*Inorganica Chimica Acta*, 9 (1974) 95–112
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# Invited Review
# Recent Advances in the Chemistry of Isocyanide Complexes

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Received October 4, 1973

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## 1. Introduction

The scope of the present review is to up-date the monography on "Isocyanide Complexes of Metals", which appeared in 1969.[131] Therefore references to material which was treated in the book are kept to a minimum, but are given each time they are required. The development of the field has been very encouraging, especially in view of the new and interesting results which are coming out continuously.

After the monography mentioned another book appeared in 1971 which is of interest to those active in this field.[215] This collection of valuable contributions is devoted mainly to organic chemistry, but inorganic and organometallic aspects are adequately covered up to *ca.* 1970.

## 2. The Ligands

### *A. Preparation of the Ligands*

Owing to their high reactivity towards polymerization, isocyanides are generally not commercially available. The classic laboratory methods[217,215,194] for obtaining reasonable amounts of pure isocyanides, namely the Hoffmann reaction, the reaction between silver cyanide and an alkyl halide, and the Ugi method,

$$\mathrm{Ar{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{EtOH} Ar{-}NC + 3\ KCl + 3\ H_2O}$$

$$\mathrm{AgCN + C_2H_5I \xrightarrow[\text{2) decomp. with KCN}]{\text{1) sealed tube}} C_2H_5{-}NC}$$

$$\mathrm{R{-}NH{-}CHO \xrightarrow{dehydration} R{-}NC}$$

are now well established. The detailed preparation of a very large number of isocyanides can be found in recent monographies and includes also difunctional isocyanides, such as di-isocianides, $\alpha$-$\beta$-unsaturated and $\beta$-substituted isocyanides.

No new general method has been reported in the last years but several improvements of the classic methods have been described; they often represent an alternative, convenient route to a specific isocyanide.

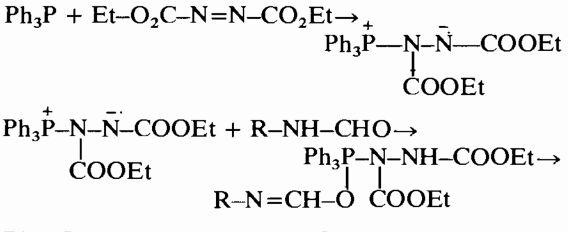
So the Hoffmann reaction which has never enjoyed popularity because the yields are generally moderate and the isocyanides obtained often contain unreacted amine, can be improved by employing the phase transfer catalysis method of generating dihalocarbene from $CHX_3$ (X = Cl, Br) and 50% aqueous NaOH.[226,227] Although the yield may be not as high as in the Ugi reaction, the preparation is convenient, e.g. for ethyl isocyanide, because affords a pure product in one step from an aqueous amine.

Improvements were suggested also for the reaction of silver cyanide: the use of dicyanoargentate(I)[196] in place of AgCN was recommended to obtain methyl or benzhydryl isocyanide in good yields. The classic reaction of AgCN was used also to prepare the unusual benzenediazoisocyanides, Ar–N=N–NC.[201,202] The Ugi reaction, i.e. the dehydration of formyl derivatives of amines, can be carried out in several additional ways:

i) by reaction with triphenylphosphine, triethylamine and carbon tetrachloride,[11]

$$\mathrm{R{-}NH{-}CHO + Ph_3P + Et_3N + CCl_4 \rightarrow R{-}NC + Ph_3PO + CHCl_3 + Et_3NH^+\,Cl^-}$$

ii) with triphenylphosphine and diethyl azodicarboxylate (i.e. in absence of base),[33]



$$\mathrm{Ph_3P + Et{-}O_2C{-}N{=}N{-}CO_2Et \rightarrow Ph_3\overset{+}{P}{-}\underset{\substack{|\\ COOEt}}{N}{-}\overset{-}{N}{-}COOEt}$$

$$\mathrm{Ph_3\overset{+}{P}{-}\underset{\substack{|\\ COOEt}}{N}{-}\overset{-}{N}{-}COOEt + R{-}NH{-}CHO \rightarrow \underset{\substack{|\\ R{-}N{=}CH{-}O}}{Ph_3P}{-}\underset{\substack{|\\ COOEt}}{N}{-}NH{-}COOEt \rightarrow}$$

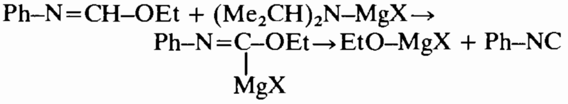
$$\mathrm{Ph_3PO + Et{-}O_2C{-}NH{-}NH{-}CO_2Et + R{-}NC}$$

iii) with a dimethylformamide solution of chlorodimethylformamidinium chloride (Vilsmeier reagent) prepared *in situ*,[225]

$$\mathrm{SOCl_2 + HC({=}O)NMe_2 \rightarrow [Me_2N{=}CHCl]^+\,Cl^- + SO_2}$$

$$\mathrm{R{-}NH{-}CHO + [Me_2N{=}CHCl]^+\,Cl^- \rightarrow R{-}NC + Me_2N{-}CHO \cdot HCl}$$

other new reactions include the action of an "amido-Grignard"[164] reagent on an alkyl N-arylformimidate or the alkylation, by means of a lithium compound, of an isocyanide with an $\alpha$-hydrogen atom:[228]



$$\mathrm{Ph{-}N{=}CH{-}OEt + (Me_2CH)_2N{-}MgX \rightarrow Ph{-}N{=}\underset{\substack{|\\ MgX}}{C}{-}OEt \rightarrow EtO{-}MgX + Ph{-}NC}$$

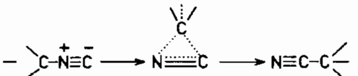
$$\mathrm{CH_3NC + BuLi \xrightarrow[-78^\circ]{THF/hexane} LiCH_2NC \xrightarrow[80\%]{Me_3SiCl} Me_3Si{-}CH_2{-}NC \rightarrow}$$

$$\mathrm{\xrightarrow[2)\ Me_3SiCl]{1)\ BuLi} (Me_3Si)_2{-}CH{-}NC \xrightarrow{\mathit{idem}} (Me_3Si)_3{-}C{-}NC}$$

Optically active isocyanides, e.g. $\alpha$-phenylethyl isocyanide, 2-phenyl-2-isocyanopropane,[230,231] were prepared from the formyl derivatives and used as ligands.[49,50]

### *B. Stability of the Ligands*

No study on the stability and on the problem of the storage of isocyanides is available, although mention is made of the instability of certain terms, e.g. phenyl isocyanide,[105] t-butyl isocyanide,[118] *p*- and *m*-fluoro phenylisocyanide.[221] Some additional data can be obtained from a review on the polymerization of isocyanides.[138] In addition to the extensive studies by Rabinovitch[215] on the isocyanide–cyanide isomerization, the thermal conversion of methyl-isonitrile to acetonitrile was studied from the theoretical point of view.[84,128,129] The thermal rearrangement of isocyanides has been considered a typical unimolecular reaction proceeding through a transition state like (*), with retention of the configuration at the asymmetric carbon atom involved:



(*)

Additional experimental evidence was obtained by examining the thermal rearrangement of some of the optically active isocyanides mentioned above. Here the reaction proceedes by means of a radical mechanism and racemization does occur.[230,231]

Quantitative data[127] are available on the acid-catalyzed solvolysis of isonitriles, which yield, in the case of methyl isocyanide, N-methylformamide and, later, methylamine and formic acid at a much slower rate.

## 3. Complexes Containing Terminal Isocyanides

### *A. Preparation*

The general methods for preparing isocyanide complexes are:

(i) The reaction between a metal derivative, often a halide, and the ligand, generally in the presence of a solvent in order to dissipate the heat of reaction and to prevent alteration of the isocyanide; sometime a reducing agent is added or the ligand itself acts as a reducing agent.

(ii) Displacement of another ligand, such as carbon monoxide, olefin, bridging halide or ammonia.

(iii) Alkylation of a cyanometallate with an alkyl halide.

Recent developments do not include any new general method, although some improvement or extension of the known methods is worth reporting. So alkylation of silver octacyanomolybdate(IV) afforded[151] molybdenum(IV) complexes, as well as other products, thus substantiating older reports.[109] In another case,[124] alkylation was carried out on a neutral, instead of an anionic complex, and a methyl isocyanide derivative was formed at a relatively high temperature (80–100° C):

$$\mathrm{(Ph_3P)_2Pt(CN)_2 + 2\,MeI \rightarrow (MeCN)_2PtI_2 + 2\,Ph_3P}$$

In the attempted alkylation of some hexacyanometallate(II), cationic $\gamma$-oxo-isocyanocomplexes were obtained smoothly:[188]

$$\mathrm{[M(CN)_6]^{4-} + 12\,Me_2CO + 6\,R_3O^+BF_4^- \xrightarrow{20^\circ\,C,\ acetone} [M(CN{-}CMe_2{-}CH_2COCH_3)_6]^{2+}(BF_4^-)_2 + 4\,BF_4^- + 6\,R_2O + 6\,ROH}$$

(M = Fe, Ru, Os)

Alkylation with methyl trifluorosulphonate or triethyloxonium fluoborate is successful in the case of $(Ph_3P)_2M(CN)_2$ (M = Ni, Pd, Pt), $K_3[Fe(CN)_6]$, and of $K[Mn(CN)_5(NO)]$ affording $[(Ph_3P)_2M(CNR)_2]^{2+}$, $[Fe(CN)\cdot(CNMe)_5]^{2+}$, and $[Mn(NO)(CNMe)_5]^{2+}$ respectively.[87]

Other preparations are known, but their general usefulness is still to be tested. The reaction of iron or molybdenum carbonyl with an N-tolylphosphineimine affords[9] the corresponding isocyanide complex:

$$Ar{-}N{=}PPh_3 + Fe(CO)_5 \xrightarrow{\text{THF, reflux}} Fe(CO)_{5-x}(CO)_x + Ph_3PO (x = 1,2)$$

The pattern is related to that of another reaction involving aryl isocyanate:[218]

$$Ar{-}NCO + Fe(CO)_5 \rightarrow (Ar{-}NC)Fe(CO)_4 + CO_2$$

The reaction of a carbene complex with hydrazoic acid[69] affords a mixture of isocyanide and nitrile complex, the latter being the minor product:

$$[Me_3SiCH_2{-}CO \rightarrow Cr(CO)_5]^- + HN_3 + MeCOCl \xrightarrow{0^\circ C} (CO)_5Cr(CN{-}Me) + (CO)_5Cr(NC{-}Me) + \ldots$$

### B. New Compounds Obtained

#### (i) Transition elements

Among the most recent complexes of isocyanides some contain a metal which had not been reported to bind this ligand, at least in the oxidation state under consideration; others are examples of uncommon coordination numbers, for the element under consideration; others contain homogeneous or heterogeneous metal–metal bond(s); and a few derive from optically active ligands.

Thorium, uranium, and osmium isocyanide complexes had been unreported. Thorium tetraiodide reacts with cyclohexyl isocyanide and moisture-sensitive $ThI_4(CN{-}R)_4$ is formed,[130] quite similar to $UI_4(CN{-}R)_4$. The compounds are the first isocyanide complexes of actinoids that do not contain stabilizing $\pi$-ligands, such as found in $(h^5\text{-}C_5H_5)_3U(CN{-}C_6H_{11})$.[120] By reduction of $OsX_3(PR_3)_3$ with zinc in the presence or methyl or phenyl isocyanide yellow $OsX_2(CN{-}R)(PMe_2Ph)_3$ was obtained,[58] which isomerized slowly in benzene solution to the pale green *fac*-isomer. The yellow isomer could be oxidized by clorine to the trivalent state, $[OsCl_2(CN{-}Me)(PMe_2Ph)_3]^+Cl^-$.

Isocyanide derivatives of chromium(O) are well established. Nevertheless, while investigating the infrared spectrum of a purified sample of $Cr(CN{-}Ph)_6$, the band at highest frequency (2065 $cm^{-1}$) was found to be due to another compound, in agreement with a published suggestion.[38] This compound is formed in the solution used for the spectrum and can be prepared satisfactorily by oxidation with iodine of the solution in dichloromethane.[96] The compound, $Cr(CN{-}Ph)_5I$, can be converted to air-stable, golden crystals by reaction with sodium tetraphenylborate, $[Cr_2(CN{-}Ph)_{10}]^{2+}(BPh_4^-)_2$. On the basis of vibrational spectroscopy a centrosymmetric structure with two bridging isonitrile groups was suggested for the cation, which is the first reported example of chromium(I) with isocyanides.

Palladium(I) and nickel(I) isocyanide complexes had been unreported. Reaction of $Pd(CN{-}CMe_3)_2$ with $Pd(CN{-}CMe_3)_2X_2$ gave yellow, stable, and chlorine bridged $(R{-}NC)_4Pd_2X_2$.[156] The bridge cannot be broken by 1,2-bis(diphenylphosphino)ethane (DPE), which gives $[(DPE)PdI]_2$, nor with triphenylphosphine, which gives $[(R{-}NC)(Ph_3P)PdI]_2$; the behaviour is quite different from that of palladium(II) halide-bridged complexes. Nickel(I) complexes were obtained by reaction of ClCOPh with $Ni(CN{-}R)_4$, brown, paramagnetic "$NiCl(CN{-}CMe_3)_2$" being formed,[158] or, without doubt, in the case of $[(h^5\text{-}C_5H_5)Ni(CN{-}Me)]_2$,[6,7] for which a structural determination was carried out. Although nickel(I) compounds are stable, attempts to react Bellucci's salt with isocyanide caused disproportionation:[148,149]

$$K_4[Ni_2(CN)_6] + 4\ R{-}NC \xrightarrow{\text{liquid } NH_3} K_2[Ni(CN)_4] + Ni(CN{-}R)_4 + 2\ KCN$$

Although nickel(II) compounds are known to be good catalysts for the homogeneous polymerization of isocyanides,[150] carefully controlled experimental conditions allowed octahedral $[Ni(t\text{-}Bu{-}NC)_4(H_2O)_2](ClO_4^-)_2$ and planar $NiCl_2(t\text{-}Bu{-}NC)(EtOH)$ to be obtained in good yields.[199,200]

Zerovalent isocyanide derivatives have been known in the case of nickel and of palladium, while those of platinum were obtained only recently by the reactions:[124,113]

$$(Ph_3P)_2Pt(C_2H_4) + 2\ R{-}NC \rightarrow C_2H_4 + (Ph_3P)_2Pt(CN{-}R)_2$$

$$(Ph_3P)_2Pt(CN{-}R)_2 + CO \rightarrow CN{-}R + (Ph_3P)_2Pt(CN{-}R)(CO)$$

$$M(PF_3)_4 + CN{-}R \rightarrow (PF_3)_3M(CN{-}R) + PF_3$$

Very many complexes of copper have been known, including derivatives of allenyl and propargyl isocyanide[238] and $C_5H_5Cu(CN{-}R)$,[74] but only recently copper(II) derivatives[198] were reported, namely $[Cu(CN{-}R)_4(H_2O)_2]^{2+}\ 2X^-$, where $R = Me_3C$ or $Me_2CCH_2CMe_3$ and $X = BF_4$ or $ClO_4$. They are purple, paramagnetic, and rather unstable; they are obtained as insoluble precipitates.

Isocyanide ligands sometimes allow a high coordination number to be reached. While platinum(II) is generally four-coordinate, five-coordinated complexes[210,124,43] can be obtained with these ligands:

$$\left.\begin{array}{l}[Pt(CN{-}Me)_2(PPh_3)_2]^{2+} + X^- \\ PtX_2(PPh_3)_2 + Me{-}NC\end{array}\right\rangle \longrightarrow [PtX(CN{-}CH_3)_2(Ph_3P)_2]^+X^-$$

$$Pt(CN{-}CMe_3)_2(PPh_3)_2 + X{-}Y \rightarrow [Pt(CN{-}CMe_3)_2(Ph_3P)_2X]^+\ Y^-$$

$(X{-}Y = I_2, MeI, CF_3I, Ph_3SnCl)$

$$(Ar{-}NC)_2PtCl_2 + p{-}FC_6H_4NH_2 \rightarrow Cl_2Pt[C(NH{-}Ar)(NH{-}C_6H_4F)](CN{-}Ar)(NH_2C_6H_4F)$$

Coordination number eight is reached in the Mo $(CN{-}R)_4(CN)_4$ complexes for which a triangular dodecahedral stereochemistry was ascertained in all cases investigated.[151,56,163] Coordination number seven[152,37] is present in several other molybdenum(II) complexes, $[Mo(CN{-}R)_7]^{2+}$, $[Mo(CN{-}R)_6X]^+$, and $Mo(CN{-}R)_5X_2$.

Recent results include many adducts between cobalt(III) or iron(II) derivatives of planar, polycyclic ligands, like N,N'-ethylenbis(salicylideniminato) (saen), dimethylglyoximato (DH) or dibenzylglyoximato (BH) groups. The compounds obtained are related to the problem of vitamin $B_{12}$ and in some case were studied on this account; they include $PhFe(saen)(C_6H_{11}NC)$, $PhCH_2Fe(saen)(C_6H_{11}NC)$,[94] $MeCo(DH)_2(CN{-}Me)$,[107] various cationic $[Co(BH)_2(C_6H_{11}NC)_2]^+$, $[Co(DH)_2(CN{-}R)_2]^+$ and neutral $Co(DH)_2X(CNR)$ derivatives.[1,2,3,4,28]

### *(ii) Typical elements*

Although no isocyanide complex is known where the metal belongs to group IA or IIA, the interaction of the ligand with the organic derivatives of these two groups, e.g. lithium or magnesium alkyls, was studied in detail. The behaviour towards other related species, like lithium hydride, was also examined.

Unless another and more reactive group is present in the isocyanide molecule, the organometallic compound gives an $\alpha,\alpha$-adduct, which mostly dimerizes or reacts with an excess of isocyanide according to the scheme:[216]

$$\begin{tikzcd} R{-}NC + R'{-}MgX \arrow[r] & R{-}N{=}CR'{-}MgX \arrow[r, "R{-}NC"] \arrow[d, "dimerization"] & R{-}N{=}CR'{-}C(MgX){=}N{-}R \\ & R{-}N(MgX){-}C(R'){=}C(R'){-}N(MgX){-}R & \end{tikzcd}$$

The same pattern, accompanied by additional reactions, is actually observed in the action of lithium alkyls on cyclohexyl, phenyl, or $p$-tolyl isocyanide, while in the especially designed 1,1,3,3-tetramethylbutyl isocyanide only $\alpha,\alpha$-addition is possible, with both lithium and Grignard reagents, affording a metal derivative of an aldimine, a versatile reagent:[223,224]

$$R{-}NC + R'M \rightarrow R{-}N{=}C^-{-}R'\ M^+$$

$(R' = \text{alkyl, hydrogen}; M = Li, Mg{-}X)$

When an active hydrogen is available, and the isocyano group activates any hydrogen atom in the $\alpha$-position, it can be exchanged:

$$R_2CH{-}NC + LiR' \rightarrow R_2C^-{-}NC\ Li^+ + R'H$$

This indeed is observed in the case of cyclohexyl,[195] methyl,[189] $\alpha$-carboalkoxymethyl,[190] or mono- and bis-trimethylsilyl isocyanide.[228] Even one of the hydrogens of the methyl group of $p$-tolyl isocyanide can be exchanged with lithium, while lithium alkyls add on the double bond of $o$- or $p$-isocyanostyrene.[195]

Two types of remarkable compounds were obtained by interaction of boron derivatives with isocyanides. Boron trihalides are good Lewis acids and they reacted with a complex as follows:[106]

$$trans\text{-}[Fe(CN{-}R)_4(CN)_2] + 2\ BX_3 \rightarrow trans\text{-}[Fe(CNR)_4(CN{\rightarrow}BX_3)_2]$$

$R = Me, Et; X = F, Cl$

The reaction of isocyanides with diorgano(alkylmercapto)boranes is rather complex[104] and is summarized in the scheme on the opposite page.

When $R = Ph$ and $R' = Me_2CH$ or $C_6H_{11}$ the 1:1 adduct (A) was isolated. In the other cases it added a second mole of $Et_2BSR$, yielding through an intermediate isothioformamidoborane, (B), not isolated, either (C) or (D). Compound (C) could be rearranged thermally to (D) which is very stable.

Amongst the remaining typical elements, new ionic zinc(II) derivatives were mentioned, e.g. $[Zn(CN{-}CMe_3)_4](ClO_4)_2$.[200]

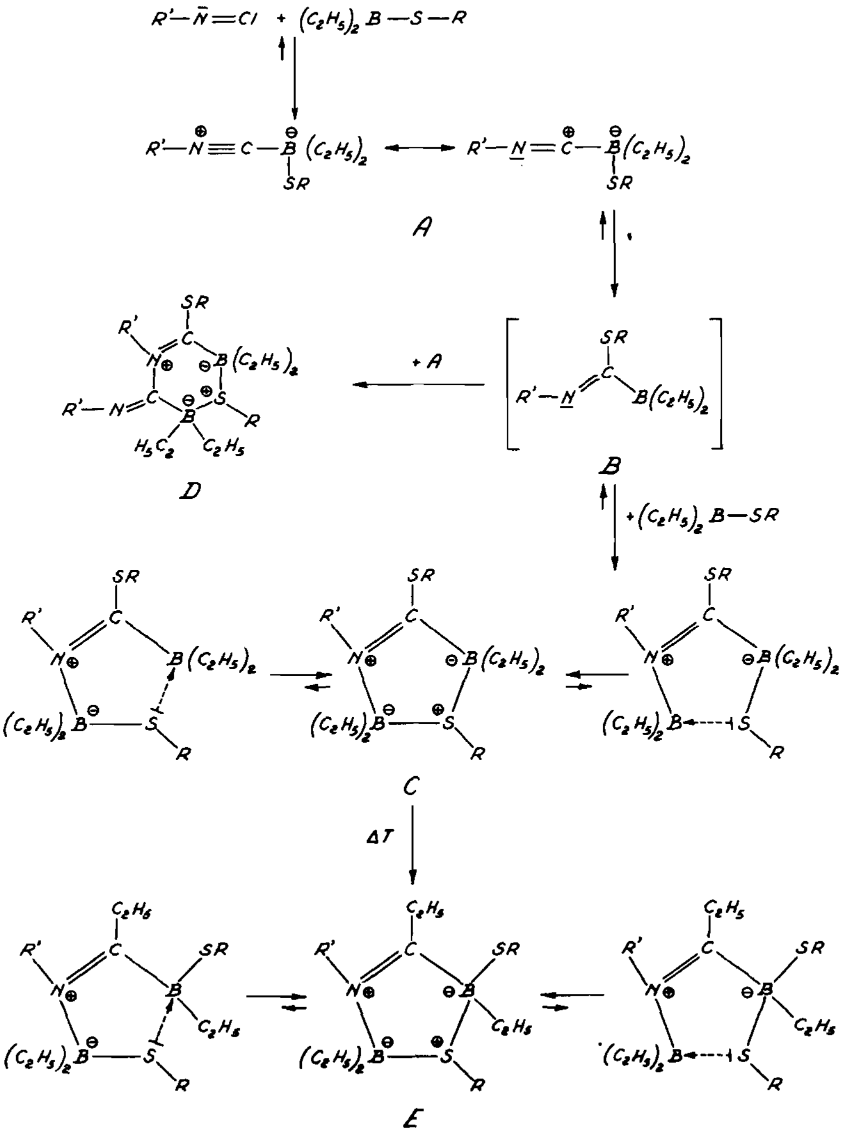
### *(iii) Optically active compounds*

Amongst the new complexes obtained mention has to be made of the optically active isocyanide derivatives, investigated by Brunner.[49,50] When four different ligands surround tetrahedrically a metal atom, optical antipodes can exist, at least in principle. In the compounds $(h^5\text{-}C_5H_5)Fe(CO)(CN{-}R)I$ and $(h^5\text{-}C_5H_5)Mo(CO)(NO)(CN{-}R)$ the group R is optically active, e.g. $\alpha$-methylbenzyl; diastereoisomers are formed and they can be separated by fractional crystallization, because they are stable in the dark and in the absence of additional ligand. In the case of molybdenum complex a Walden-type inversion at the asymmetric metal atom was also observed.

### *(iv) Complexes containing metal–metal bond(s)*

Isocyanide complexes containing metal–metal bond(s) can be divided into three classes: those having a homonuclear metal–metal interaction, i.e. a weak metal–metal bond; those having a true homonuclear bond, with or without bridging ligands; those having a heteronuclear metal–metal bond.

Certain isocyanide, like phenyl or $p$-tolyl isocyanide, are fairly flat molecules. Consequently in the products of the reaction between these molecules and potassium



tetrachloroplatinate(II) a metal–metal interaction between cations and anions, $[Pt(CN\text{–}R)_4]^{2+}$ and $[PtCl_4]^{2-}$ respectively, is possible. Such an interaction, analogous to that established in Magnus' Green Salt, explains the intense colours observed when R = Ph or *p*-tolyl. Coherently, salts deriving from cyclohexyl or other aliphatic isocyanides are pale red, the colour of the $[PtCl_4]^{2-}$ ion, because there is no metal–metal interaction.[36]

Homonuclear Pd–Pd bonds were evidenced by single crystal X-ray analysis on di-$\mu$-(sulphur dioxide)-pentakis(t-butyl isocyanide)*triangulo*-tripalladium,[159] obtained from sulphur dioxide and $Pd(CNR)_2$ and originally formulated as a dimeric 1 : 1 adduct.[153] The Pd–Pd bonds are not equal, the two with $SO_2$-bridge being shorter than the other.

All the other isocyanide complexes containing a metal–metal bond are carbonyl or cyclopentadienyl derivatives. Often the metal–metal bond is accompanied by bridging carbonyl or isocyanide groups. The metal involved are iron, cobalt, nickel, molybdenum and rhodium; representative compounds are listed in Table I.

TABLE I. Compounds with homonuclear metal–metal bond(s)[a]

| Compound | Reference |
|---|---|
| $[\mathrm{CpNi(CNR)}]_2'$ | 6, 7, 232 |
| $\mathrm{CpMo(CO)_3{-}Mo(CO)_2(CNMe)Cp}$ | 5 |
| $\mathrm{CpFe(CO)_2{-}Fe(CO)(CN{-}CMe_3)Cp}$ | 112 |
| $\mathrm{CpFe(CO)_2{-}Fe(CO)(CNMe)Cp}$ | 206 |
| $\mathrm{CpFe(CO)(\mu\text{-}CO)Fe(CO)(\mu\text{-}CNPh)Cp}$ | 115 |
| $[\mathrm{(R{-}NC)_mCo_2(CO)_{8-m}}]$ (m = 1, 2, 3) | 47 |
| $\mathrm{Co_4(CO)_{12-n}(\mathit{p}\text{-}MeC_6H_4{-}NC)_n}$ (n = 1, 4) | 186 |
| $\mathrm{Rh_4(CO)_{12-p}(\mathit{p}\text{-}MeC_6H_4{-}NC)_p}$ (p = 1, 2, 4) | 186 |
| $\mathrm{Rh_6(CO)_{10}(\mathit{p}\text{-}MeC_6H_4{-}NC)_6}$ | 186 |

[a] Cp indicates $h^5$-$\mathrm{C_5H_5}$.

The complexes with a heteronuclear metal–metal bond include generally tin or mercury. They are generally prepared by insertion or exchange reaction or through oxidative addition:[41,78,45,167,168,83,23,99]

$$\mathrm{M(CN{-}R)(carbene)Cl_2 + SnCl_2 \rightarrow M(CN{-}R)(carbene)(SnCl_3)_2}$$

(carbene is RO–C–NHR′ or R–NH–C–NHR′ and M = Pd, Pt)

$$\mathrm{Pd(CN{-}R)_2Cl_2 + 2\ CsGeCl_3 \rightarrow 2\ CsCl + (R{-}NC)_2Pd(GeCl_3)_2}$$

$$[\mathrm{M(CN{-}R)_4}]^+ + \mathrm{X{-}Y} \rightarrow \mathit{trans}\text{-}[\mathrm{M(CNR)_1XY}]^+$$

where X–Y indicates mercury(II) chloride, tin(IV) chloride, triphenylchlorotin(IV) and M is rhodium or iridium.

*(v) Complexes of ligands which have not been common with isocyanides*

Isocyanides have been used together with many other ligands, including carbon monoxide, nitric oxide, phosphines, phosphites, arsines, cyclopentadienyl. Recent results include the preparation of complexes containing additional types of ligands: hydrides, $\mathrm{PF_3}$, $\mathrm{SO_2}$, monodentate perchlorate, many unsaturated ligands and carbenes.

The hydrido containing isocyanide complexes could not be obtained by reduction with a hydride; they can be obtained indirectly, generally by addition of R–NC to coordinatively unsaturated molecules, by displacement of another ligand or by protonation:[12,13,132,133,134,63,62,83]

$$\mathrm{IrH_3(AsPh_3)_2 + R{-}NC \rightarrow Ir(AsPh_3)_2(R{-}NC)H_3}$$

$$\mathrm{IrH_3(AsPh_3)_2(R{-}NC) + H{-}X \rightarrow H_2 + IrH_2Cl(AsPh_3)_2(R{-}NC)}$$

$$\mathrm{IrH_5(PEt_2Ph)_2 + Me{-}NC \rightarrow H_2 + IrH_3(PEt_2Ph)(CN{-}Me)}$$

$$\mathrm{RhHCl_2(t\text{-}BuPPr_2)_2 + Me{-}NC \rightarrow RhHCl_2(t\text{-}BuPPr_2)_2(CN{-}Me)}$$

$$\mathrm{RuHCl(CO)(PPh_3)_3 + R{-}NC \rightarrow Ph_3P + RuHCl(CO)(CNR)(PPh_3)_2}$$

$$\mathrm{RuHCl(CO)(CN{-}R)(PPh_3)_2 + AgClO_4 \rightarrow RuH(OClO_3)(CO)(CN{-}R)(PPh_3)_2}$$

Another monodentate perchlorate group[38] can be found in the complex obtained by reaction of iron(II) perchlorate with aryl isocyanide *(caution: with iron(III) perchlorate an explosion resulted)*:

$$[\mathrm{Fe(H_2O)_6}](\mathrm{ClO_4})_2 + 5\ \mathrm{Ar{-}NC} \rightarrow [\mathrm{Fe(CN{-}Ar)_5(OClO_3)}]\mathrm{ClO_4 \cdot H_2O}$$

Although it contains six-coordinate iron(II) and should consequently be coordinatively saturated, the oxygen bonded perchlorate is labile and the complex behaves as it were unsaturated:[42]

$$[\mathrm{Fe(CN{-}Ar)_5(OClO_3)}]^+ + \text{ligand} \rightarrow [\mathrm{Fe(CN{-}Ar)_5}(\text{ligand})]^{2+} + \mathrm{ClO_4}^-$$

The ligand may be phosphines, arsines, stibines, nitriles, halides, and even isonitrile, so that a complex containing two different isocyanides can be obtained, e.g. $[\mathrm{Fe(CN{-}Ar)_5(CN{-}C_6H_{11})}](\mathrm{ClO_4})_2$. All these mixed complexes are very stable and the iron–ligand bonds are not easily broken. Complexes with other ligands which have been unusual together with isocyanides include $\mathrm{M(PF_3)_3(CN{-}R)}$, (M = Ni, Pt)[113] and $\mathrm{SO_2}$ complexes of nickel and palladium, $\mathrm{Ni(SO_2)(t\text{-}BuNC)_3}$,[153] $(\mu\text{-}\mathrm{SO_2})_2(\mathrm{t\text{-}Bu{-}NC})_5\mathrm{Pd_3}$,[159] as well as of rhodium(I).[83]

Complexes with unsaturated ligands include olefins[160,161,46] or $p$-quinones:[166]

$$\mathrm{Pd(CN{-}Ph)_2} + \text{ligand} \rightarrow \mathrm{Pd(CN{-}Ph)_2}(\text{ligand})$$

$$\mathrm{Pd(CN{-}Ph)_2[(NC)_2C{=}C(CN)_2] + Ph_3P \rightarrow Pd(CN{-}Ph)_2[(NC)_2C{=}C(CN)_2](Ph_3P)}$$

Generally a 1:1 adduct is formed whereas a 1:2 adduct is formed with tetrachloro-$p$-benzoquinone. Other unsaturated ligands may be present with isocyanides: diazoalkanes,[153,157] perfluorodiazoalkanes[67] (and products arising from their rearrangement), azobenzene,[160,86] nitrosocompounds,[153] etc. Sometimes the unsaturated ligand reacts with the isocyanide under the catalytic influence of the metal complex:[85] reaction of diphenylacetylene and an arylisocyanide complex gave 1,2-diarylimino-3,4-diarylcyclobut-3-ene.[204] Complexes containing carbene ligands will be treated further on.

## 4. Complexes Containing Bridging Isocyanide Ligand(s)

Apart from the complex $[(h^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2{-}Fe(CO)(CNC_6H_5)}(h^5\text{-}\mathrm{C_5H_5})]$ for which the presence of a bridging isocyanide has been proved by an X-ray structure determination,[115] little was known about the possibility of the isocyanide to act as a bridging group. On the basis of i.r. evidence, a bridging structure has been suggested also in the case of $[(h^5\text{-}\mathrm{C_5H_5})\mathrm{Ni(CNPh)}]_2$, while the related $[(h^5\text{-}C_5H_5)Ni(CNC_6H_{11})]_2$ was reported to have a bridging structure in the solid state and to exist in solution as an equilibrium mixture of bridged and non bridged isomers.[232] Since it was of interest to establish if isonitriles ligands may give rise in solution to equilibria between bridging and non-bridging groups, similar to that established in the case of the carbonyl groups, new complexes of the series $[(h^5\text{-}C_5H_5)Ni(CNR)]_2$, ($R = CH_3$, $CD_3$, $CH(CH_3)_2$) were prepared and the problem was reinvestigated.[6] On the basis of more accurate infrared data and, in the case of $[(h^5\text{-}C_5H_5)Ni(CNCH_3)]_2$ of an X-ray structure determination, it was concluded that all these dimers, both with aryl and alkyl isocyanides, exist only in the bridged forms, and no equilibrium between isomers was detected. The non existence of such an equilibrium does not exclude however the possibility of a dynamical rearrangement of structures in solution. Indeed, recently, it has been proved[5] that the isocyanide ligand in solution has a mobility similar to that of the carbonyl groups.

## 5. Reactions of Isocyanide Complexes

### *A. Oxidation and Reduction*

The isocyanide complexes can be oxidized by halogens or nitric acid, or by oxidative addition reaction, or anodically.

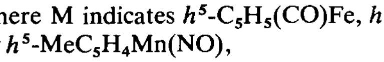
The oxidative addition and the electrochemical oxidation are treated in section 5B and 5C resp.; the chemical oxidation is often successful and was used to prepare osmium(III)[58], manganese(II),[147] or chromium(I)[96] from the corresponding osmium(II), manganese(I) or chromium(O) complexes. The successful oxidation suggests that the complexes involved are not labile, i.e. that the equilibrium of the type

$$M(CNR)_m{}^{n+} \rightleftarrows M(CNR)_{m-1}{}^{n+} + CNR$$

is not displaced forward. If this were true, then the isocyanide should be oxidized very quickly, yielding isocyanide dihalide or isocyanate. Isocyanides are good reducing agents and, therefore, they and their complexes are reduced only with difficulty.

Reduction of isocyanide complexes was attempted and two pathways are reported:

i) addition of the reducing agent, $BH_4^-$, across the $C{\equiv}N$ bonds in the coordinated isocyanide ligands, i.e.:[54,212]



where M indicates $h^5\text{-}C_5H_5(CO)Fe$, $h^5\text{-}C_5H_5Mo(CO)_2$ or $h^5\text{-}MeC_5H_4Mn(NO)$,

ii) fragmentation of the isocyanide ligand. So, reduction of *cis*-$PtCl_2(CNPh)(PEt_3)$ by borohydride ion gave[16,17] methane, ethane, and ethylene, all originating from the carbon atom of the isonitrile, as they do from enzymatic reactions. The same reduction to hydrocarbon by means of borohydride was obtained[191,192,193] using a homogeneous catalyst system composed of a molybdate and a thiol component, probably by multielectron reduction steps. The conventional reduction of a metal complex by an isocyanide in alkaline alcohol did not yield other low-valent metal complexes, in addition to those already obtained, e.g. $Pd(CNR)_2$. This reaction system afforded new types of complexes:[140,144,139,141,143]

$$(Ph_3P)AuCl \xrightarrow{\text{KOH, ROH, Ar–NC}} (Ph_3P)Au\text{–}C(OR){=}NAr$$

$$(Ph_3P)AuCl \xrightarrow{\text{KOH, ROH, } C_6H_{11}\text{–NC}} [Au\text{–}C(OR){=}NC_6H_{11}]_3$$

$$(Ph_3P)_2PtCl_2 \xrightarrow{\text{KOH, ROH, Ar–NC}} (Ph_3P)(Ar\text{–}NC)Pt\text{–}[\text{–}C(OR){=}NAr]_2$$

$$(RNC)AgCl \xrightarrow{\text{KOH, ROH, R'NC}} [Ag\text{–}C(OR){=}NR']_3$$

$$(Ph_3P)_2HgCl_2 \xrightarrow{\text{KOH, ROH, R'NC}} Hg\text{–}[\text{–}C(OR){=}NR']_2$$

### *B. Oxidative Addition Reactions*

Oxidative addition reactions have been extensively investigated to establish the influence of the ligands surrounding the metal ion and to predict the stereochemistry of the resulting molecule. Although most studies have involved phosphine or carbonyl complexes of $d^8$ ions, recent results include isocyanide and isocyanide containing complexes. Generally it is found that increasing the $\sigma$-basicity and/or decreasing the $\pi$-ability a greater stability of the oxidized product is observed: it should be remembered that isocyanide are moderately good $\sigma$-donor ligands and are probably intermediate between $PR_3$ and CO as $\pi$-acceptors.

Correspondingly more oxidative addition reactions on square-planar rhodium(I) or iridium(I) isocyanide complexes are observed than in the corresponding carbonyl complexes.

The complexes investigated include square-planar $[(RNC)_4Rh]^+$,[162,48,23,83] *trans*-$[(RNC)_2(R_3P)_2Rh]^+$,[162] *trans*-$[(RNC)_2Rh(CO)X]$,[162] $(Ph_3P)_2(MeNC)RhCl$,[23] five-coordinated $[(Ph_3P)_2M(CNR)_3]^+$[83] ($M = Rh$, Ir), and $[Ir(CNMe)\{(Ph_2PCH_2)_2\}_2]^+$.[32] The oxidizing agent may be a halogen, an alkyl halide, mercury(II) halide, tin(IV) tetrachloride, oxygen (reversibly).[23] The addition is rather solvent-dependent and takes place in the axial, mutually *trans* positions in the case of four-coordinate complexes.

In the five coordinated starting compounds oxidative addition takes place without loss of any of the existing ligand when a chelating ligand is present e.g. in the case of $[Ir(CNMe)(dpe)_2]^+$ while the reaction pathway is less predictable in the other cases:

$$[L_4M]^+ + X\text{–}Y \rightarrow [L_4MXY]^+$$
$$[LIr(dpe)_2]^+ + X\text{–}Y \rightarrow [LIrX(dpe)_2]^+Y^-$$
$$[(Ar_3P)_2Ir(CNR)_2]^+ \rightarrow [(Ar_3P)_2Ir(CNR)_3X]^{2+} \rightarrow$$
$$[(Ar_3P)Ir(CNR)_3X_2]^+ \rightarrow \{[Ir(CNR)_3X_2]_2\}^{2+}$$

Oxidative addition reactions are not limited to $d^8$ ions.

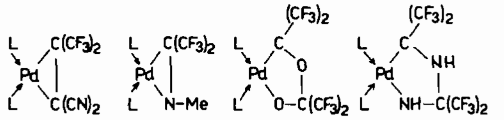
Zerovalent isocyano complexes of platinum,[124] palladium,[46,156,88] and nickel,[156,101,102] i.e. $d^{10}$ ions, undergo such reaction and the corresponding square planar divalent metal derivatives are obtained smoothly, e.g.[124]

$$Pt(CNR)_2(PAr_3)_2 + X\text{–}Y \rightarrow [(RNC)_2(Ar_3P)_2PtX]^+\,Y^-$$

although with nickel(O) more complicate reactions may follow.[158]

The group X–Y may range from an alkyl halide or an organo-element halide, to a halogen, oxygen or tetracyanoethylene.

With fluorinated hydrocarbons the reaction offers interesting results. Two type of products were obtained:[101,102] besides the ones arising from the regular oxidative addition, e.g. $(t\text{-}BuNC)_2Pd(CF_2{=}CF_2)X$, other products having a cyclic palladium or nickel containing ring, are formed



from Pd $(t\text{-}BuNC)_2$ and $(CF_3)_2C{=}C(CN)_2$, hexafluoropropylidenemethylamine, hexafluoroacetone and hexafluoropropylidenamine.

Oxygen complexes of isocyanide include nickel, palladium, ruthenium and rhodium derivatives: $M(O_2)(t\text{-}BuCN)_2$ (M = Pd, Ni),[153,154] $RhX(O_2)L_2(t\text{-}BuNC)$ (X = Cl, Br; L = $Ph_3P$, $Ph_3As$), $Ru(O_2)(CO)(CNR)PPh_3)_2$[62,63] and $RhX(O_2)(PPh_3)_2(RNC)$, $RhCl(O_2)(Ph_3As)_2(t\text{-}BuNC)$, $[Rh(O_2)(PPh_3)_2(t\text{-}BuNC)_2]Cl$.[145] Some of the rhodium complexes hold dioxygen irreversibely, while others do that reversibely. Spectroscopic studies[146] have shown that the dioxygen molecules is coordinated "side-on" and not "end-on" as in the cobalt(II) complexes. Gold(I) has a $d^{10}$ configuration, but attemps to carry out oxidative-addition with iodine in dichloromethane failed with $[(p\text{-}CH_3C_6H_4NC)_2Au]ClO_4$, while it succeeded[142] with the corresponding carbene $\{[(p\text{-}CH_3C_6H_4NH)_2C]_2Au\}^+$, in agreement with a better $\sigma$-donor character of the carbene group.

### C. Electrochemical Investigations

Polarographic studies[122] were carried out on $[(MeNC)_5Co](NO_3)_2$. Electrochemical oxidation was studied in the case of manganese,[207,208] chromium[208,70,135] and molybdenum[135] complexes of the types $[(RNC)_6Mn]^+$, $[(RNC)_x(CO)_{6-x}Mn]^+$, $(RNC)_6Cr$, $M(CNR)_x(CO)_{6-x}$ (M = Cr, Mo), (n = 1–3).

The results obtained by the groups interested in the problem are in excellent agreement between themselves and with established ideas.[131] The oxidation of aryl isocyanide derivatives is more difficult, i.e. it takes place at higher $E_{1/2}$, than the oxidation of alkyl derivative. The effect of a substituent on the aryl group can be observed and predicted qualitatively.[70,135] The $E_{1/2}$ values decrease on increasing x in mixed isocyanide–carbonyl complexes, thus reflecting the stepwise replacement of a good $\pi$-acceptor by a less effective one (the isocyanide), in agreement with established results from i.r. spectra.

The electrochemical oxidation of $[Mn(CNR)_6]^+$ ions produces $Mn^{II}$ complexes, already available by oxidation with nitric acid or otherwise,[19] and gives evidence of manganese(III) species, which have not been isolated.

### D. Photochemical Reactions

Both the isocyanides and their complexes undergo photochemical reactions. The ligand can be photochemically isomerized to the corresponding cyanide, either in the gas phase[215] or in solution.[171,172] In the latter case the photo-induced isomerization of an arylisocyanide in methanol receives assistance from a strong electron donating substituent in the *para* position, while in aprotic solvents (dichloromethane, benzene, cyclohexane) the rearrangement was slowed down much.

Remarkable results are obtained through the action of light on four-coordinate iridium(I) cations, e.g.,[32]

$$\underset{\text{blue}}{[Ir(CNMe)_4]^+} + \text{ligand} \underset{\text{heat}}{\overset{h\nu}{\rightleftarrows}} \underset{\text{red–orange}}{[Ir(CNMe)_4(\text{ligand})]^+}$$

The forward reaction is likely to be the first example of photo-association, i.e. the photochemical formation of a metal-ligand bond, a possibility which had been recognized previously.[24] Another daylight-induced reaction is[32]

$$[Ir(CNMe)_4]^+ + (Ph_2PCH_2)_2 \rightarrow [Ir(CNMe)\{(Ph_2PCH_2)\}_2]^+$$

and the racemization[50] of (+)- or $[(-)\text{-}(h^5\text{-}C_5H_5)Fe(CO)(CNCHMePh)]^+I$. Photochemical decomposition of *cis*- and *trans*- $[Fe(CNMe)_4(CN)_2]$ was studied kinetically.[68]

### E. Insertion Reactions into Metal–Carbon, Metal-Nitrogen and Metal–Halogen Bonds

The insertion reaction of isocyanides into metal–carbon $\sigma$-bonds has been reported only recently, although the analogous reaction of carbonyl group had been already extensively studied.

The first isocyanide insertion products obtained[237] were $\pi$-cyclopentadienyl(cyclohexylisocyanide)[alkyl(cyclohexylimino)methyl]nickel,

$$\pi\text{-}C_5H_5Ni(PPh_3)R + 2\,R'NC \rightarrow \pi\text{-}C_5H_5Ni(CNR')[C(=NR')R]$$

In this case none of the possible intermediates, i.e. $\pi$-$C_5H_5Ni(CNR')R$ or $\pi$-$C_5H_5Ni(PPh_3)[C(=NR')R]$ was isolated, and the mechanism of the reaction was not ascertained.

An intermediate (*) was isolated in the related insertion into a Pt–C bond,[209]

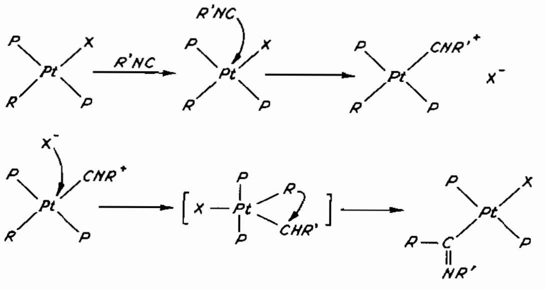
$$trans\text{-}[(Ph_3P)_2Pt(R)X] + CH_3NC \xrightarrow{\text{benzene}} (Ph_3P)_2Pt(R)X\cdot CNCH_3\ (*)$$

$$(Ph_3P)_2Pt(R)X\cdot CNCH_3 \xrightarrow[\text{reflux}]{\text{benzene}} (Ph_3P)_2PtX[C(=NCH_3)R]$$

$$(R)X = (CH_3)I,\ (C_6H_5)Cl,\ (C_6H_5)Br,\ (C_6H_5)I$$

The intermediate, a 1 : 1 adduct of the parent square-planar complex, is probably an ionic derivative, *trans*-$[(Ph_3P)_2Pt(R)(CNCH_3)]^+\,X^-$.

In this hypothesis, the following path of reaction was suggested:

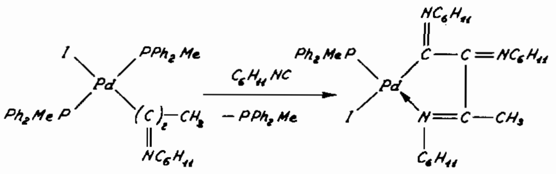


Many other examples have been reported later, including insertion into Mo–C, Fe–C and Pd–C bonds; in any case an imino complex was obtained, e.g.[235] $\pi$-$C_5H_5Mo(CO)_3[C(=NC_6H_{11})(p\text{-}CH_2\text{–}C_6H_4X)]$, $\pi$-$C_5H_5Fe(CO)_2[C(=NC_6H_{11})CH_2C_6H_5]$[233] and *trans*-$Pd(PR_3)_2X[C(=NR')CH_3]$ or $\{(MePh_2P)PdI[C(=NR)CH_3]\}_2$.[234]

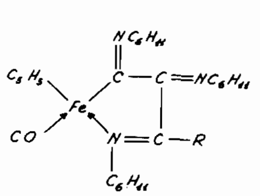
Also the insertion of isocyanides into the palladium allyl $\sigma$-bond was reported to afford dimeric imino-complexes:[119]

$$[\pi\text{-}C_3H_5PdCl]_2 \xrightarrow{\text{RNC}} \pi\text{-}C_3H_5Pd(CNR)Cl \rightarrow \{(RNC)ClPd[C(=NR)CH_2CH=CH_2]\}_2$$

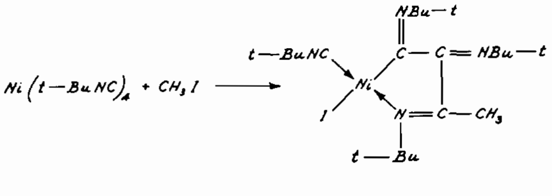
A typical feature of these reactions seems to be the possibility of multiple insertion of isocyanide molecules into a metal–carbon bond.[236] So the monoimino palladium complex *trans*-$Pd(PR_3)_2I[C(=NC_6H_{11})CH_3]$ can react with other molecules of cyclohexylisocyanide, yielding the bis-imino complex, $(R_3P)_2PdI[(C=NC_6H_{11})_2CH_3]$. A third molecule can insert giving a tris-imino complex with a five-membered chelate structure:



Other examples include the reaction of $\pi$-$C_5H_5Fe(CO)_2R$ with an excess of isocyanide, yielding[233]

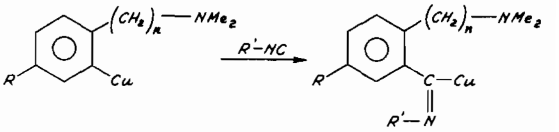


Imino complexes of this type were obtained also by a different route, i.e. by oxidative addition of alkyl halides to isocyanide complexes of Ni(O),[155]



The complex may undergo successive insertion reactions and was found to be active in the catalytic polymerization of isocyanides. Polymerization with a repeating unit —C(=NR)—C(=NR)— was obtained also by treatment of $\pi$-$C_5H_5Mo(CO)_2(\pi\text{-}C_3H_5)$ with cyclohexylisocyanide.[236]

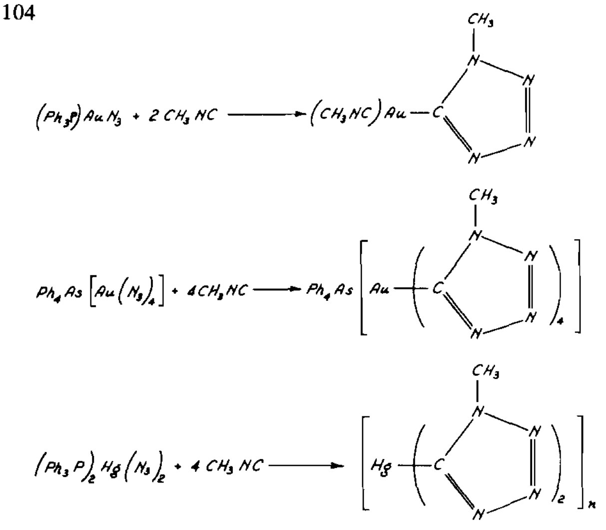
An insertion into a group IB metal–carbon bond has been also reported:[220] aryl–copper(I) complexes, such as



react with isocyanides to afford $\alpha$-cupriobenzylideneamines, dimeric in benzene, for which a six-membered ring structure formed by two –Cu–C=N→ units, has been suggested. The reaction seems to be general for aryl–copper compounds.

Insertion of isonitriles into a metal–nitrogen bond resulted from the reaction of azide complexes with isocyanides.[29]

The resulting complexes are tetrazole derivatives with a metal–carbon bond:



Several other examples are reported, including platinum and palladium derivatives. The behaviour of the coordinated isocyanide, in this case, is the same of that of the free ligand, which is known to give substituted tetrazoles by reaction with organic azides.

Insertion into a metal–halogen bond has been recently described in the case of the reaction of methyl isocyanide with niobium or tantalum pentachlorides:[82]

$$MCl_5 + 2\,CH_3NC \xrightarrow[20^\circ]{Et_2O} \{MCl_4[C(Cl){=}NCH_3](CNCH_3)\}$$

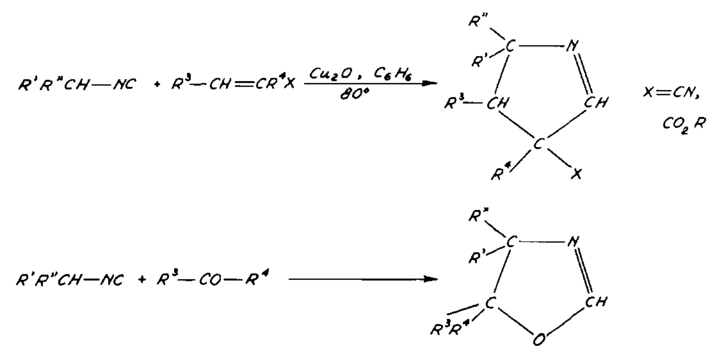
(M = Nb, Ta)

The complexes are dimeric and probably are bridged by the imino nitrogen.

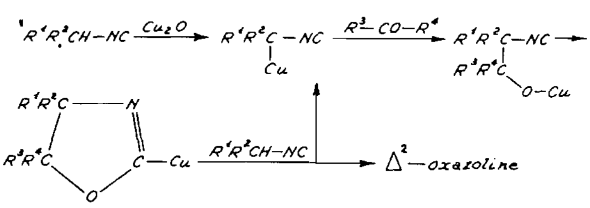
## 6. Synthesis of Organic Products through Isocyanide Complexes of Metals

A good and detailed account of the results obtained up to 1970 can be found in a book;[215] here only recent results are given.

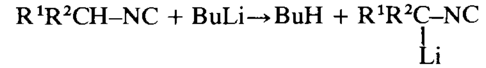
Isocyanides containing an $\alpha$-hydrogen atom may react[97,177] with the carbon–carbon double bond of $\alpha,\beta$-unsaturated carbonyl and nitrile compounds, yielding $\Delta^1$-pyrrolines or $\Delta^2$-oxazolines respectively:



The last reaction can be carried out without copper(I) oxide,[110] but then either a stoichiometric amount of alkyllithium or an NaCN/EtOH system is required. Both routes, involving either copper or lithium derivatives, require abstraction of the $\alpha$-hydrogen atom, affording an $\alpha$-metallated isocyanide on which the insertion takes place:



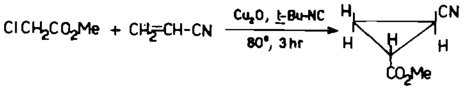
The same mechanism is operative with lithium alkyls; in this case the first step is:



$$R^1R^2CH\text{–}NC + BuLi \rightarrow BuH + R^1R^2\underset{\displaystyle Li}{\underset{|}{C}}\text{–}NC$$

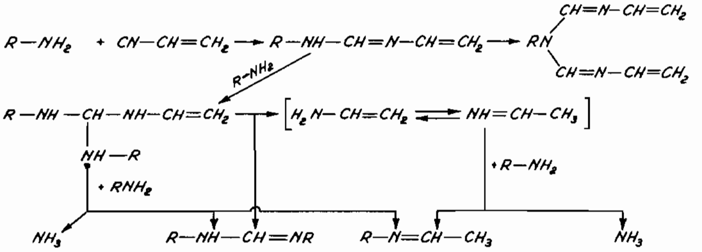
The mechanism require the $\alpha$-hydrogen to be "acid", in agreement with the results recorded in section 3.B.(ii). Moreover,[175] optically active phenylethylisocyanide is racemized readily at room temperature over $Cu_2O$ at a rate which depends on the nature of the substituent in the *para* position of the aromatic ring ($p$-Cl > H > $p$-Me), as required by an involvement of an $\alpha$-hydrogen atom.

The reaction of ketones, esters or nitriles having an $\alpha$-halogen with activated olefins, like methyl acrylate, acrylonitrile or dimethyl maleate afforded the corresponding cyclopropane derivatives:[182,176]



The synthesis is stereoselective: nearly always only the stereoisomer where the activating groups are *trans* to each other is produced. Maleate is the exception, isomerization to fumarate occurring concurrently with cyclopropane formation, and, consequently, two isomers are formed. Both isomers are formed if the reaction is carried out in the presence of a strong base instead of the copper(I) oxide/isocyanide catalyst; in addition, if dimethylformamide or hexamethylphosphoramide are used as solvent, always without catalyst, only the stabler isomer is formed.

The reaction of vinyl or phenyl isocyanide with amines, alcohols, thiols, N-alkyl derivatives of amides, carbamate, urea and thiourea proceeds at room temperature in the presence of $Cu_2O$. The reaction pattern is:[183]

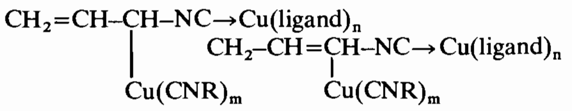


The relative amount of N,N-di(N'-vinylformimidoyl) alkylamine, N,N'-dialkylformamidine and of N-ethylidenalkylamine (alkyl may be ethyl, vinyl or cyclohexyl) depends on the ratio of the reagents. Saturated isocyanides do not react in the same or more rigorous conditions, thus showing the unique character of vinyl isocyanide. With alcohols (or thiols) 1:1 or 1:2 addition takes place leading to formimidates or to N-ethylidene-N-dialkoxymethylamine (or thio derivatives) respectively.

Allyl isocyanide isomerizes to propenyl isocyanide under action of a catalyst, the best being $Cu_2O$:[184]

$$CH_2{=}CH\text{–}CH_2NC \rightarrow CH_3\text{–}CH{=}CH\text{–}NC$$

The following intermediates are assumed for the isomerization:



$$\underset{\displaystyle Cu(CNR)_m}{CH_2{=}CH\text{–}CH\text{–}NC} \rightarrow Cu(ligand)_n \qquad \underset{\displaystyle Cu(CNR)_m}{CH_2\text{–}CH{=}CH\text{–}NC} \rightarrow Cu(ligand)_n$$

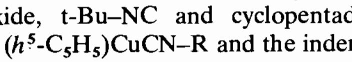
and, indeed, the reaction of allyl isocyanide with allyl bromide over $Cu_2O$ affords 4-isocyano-1,5-hexadiene which in turn can undergo isomerization to 4-isocyano-1,4-hexadiene:

$$CH_2{=}CH\text{–}CH_2\text{–}NC + BrCH_2\text{–}CH{=}CH_2 \rightarrow CH_2{=}CH(NC)\text{–}CH_2\text{–}CH{=}CH_2 \rightarrow CH_3\text{–}CH{=}C(NC)\text{–}CH_2\text{–}CH{=}CH_2$$

As a consequence of the isomerization allyl isocyanide reacts with alcohols, secondary amines or amides (e.g. ε-caprolactam) and affords N-propylidendialkoxymethylamine, the two isomeric formamidines or N-(N'-propenylformimidoyl)amide resp.:

$$CH_3\text{–}CH_2\text{–}CH{=}NCH(OR)_2$$

$$\left\{\begin{array}{l} (CH_2)_5N\text{–}CH{=}N\text{–}CH_2\text{–}CH{=}CH_2 \\ (CH_2)_5N\text{–}CH{=}N\text{–}CH{=}CH\text{–}CH_3 \end{array}\right.$$



$$R\text{–}CO\text{–}\underset{\displaystyle CH{=}N\text{–}CH{=}CH\text{–}CH_3}{N}\text{–}R'$$

Another example of isomerization of an unsaturated isocyanide is [238]

$$HC{\equiv}C\text{–}CH_2\text{–}NC \rightarrow CH_2{=}C{=}CH\text{–}NC$$

propargyl allenyl isocyanide

The transformation is catalyzed by trace amount of base, while $Cu_2O$ caused explosive decomposition of the energy-rich compound; it can be carried out cleanly and quantitatively by using a catalytic amount of 1,5-diaza-bicyclo[4,3,0]non-5-ene at room temperature on an acetonitrile solution of the copper(I) complex:[238]

$$[Cu(CNCH_2\text{–}C{\equiv}CH)_4]X \rightarrow [Cu(CN\text{–}CH{=}C{=}CH_2)_4]X \quad (X = ClO_4, BF_4)$$

The isocyanide is recovered by action of aqueous cyanide and subsequent extraction with a water-immiscible organic solvent.

Two copper(I) isocyanide complexes containing a carbon–copper σ-bond were isolated by reaction of copper(I) oxide, t-Bu–NC and cyclopentadiene or indene. Both ($h^5$-$C_5H_5$)CuCN–R and the indenyl complex catalyze the reaction between cyclopentadiene, or indene, and a carbonyl compound to yield fulvenes:[179]

$$C_5H_6 + Me_2CO \xrightarrow{\text{catalyst, } 95\%} \overline{CH{=}CH\text{–}CH{=}CH\text{–}C}{=}CMe_2$$

The complex copper catalyst has the same effect as the $Cu_2O$/CN–R mixture, both in the above mentioned reaction and in the dimerization of acrylonitrile or in a Michael type addition:

$$2\ R\text{–}CH{=}CHX \rightarrow R\text{–}CH{=}CX\text{–}CHR\text{–}CH_2X \quad (X = CN, CO_2R)$$

$$R'H + R''\text{–}CH{=}CHX \rightarrow R'R''CH\text{–}CH_2X$$

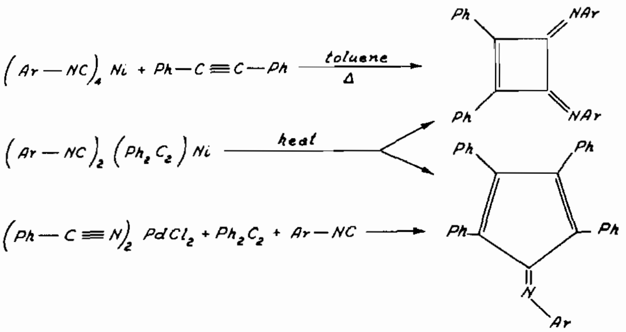
The former reaction is catalyzed[178] also from mixtures of copper(II), nickel(II), iron(II), or cobalt(II) acetylacetonate and isocyanide, but then the products include acrylonitrile polymer and, sometime, polymerized cyclohexyl isocyanide. The same reaction is not observed in the case of $\beta$-unsubstituted $\alpha,\beta$-unsaturated carbonyl and nitrile compounds;[180] acrylates and acrylonitrile are not dimerized but are co-dimerized with $\beta$-alkyl substituted monomers, probably with a mechanism involving an allyl carbanion complex intermediate.

An intermediate containing a nitrene and an isocyanide bound to the same metal atom is assumed to be the catalytically active species for the reaction[181]

$$\text{R–NC} + \text{R}'\text{N}_3 \xrightarrow{\text{Fe(CO)}_5,\ 90^\circ} \text{R–N=C=N–R}'$$

The reaction products, which do not include either $(\text{R–N=})_2\text{C}$ or $(\text{R}'\text{–N=})_2\text{C}$, cannot be obtained in the presence of iron carbonyl; even $Cu_2O$ gives only a trace of carbodiimide. The mechanism suggested involves an isocyanide complex.

Besides copper or iron isocyanide complexes, other transition metal derivatives are catalytically active, although no system is known to be as active as $Cu_2O$/CN–R. Zerovalent arylisonitrile complexes catalyze cycloaddition of acetylenes to isocyanides:[205,204,203]



These reactions can be compared with similar reactions involving carbon monoxide, which afford, e.g., tetraphenylcyclopentadienone.

## 7. Reaction of Isocyanide Complexes Involving Attack on the Isocyano Group

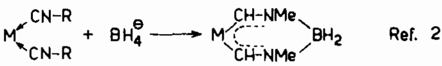
Very many reactions involve attack on the isocyano group coordinated to a metal, because upon coordination the group becomes more available to nucleophiles than in the free molecule. For example, alcohols have been often used as solvents in many reactions involving isocyanides, which are generally unaffected. But upon coordination to a suitable metal, reaction is possible and complexes of a molecule, (RO)(R'NH)C, which cannot exist free, are obtained.

Here only the general pattern of these reactions and the relevant references are given because three recent reviews cover, completely or to a big extent, this fashionable field of investigation.

$\text{M}\leftarrow\text{CN–R} + \text{R}'\text{OH} = \text{M}\leftarrow\text{C(OR}')\text{=(NHR)}$ Ref. 41,16,18,17,36,35,66,65,59

$\text{M}\leftarrow\text{CN–R} + \text{R}'\text{NH}_2 = \text{M}\leftarrow\text{C(NH–R)(NH–R}')$ Ref. 41,18,10,66,16,48,52,43, 40,65,79,80,136,125

$\overset{+}{\text{M}}\text{–CN–R} + \text{R}'_n\text{M} = \text{M–CR}'\text{=N–R} + \text{R}_{n-1}\text{M}^{\oplus}$ Ref. 211, 206, 81



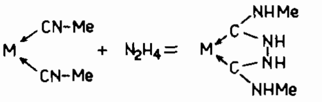
Ref. 212

$\text{M}\leftarrow\text{CNR} + \text{OH}^{\ominus} \longrightarrow [\overset{+}{\text{M}}\text{–C(OH)=NR}] \longrightarrow \text{M–CO–NHR}$ Ref. 214,123

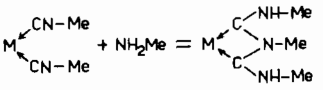
$\overset{\oplus}{\text{M}}\leftarrow\text{CNR} + \text{RO}^{\ominus} = \text{M–C(OR)=NR}$ Ref. 213,140,143,139,141

$\overset{\oplus}{\text{M}}\leftarrow\text{CNR} + \text{SH}^{\ominus} = \text{M–CS–NHR}$ Ref. 214,81,65

$\overset{\oplus}{\text{M}}\leftarrow\text{CN–R} + {}^{\ominus}\text{NHR} = \text{M–C(=NR)–NHR}$ Ref. 214,123,40



Ref. 173,174,53,51, 21, 22



Ref. 137

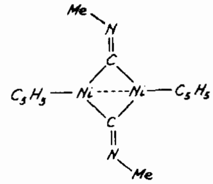
## 8. Structural Studies

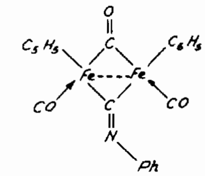
### A. Structural Data

These data have been used often to check the correctness of structural formulae suggested on the basis of other lines of evidence, e.g. chemical reactivity and various types of spectra. In addition X-ray structural data have been used to investigate the mode of bonding of isocyanide ligands.

The C–N–R arrangement is generally found to be nearly linear or linear both in the ligands and in the complexes. In the latter two types of exceptions are found where the C–N–R grouping is not linear:

(a) bridging isocyanide ligand, found in [7,115]





but not in the homologous iron complex[206] having a methyl in place of the phenyl group. The C=N–C angle of the bridging ligand is 136 and 131° respectively and the C=N bond length is perhaps shorter in the nickel complex than in $[(\text{Me–NC})_6\text{Co}]^{n+}$ (n = 1,2).[72,73]

(b) distortions due to packing forces. The most evident case is perhaps that of *cis*-$[\text{Fe(CN)}_2(\text{CN–Me})_4] \cdot 4\text{CHCl}_3$:[229] the crystal contains at least 60% chloroform by volume and the Fe–C–NMe angles are *ca.* 160°; in addition "the crystal was not suitable for the measurements of bond lengths in either the component molecules" and the distances and angles were recorded only to establish the authenticity of the structure. Another case was found in *cis*-$[\text{Pt(CN–Ph)}_2\text{Cl}_2]$,[116] where the Pt–C–N angle was found to be 177.8(17)° and

170.8(18)°: the bending is probably due to crystal packing forces rather than to electronic effects, which would affect both angles *equally*. A bigger bend, 165.5 (30)°, was mentioned in the case of *cis*-Pt(CN–Ph) $(PEt_3)Cl_2]$, but full details are not yet available.[15]

X-ray data were also used to asses the $\pi$-bonding ability and the *trans* influence of the isocyanide ligand.[131] The views generally accepted were confirmed mainly through the discussion of the structure of $Mn(CO)_3(CNMe)_2Br$,[185] *cis*-$[PtCl_2(CN\text{–}Ph)_2]$,[116] and the octa-coordinated, dodecahedral complexe $Mo(CN)_4(CNMe)_4$.[163,151] In summary, the isocyanide ligand is capable of accepting $\pi$-electron density from the metal, even if a stronger $\pi$-acceptor (such as a carbonyl) is present. The quantitative amount of $\pi$-bonding is not easily established, especially because of the disagreement between the interpretation of the infrared spectra following a simple valence bond model and the results of structural data.[39,131,72] Nevertheless, according to established ideas, a more significant contribution to $\pi$-bonding was found in the $[Mo(CNR)_6I]^+$ ion than in the dodecahedral species $Mo(CN)_4(CNMe)_4$, the Mo–CNR distance being 2.08 and 2.148(8) Å respectively.

In addition the available data do not reveal any significant difference between the CN bond length in the complexes of terminal isocyanides and that found in the free ligand. The difference could be smaller than the standard deviations; in any case, very many accurate data are required to settle the point. Besides, any difference is likely to be small for bonds of order 2–3, as has been shown in the case of metal carbonyls.[75]

In Table II the compounds are listed for which an X-ray crystal structure is available.

TABLE II. X-ray crystal structures of isocyanide complexes.

| Compound | Reference |
|---|---|
| $Mo(CNMe)_4(CN)_4$ | 151, 56 |
| $[(t\text{-}Bu\text{–}NC)_6MoI]I$ | 126 |
| *fac*-$[Mo(CO)_3(CNMe)_2Br]$ | 185 |
| $[Fe(CNMe)_6]Cl_2 \cdot 3H_2O$ | 165 |
| *cis*-$[Fe(CNMe)_4(CN)_2] \cdot 4CHCl_3$ | 229 |
| *trans*-$[Fe(CNMe)_4(CN)_2]$ | 111 |
| $Cp_2Fe_2(CO)_3(\mu\text{-}CNPh)$ | 115 |
| $[Fe(CNMe)_4(MeNH\text{–}C\text{–}NMe\text{–}C\text{–}NHMe)](PF_6)_2$ | 137 |
| $[Co_2(CNMe)_{10}](ClO_4)_4$ | 73 |
| $[Co(CNMe)_5](ClO_4)$ | 72 |
| *trans*-$[(p\text{-}MeC_6H_4NC)_4CoI_2]$ | 98 |
| $(t\text{-}BuNC)_2Ni\text{–}C(CF_3)_2\text{–}NH\text{–}C(CF_3)_2\text{–}O$ | 77 |
| $[CpNi(CNMe)]_2$ | 7 |
| $(t\text{-}BuNC)_2(Ph\text{–}N{=}N\text{–}Ph)Ni$ | 86 |
| $(t\text{-}BuNC)_2(Ph\text{–}C{\equiv}C\text{–}Ph)Ni$ | 85 |
| *trans*-$[PdI_2(t\text{-}BuNC)_2]$ | 20 |
| $[(MeNC)_2Pt(MeNH\text{–}C{=}N\text{–}NMe\text{–}C\text{–}NHMe)]BPh_4$ | 55 |
| *cis*-$[PtCl_2(CNPh)_2]$ | 116 |
| *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$ | 117 |
| *cis*-$[PtCl_2(CNPh)(PEt_3)]$ | 15 |
| $Cu(CNMe)I$ | 93 |

The *trans* influence of the isocyanide was determined to be smaller than that of a tertiary phosphine by examining the two Pt–Cl distances in *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$:[117] they are 2.314(10) *trans* to chlorine and 2.390(8) *trans* to phosphorus. The conclusion is in agreement with the results obtained examining the $\nu$(M–X) in a series of (ligand)AuX and *cis*-$[(ligand)_2PtCl_2]$ compounds (X = Cl, Br),[39] and other platinum analogues investigated from different points of view.[64]

## B. Infrared and Raman Spectra

The evidence collected by examining the spectra of more than one hundred isocyanides shows conclusively that "the stretching frequency $\nu$(CN) of these molecules is completely unsuitable as a probe to obtaine detailed information on the electronic distribution within the isocyano group".[197]

Nevertheless, some information, e.g. on the bonding between the metal and the ligand, can be obtained by comparing the position of $\nu$(CN) in a complex and the same vibration in the free ligand. In principle, the same and complementary information should be provided by $\nu$(M–C) or by $\delta$(M–CN), which, unfortunately, are assigned only in few cases, e.g. in certain cobalt(I), cobalt(II),[103,44] iron(II), manganes(I)[91] and platinum(II)[65,60] isocyanides; besides it is by no means sure that they are "pure" vibrations.

The difference between the CN stretching frequency in the complex and in the ligand ($\Delta\nu$) can be positive or negative. Generally $\Delta\nu$ is negative when the metal is in a low oxidation state, as in $Cr(CNPh)_6$,[96] $Ni(CNPh)_4$, $(Ph_3P)_2Pt(CNCMe_3)_2$,[124] provided that no other ligand of the type of carbon monoxide or of phosphorus trifluoride is present. If any of these is present, then $\Delta\nu$ is small and approaches zero: *ca.* +30 in $(Ph_3P)_2Pt(BuNC)(CO)$[124] and *ca.* –10 in $(PF_3)_3Pt(CNC_6H_{11})$.[113] On the other hand, when the metal is in an intermediate or high oxidation state, e.g. $AlR_3 \cdot CNR'$,[108] $UI_4(CNR)_4$[130] or $(Mo(CN)_4(CNR)_4$,[151] $\Delta\nu$ is positive (up to *ca.* 150 $cm^{-1}$).[65] In addition when the same cation can be found in two oxidation states, e.g. $[Mn(CNR)_6]^{n+}$ (n = 1,2),[219] the bigger $\Delta\nu$ is found in the higher oxidation state. Furthermore, when a metal in a fixed oxidation state is surrounded by a variable number *n* of ligands, as in $[Ag(CNR)_n]^+$ (n = 2,4), the bigger $\Delta\nu$ accompanies the higher *n*.[76]

On a simple valence bond scheme the conclusion had been reached that a positive $\Delta\nu$ would indicate scarce or non existent $\pi$-bonding, while a negative $\Delta\nu$ would indicate a significant amount of such a bonding.[76] While this widely accepted conclusion may be right, surely in extreme cases ($(R_3B \cdot CNR')$ and $(CNR)_4Ni)$, it is not sufficient from the quantitative point of view, according to X-ray evidence.[116,117,151,72]

CN stretching frequencies in the infrared and raman spectra, as well as their satellites due to $^{13}C$ and $^{15}N$,[34] have been used to predict structures and to check suggested formulae, e.g. $[(MeNC)_5Co–I–Co(CNMe)_5]^{3+}(ClO_4^-)_3$[44] or $[(MeNC)_5Co]I$, or to distinguish *cis*- and *trans*-isomers of $Fe(CNR)_4(CN)_4$. Nevertheless, very often some bands are missing owing to accidental degeneracy, as in $[Fe(CNR)_5X]^{+}$[42] (three bands are expected, only one is observed) or in $Mo(CNR)_4(CN)_4$[151,163] (two ir and three raman bands expected against one each found by different groups of researchers). On the contrary two cases had been reported where one band is predicted and more had been found, $Cr(CNPh)_6$ and $[Fe(CNMe)_6]^{2+}$;[89] but more recent evidence changed the situation.[96,91]

Force constants were computed using a modified Cotton–Kraihanzel force field in the case of *cis*- and *trans*-$[Fe(CNMe)_4(CN)_2]$[34] and of $[(p\text{-}MeOC_6H_4NC)_6Mn]NO_3$;[219] no data are available on the intensity of the carbon–nitrogen stretching frequency.

### C. Nmr Spectra

Nmr spectra of isocyanide complexes are generally recorded as a part of standard caracterization, which in some case requires temperature-dependent $^{13}C$ spectra.[151] Variable temperature proton spectra gave evidence[121] for the free rotation of tetracyanoethylene in its square pyramidal adducts with $[(ArNC)_4Rh](ClO_4)$ and for the possibility of a dynamical rearrangement[5] of structures in solution. Proton magnetic resonance spectra of 2:1 adducts between isocyanide and nickel(II) acetylacetonate were used to check spin density calculations.[187]

More specialized investigations were carried out on $^{13}C$ spectra,[61] which were used to evaluate the *trans*-influence of various C-bonded ligands in a series of platinum complexes, with the following result: $C(OMe)Me > CO \geq MeNC > C_6F_5C{\equiv}N$. The isocyanide $^{13}C$ terminal carbon resonance is shifted[92] upfield from the range observed in uncomplexed ligands, but sometimes the signal cannot be detected.[71,14] The $^{14}N$ resonance, on the contrary, is shifted downfield upon complexation, e.g. from +200 to +151 ppm on going from PhNC to $Cr(CNPh)_6$.[30,31]

### D. Mössbauer Spectra and Other Data

Mössbauer spectra are available for isocyanide complexes of iron(II),[25,27,26,8] for various tin[25,8] or boron[106] containing complexes of the same metal, and for (*p*-tolyl isocyanide)trichlorogold(III).[57]

According to Mössbauer center shifts measured in the series *trans*-$[FeHL(Ph_2PCH_2CH_2PPh_2)]^+$ the $\sigma$-donor plus $\pi$-acceptor ability increases in the order $MeCN < PhCN \sim N_2 < P(OPh)_3 \sim P(OMe)_3 < t\text{-}BuNC < p\text{-}MeOC_6H_4NC < CO$. For the tin containing iron complexes, like *cis*-$FeCl(SnCl_3)(ArNC)_4$ or *cis*-$Fe(SnCl_3)_2(ArNC)_4$, the chemical shifts suggest clearly that the tin atoms are in the tetravalent state; nevertheless, to preserve the additivity of the values of chemical shifts and quadrupole splittings relative to the iron nuclei, Fe in the complexes should be in the $Fe^{II}$ oxidation state.

In the boron containing complexes,[106] *cis*-$[Fe(CNR)_4(CNBX_3)_2]$ (X = F, Cl), the combined spectral evidence available and that for the corresponding boron-free parent complex suggest that the CNR and $CNBX_3$ ligands are very similar in their bonding properties to iron.

In the other spectroscopic techniques much place is available for further research, magnetic properties and electronic spectra being at the present used mainly for identification purposes only.

In a magnetic and spectral investigation[219] on $[Mn(p\text{-}\ OC_6H_4NC)_6](NO_3)_2$, the optical electronegativity of the ligand was found to be lower than that of the cyanide and of the bromide ion ($\chi_{opt} = 2.8$) and very near to that of acetylacetonate or diethyldithiophosphate. In a following investigation[91] the electronic properties of the isoelectronic complexes $[Fe(CNMe)_6^-]^{2+}$ and $[Mn(CNMe)_6]^+$ were investigated by semiempirical M.O. calculations; $\chi_{opt} = 2.2$ was calculated for the isocyanide ligand and, considering the value of $\chi_{opt}$ for $Fe^{3+}$ (2.1), it has been predicted that no $[Fe(CNR)_6]^{3+}$ complex should be stable. In addition, $\Delta_{oct}$ should be *ca.* 34,000 $cm^{-1}$,[81,90] a value similar to that proposed by Jorgensen[114] and by Gray[100] for $d^5$ and $d^6$ cyanometallates and for $d^6$ carbonyls. The value is in agreement with the known effect of the isocyanide ligand on magnetic properties.

Miscellaneous structural data include chlorine-35 nuclear quadrupole resonance frequencies in platinum(II) complexes[95] and e.s.r. spectra of five- and six-coordinate cobalt complexes in zeolites.[222]

## Acknowledgement

Financial support by the "Facoltà di Scienze, Università di Camerino" is acknowledged.

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