$ (cm^{-1})[a] (terminal)	$\nu_{C\equiv N}$ (cm^{-1})[a] (bridging)	Ref.
$[Co(CN)_2(dpe)_2]ClO_4$	Yellow	2113		49
$[Co(CN)_2(dpe)_2]CoCl_3$	Green	2108	2146	49
$[Co(CN)_2(dpe)_2]CoBr_3$	Green	2106	2132	49
$[Co(CN)_2(dpe)_2]Co(NCS)_3$	Green	2112	2148	49
$[Co(CN)_2(dpe)_2]MnCl_3$	Yellow	2108	2139	49
$[Co(CN)_2(dpe)_2]FeCl_3$	Green	2109	2137	49
$[Co(CN)_2(dpe)_2]NiCl_3$	Green	2108	2152	49
$[Co(CN)_2(dpe)_2]ZnCl_3$	Yellow	2107	2151	49
$[Pt(CN)(H)(PEt_3)_2]$	White	2137		122
$[Pt(CN)(H)(PEt_3)_2]_2MnCl_2$	White		2149	122
$[Pt(CN)(H)(PEt_3)_2]_2FeCl_2$	White		2152	122
$[Pt(CN)(H)(PEt_3)_2]_2CoCl_2$	Blue		2159	122
$[Pt(CN)(H)(PEt_3)_2]_2NiCl_2$	Violet		2169	122
$[Pt(CN)(H)(PEt_3)_2]ZnCl_2$	White		2164	122
$[Pd(CN)_2(PBu_3)_2]$	White	2126		122
$[Pd(CN)_2(PBu_3)_2MnCl_2]_n$	White		2135	122
$[Pd(CN)_2(PBu_3)_2FeCl_2]_n$	White		2151	122
$[Pd(CN)_2(PBu_3)_2CoCl_2]_n$	Blue		2161	122
$[Pd(CN)_2(PBu_3)_2NiCl_2]_n$	Violet		2168	122
$[Pd(CN)_2(PBu_3)_2ZnCl_2]_n$	White		2164	122
$[Ni(CN)_2(PBu_3)_2]$	Yellow	2110		122
$[Ni(CN)_2(PBu_3)_2MnCl_2]_n$	Yellow		2137	122
$[Ni(CN)_2(PBu_3)_2FeCl_2]_n$	Yellow		2139	122
$[Ni(CN)_2(PBu_3)_2CoCl_2]_n$	Blue		2145	122
$[Ni(CN)_2(PBu_3)_2NiCl_2]_n$	Violet		2157	122
$[Ni(CN)_2(PBu_3)_2ZnCl_2]_n$	Yellow		2152	122
$[Co(CN)_2(PMe_2Ph)_3]$	Red	2075, 2095		122
$[Co(CN)_2(PMe_2Ph)_3MnCl_2]_n$	Red		2085, 2110	122
$[Co(CN)_2(PMe_2Ph)_3FeCl_2]_n$	Red		2090, 2110	122
$[Co(CN)_2(PMe_2Ph)_3CoCl_2]_n$	Green		2095, 2115	122
$[Co(CN)_2(PMe_2Ph)_3NiCl_2]_n$	Violet		2105, 2125	122
$[Co(CN)_2(PMe_2Ph)_3ZnCl_2]_n$	Red		2100, 2120	122

[a] In Nujol mulls.



(iv)

P P = dpe; M′ = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}.

It is interesting to observe that in the last case coordinative ability is displayed by only one of the two cyanide groups of the donor complex $[Co(CN)_2(dpe)_2]^+$, which in this way behaves similarly to a monofunctional organonitrile[149]. This behaviour is in contrast with that of the complexes of categories (ii) and (iii) where the donor complexes $[M(CN)_2(PBu_3)_2]$ and $[Co(CN)_2(PMe_2Ph)_3]$ behave as dinitriles and generate polymeric chains.

As expected, the ν_{CN} stretching frequency in the adducts of the types (i)–(iii) is higher than in the donor complexes (Table 10). However, the single ν_{CN} absorption of the complex ion $[Co(CN)_2(dpe)_2]^+$ gives rise to two absorptions, one at a higher frequency, attributed to the bridged CN group, the other at a lower frequency ascribable to the ν_{CN} stretch of the terminal CN group[49].

Complex (iv) is an example of inorganic zwitterion in which the positive charge of the $[Co(CN)_2(dpe)_2]^+$ cation is balanced by the negative charge of an $M'X_3^-$ group.

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