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ISOCYANIDE INSERTION AND RELATED REACTIONS

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A. INTRODUCTION

Isocyanides are among the few substances with a lone electron pair on a carbon atom. Their structure is isoelectronic with carbon monoxide and can be considered as a hybrid of the three resonance forms I, II and III (eqns. (1) and (2)).

$$.\overset{-}{C}\equiv\overset{+}{O}. \leftrightarrow .C{=}\dot{O}. \leftrightarrow :\overset{+}{C}-\underset{..}{\ddot{O}}.^{-} \qquad (1)$$

$$.\overset{-}{C}\equiv\overset{+}{N}-R \leftrightarrow .C{=}\ddot{N}-R \leftrightarrow :C{=}\overset{+}{N}{=}\overset{-}{R} \qquad (2)$$

I II III

The presence of a lone pair on the terminal carbon atom enables isocyanides to act as carbon ligands in coordination compounds[1] and to behave as Lewis bases similar to carbon monoxide and phosphines. A characteristic property of isocyanides as ligands is the capacity to function as stronger π-acceptors than phosphines and as weaker π-acceptors than carbon monoxide[2]. An important advantage of the use of isocyanides as ligands is the possibility of varying the substituent bonded to the nitrogen. Accordingly, we can vary the properties of the isocyanides in the same manner as phosphine ligands can be altered.

The insertion reaction is one of the most important reactions in organometallic chemistry and is thought to be an intermediate step in organic syntheses catalyzed by transition metal complexes and in catalytic polymerization reactions.

Several simple molecules, such as carbon monoxide, sulfur dioxide and olefins are known to insert into metal—carbon σ-bonds[3]. Among them, the insertion of carbon monoxide is the best studied and most firmly established. Similar insertion reactions would be expected with isocyanides, since they are isoelectronic with carbon monoxide, but they have received little attention.

Reactions which may be formally considered as the insertion of isocyanides into cobalt—carbon σ-bonds have been reported by Johnson et al.[5]. Thus, the treatment of 2-, 3- and 4-pyridomethylpentacyanocobaltate(III) ions with base gives the corresponding pyridylacetonitrile. The insertion of hydrogen isocyanide into cobalt—carbon σ-bonds has been suggested in the mechanism proposed. However, intermediate complexes could not be isolated in the reactions.

The authors have found that isocyanides insert into carbon—nickel σ-bonds to give the corresponding imino complexes when reacted with π-cyclopentadienyl(triphenylphosphine)nickel alkyls[6]. These compounds were the first isocyanide insertion products to be isolated. Studies of this type of reaction have since been conducted in several laboratories.

Recently the reactions of nucleophiles with coordinated isocyanides have been studied extensively. Among them, the coordinated isocyanide complexes of palladium, platinum and iron are known to react with amines or alcohols, affording the corresponding carbene complexes

This review includes recent developments in the insertion reactions of isocyanides into transition metal—carbon σ-bonds and related reactions.

B. INSERTION OF ISOCYANIDE

(i) Reactions with carbon—metal σ-bonded complexes

(a) Insertion into carbon—molybdenum σ-bonds.

It is well known that tricarbonyl-π-cyclopentadienylmolybdenum alkyls undergo carbonyl insertion to give the corresponding acyl complexes when reacted with Lewis bases such as carbon monoxide[7] or phosphorus ligands[8].

$$\pi\text{-}C_5H_5Mo(CO)_3R + L \rightarrow \pi\text{-}C_5H_5Mo(CO)_2LCOR \qquad (3)$$

Isocyanides react with complexes of the type π-$C_5H_5Mo(CO)_3R$ under a variety of conditions to afford either the carbonyl or isocyanide insertion products, depending on the nature of the isocyanides and the alkyl—molybdenum complexes[9,10]. The reaction of π-$C_5H_5Mo(CO)_3CH_3$ with cyclohexyl or *tert*-butyl isocyanide in benzene at room temperature results in carbonyl insertion, affording the corresponding acyl complexes, viz.

$$\pi\text{-}C_5H_5Mo(CO)_3CH_3 + RNC \rightarrow \pi\text{-}C_5H_5Mo(CO)_2(CNR)COCH_3 \tag{4}$$

A similar result is also obtained by the reaction of $\pi\text{-}C_5H_5Mo(CO)_3CH_2Ph$ with *tert*-butyl or 2,6-dimethylphenyl isocyanide. However, the benzyl derivatives, $\pi\text{-}C_5H_5Mo(CO)_3R$ (R = CH_2Ph, $p\text{-}CH_2C_6H_4OCH_3$ or $p\text{-}CH_2C_6H_4Cl$), react with cyclohexyl isocyanide at room temperature and undergo competitive carbonyl and isocyanide insertion, yielding both the corresponding acyl and imino complexes. The relative yield of the two isomers depends on the nature of the *p*-substituted benzyl group (Table 1).

$$\begin{aligned}&\pi\text{-}C_5H_5Mo(CO)_3p\text{-}CH_2C_6H_4X + C_6H_{11}NC \rightarrow\\ &\qquad \pi\text{-}C_5H_5Mo(CO)_3[C(p\text{-}CH_2C_6H_4X){=}NC_6H_{11}]\\ &\qquad\qquad + \pi\text{-}C_5H_5Mo(CO)_2(CNC_6H_{11})CO\,p\text{-}CH_2C_6H_4X\end{aligned} \tag{5}$$

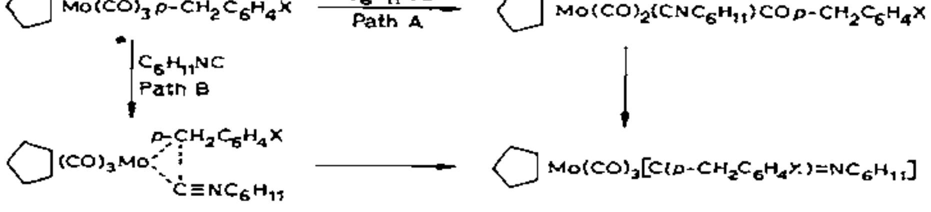
TABLE 1

The relative yield of the two isomers [a]

X	NMR τCH_2	Imino complex (%)	Acyl complex (%)
Cl	7.16	72	
H	7.12	51	4
p-OCH_3	7.06	40	13

[a] Isolated yield.

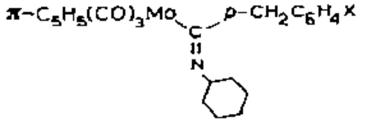
Two mechanisms concerning the isocyanide insertion are considered. The first results from initial formation of the acyl complex $\pi\text{-}C_5H_5Mo(CO)_2(CNC_6H_{11})CO\,p\text{-}CH_2C_6H_4X$, followed by a rapid migration of the benzyl group to the coordinated isocyanide ligand (Path A). The second path involves direct attack of isocyanide on molybdenum, accompanied by a transfer of the alkyl group to the isocyanide ligand (Path B). All attempts to rearrange the acyl complex to the imino complex have been unsuccessful. This speaks in favor of direct isocyanide insertion (Path B).



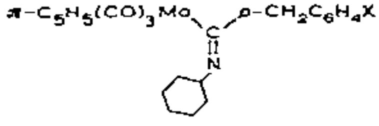
It is deduced from the NMR spectra that the benzylic methylene protons of the starting materials, π-$C_5H_5Mo(CO)_3$-p-$CH_2C_6H_4X$, are shielded in the order OCH_3, H, Cl, suggesting a transfer of an electron from molybdenum to the methylene group by an inductive effect of the *para* substituent. Table 1 indicates that the high electron density of the methylene group facilitates a transfer of alkyl group to isocyanide ligand. One reason for this is connected with the higher contribution of resonance form IV than that of V.

$$\underset{\text{IV}}{R{-}\overset{+}{N}{\equiv}C{-}\overset{-}{M}} \leftrightarrow \underset{\text{V}}{R{-}N{=}C{=}M}$$

The benzylic methylene protons of the imino complexes prepared show two peaks in the NMR spectra, suggesting the presence of two isomers They can be interpreted as *syn* (VI) and *anti* (VII) forms.

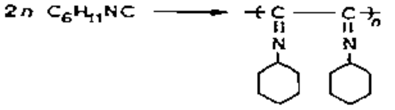


VI



VII

Treatment of $C_6H_{11}NC$ with alkyl-molybdenum derivatives having strong electron-attracting groups such as CH_2Cl and CH_2CN does not yield an insertion product, because of the greater strength of the carbon—molybdenum σ-bond. The same trend has been observed in the reactions of complexes containing M—CH_2CN linkages with carbon monoxide[11]. The reaction of π-$C_5H_5Mo(CO)_2(\pi$-$C_3H_5)$ with $C_6H_{11}NC$ leads to an unexpected result[12], the reaction at room temperature occurs readily, affording the poly-cyclohexyl isocyanide.



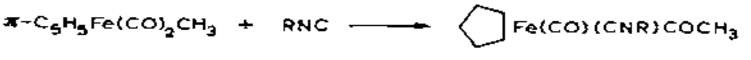
(6)

However, no reaction occurred with *tert*-butyl isocyanide, both starting materials being recovered, indicating the steric effect of isocyanide

(b) Insertion into carbon—iron sigma-bonds

Dicarbonyl-π-cyclopentadienyliron alkyls, in a manner similar to π-$C_5H_5Mo(CO)_3R$, react with carbon monoxide[13] and phosphorus ligands[14–16] to afford the acyl complexes. This reaction is often reversible.

The reaction of π-$C_5H_5Fe(CO)_2CH_3$ with $C_6H_{11}NC$ or $(CH_3)_3CNC$ in refluxing THF for 20 h gives the corresponding acyl complex, viz.

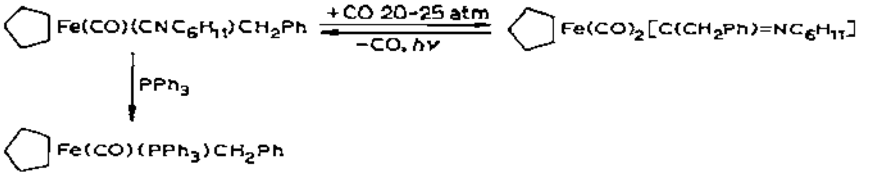


(7)

The treatment of π-$C_5H_5Fe(CO)_2CH_2Ph$ with *tert*-butyl isocyanide gives π-$C_5H_5Fe(CO)(CNC(CH_3)_3)CH_2Ph$ without producing the acyl complex[17]. The complex, π-$C_5H_5Fe(CO)(CNR)CH_2Ph$ (R = C_6H_{11} or $(CH_3)_3C$) can also be prepared from π-$C_5H_5Fe(CO)(CNR)I$ and $PhCH_2MgCl$.

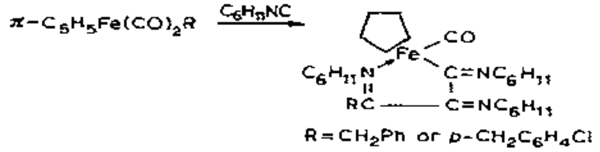
The treatment of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ with 20–25 atm of carbon monoxide in THF or benzene at room temperature for several days gives the isocyanide insertion product[18], π-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$. It is interesting to note that the reaction of π-$C_5H_5Fe(CO)_2CH_3$ and CO is known[19] to require a temperature of 125°C and a CO pressure of 200 p.s.i. to produce π-$C_5H_5Fe(CO)_2COCH_3$. Although difficult to accomplish thermally the decarbonylation of this acyl complex goes at ambient temperature when UV light is used.

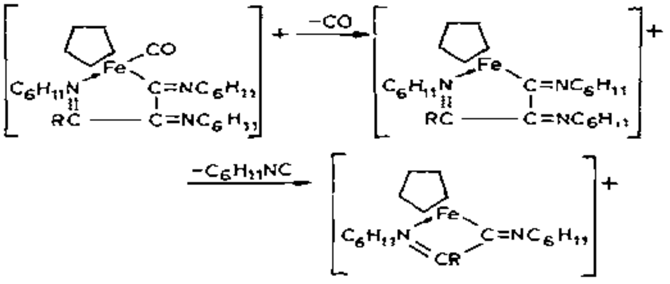
Similarly, the ultraviolet irradiation of π-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ in THF for 21 h brings about a decarbonylation reaction[18], producing π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$.



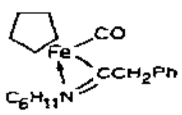
After treatment of π-$C_5H_5Fe(CO)(CNC(CH_3)_3)CH_2Ph$ with CO, only the starting material is recovered, an observation explicable in terms of steric hindrance of the bulky isocyanide The reaction of π-$C_5H_5Fe(CO)(CNR)CH_2Ph$ ($R = C_6H_{11}$ or $(CH_3)_3C$) with PPh_3 undergoes a substitution reaction to produce π-$C_5H_5Fe(CO)(PPh_3)CH_2Ph$.

Multiple insertion of isocyanide molecules into an Fe–C bond has also been reported[17]. Treatment of benzyl derivatives of dicarbonyl-π-cyclopentadienyliron with an excess of cyclohexyl isocyanide in refluxing THF results in a successive insertion of three isocyanide molecules, yielding the tris-imino complex (reaction (8)). The structure has been confirmed by IR, NMR and mass spectroscopy The mass spectra exhibited metastable ions which permit a partial elucidation of the fragmentation scheme The spectra indicated the successive loss of carbon monoxide and cyclohexyl isocyanide molecules.

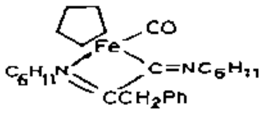

(8)



All attempts to isolate this type of mono- or bis-imino complex (VIII or X) which may be considered as an intermediate were unsuccessful. A similar tris-imino complex can also



VIII

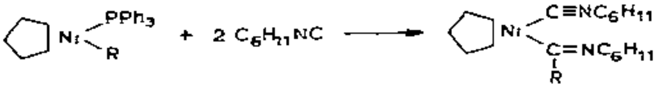


IX

be prepared from the reaction between π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ and an excess of $C_6H_{11}NC$ in refluxing THF. However, after treatment of π-$C_5H_5Fe(CO)_2[C(CH_2Ph)=NC_6H_{11}]$ with $C_6H_{11}NC$ in refluxing THF, the starting material is recovered without producing a tris-imino complex.

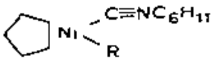
(c) Insertion into carbon–nickel sigma-bonds

Triphenylphosphine–π-cyclopentadienylnickel alkyls ($R = CH_3$, n-C_4H_9, Ph, p-C_6H_4Cl or $C{\equiv}CC_2H_5$) react[6] with cyclohexyl isocyanide at room temperature, undergoing isocyanide insertion to yield the imino complex. The IR spectra of

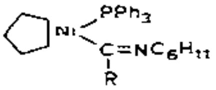


(9)

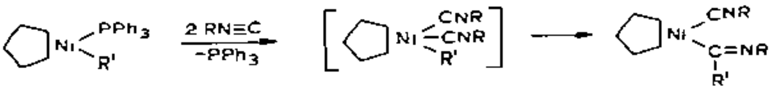
these imino complexes show two characteristic bands in the ranges 2130–2140 cm^{-1} and 1580–1620 cm^{-1}, the former band is due to the coordinated isocyanide group and the latter to a carbon–nitrogen double bond. No complexes of the type X and XI, which may be considered as intermediates in the formation of imino complexes, can be isolated under a variety of conditions. The insertion reaction probably proceeds as follows.



X

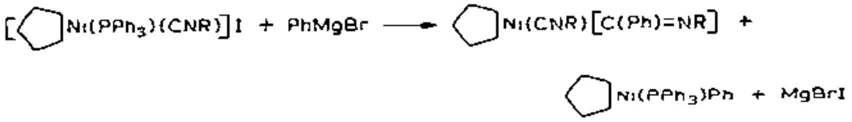


XI

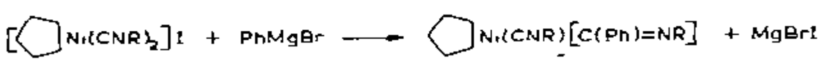


(10)

Similar imino complexes can also be prepared from the reactions of Grignard reagents with nickel halides containing coordinated isocyanides, viz.



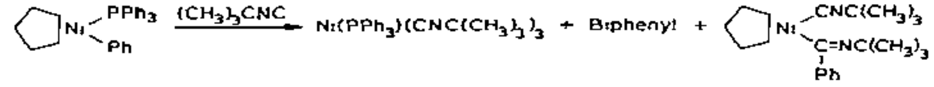
(11)



(12)

No reaction occurs between nickel alkyls having o-methyl substituents (o-tolyl or mesityl) and cyclohexyl isocyanide, due to steric hindrance of the bulky substituents The reaction of π-$C_5H_5Ni(PPh_3)Ph$ with bulky *tert*-butyl isocyanide gives

$Ni(PPh_3)(CNC(CH_3)_3)_3$ and biphenyl as main products and a small amount of π-$C_5H_5Ni(CNC(CH_3)_3)[C(Ph)=NC(CH_3)_3]$ On the other hand, it is known that



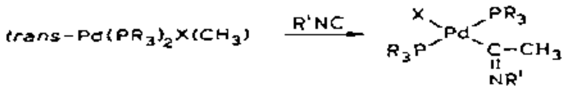
(13)

$Ni(PPh_3)(CO)_3$ and 1-phenyl-1,3-cyclopentadiene were obtained when π-$C_5H_5Ni(PPh_3)Ph$ reacted with 80 atm of carbon monoxide for several days at room temperature[20].

(d) Insertion into carbon–palladium sigma-bonds

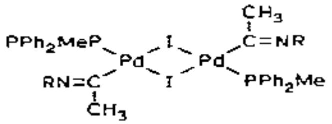
It is known that the square planar complexes, $M(PEt_3)_2X(R)$, where M = Pd or Pt, X = halogen and R = alkyl, are directly carbonylated to give acyl complexes when reacted with carbon monoxide[21] Insertion of isocyanide into metal–carbon σ-bonds in these square planar complexes has also been observed[22,23].

trans-$Pd(PR_3)_2X(CH_3)$ (PR_3 = PPh_3, $PPhMe_2$, PMe_3, $PBu^n{}_3$, or $PPh_2C_6H_{11}$; X = Br or I) reacts with an equimolar amount of R′NC (R′ = C_6H_{11}, $(CH_3)_3C$, Ph or $PhCH_2$) at low temperature to give the corresponding mono-imino complex, viz



(14)

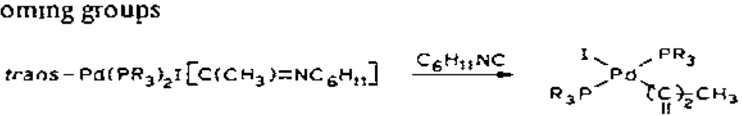
A *trans* structure was confirmed by the NMR spectrum, which revealed virtual coupling of the P–CH_3 proton resonances On the other hand, reaction of *trans*-$Pd(PPh_2Me)_2I(CH_3)$ with $C_6H_{11}NC$ or $(CH_3)_3CNC$ produces the dimer The NMR data show the presence of



XII

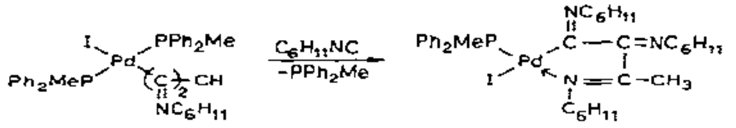
two isomers. No reactions occur between alkyl palladium complexes and isocyanides having a bulky group such as 2,4-dimethylphenyl, and treatment of the *o*-tolyl complex with *tert*-butyl or 2,4-dimethylphenyl isocyanide recovers both starting materials, explicable in terms of steric hindrance of the isocyanide or alkyl group, respectively

The mono-imino complex, *trans*-$Pd(PR_3)_2I[C(CH_3)=NC_6H_{11}]$ (PR_3 = $PPhMe_2$, PMe_3 or $PBu^n{}_3$) reacts readily with cyclohexyl isocyanide to yield the bis-imino complex (eqn. (15)). No further insertion of *tert*-butyl isocyanide into *trans*-$Pd(PR_3)_2[C(CH_3)=NC(CH_3)_3]$ occurs, which is interpreted to result from the steric hindrance of iminoacyl towards incoming groups



(15)

The bis-imino complex, *trans*-Pd$(PPh_2Me)_2I[CH_3(C{=}NC_6H_{11})_2]$ induces reaction with $C_6H_{11}NC$, giving the tris-imino complex with a five-membered chelate structure (reaction (16)).

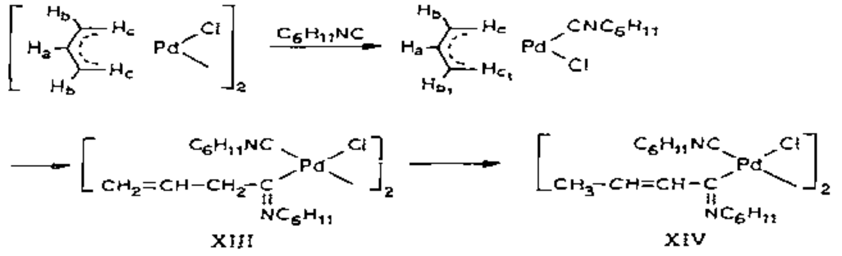


(16)

The mechanism by which the isocyanide molecule inserts stepwise into the palladium–carbon sigma bonds is probably similar to one proposed for the insertion into platinum–carbon σ-bonds (see sect. B(i)(*e*), below).

It has been reported by Kajimoto et al.[25] that the reaction between π-allylpalladium chloride and cyclohexyl isocyanide involves an isocyanide insertion, affording the imino complex. $[\pi\text{-}C_3H_5PdCl]_2$ reacts with $C_6H_{11}NC$ to give bis[μ-chloro(cyclohexyl isocyanide)-(1-cyclohexylimino-3-butenylpalladium] (XIII). When XIII is allowed to stand overnight, migration of the allylic double bond takes place, producing bis[μ-chloro(cyclohexyl isocyanide)(1-cyclohexylimino-2-butenylpalladium] (XIV).

The mechanism of this reaction deduced from the NMR spectra is as follows



(17)

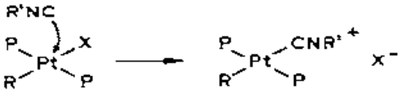
(e) Insertion into carbon–platinum sigma bonds

Insertion of isocyanide into Pt–C bonds has been studied by Treichel and Hess[26] and by us[27].

trans-Pt$(L)_2X(R)$ (R = CH_3 or Ph, L = PPh_3 or $PPhMe_2$, X = Br or I) reacts with R'NC in a 1 : 1 molar ratio at room temperature to give the ionic four-coordinate complex, [*trans*-Pt$(L)_2(CNR')R]X$. When [*trans*-Pt$(PPh_3)_2(CNR')R]X$ is refluxed in benzene, migration of the alkyl group to the coordinated isocyanide ligand takes place, affording *trans*-Pt$(PPh_3)_2X[C(R){=}NR']$. No insertion reaction occurs when [*trans*-Pt$(PPhMe_2)_2(CNC_6H_{11})CH_3]I$ is treated in a similar fashion to that in the above-mentioned reaction. However, on refluxing in toluene, an insertion does proceed, affording the corresponding mono-imino complex. *trans*-Pt$(PPh_3)_2Br[C(Ph){=}NCH_3]$ further reacts with methyl isocyanide to give the 1:1 adduct, $Pt(PPh_3)_2[C(Ph){=}NCH_3]Br\cdot CH_3NC$.

Square-planar palladium complexes are usually more labile than the platinum analogs, and in agreement with this trend isocyanide insertion into the platinum alkyls will occur more readily than that into the platinum derivatives. In fact, an insertion of isocyanide into Pd—C bonds occurs even at 0°C. The initial formation of a salt-like complex, accompanied by insertion of the isocyanide into the Pt—C bonds at an elevated temperature, is in complete agreement with the result.

The mechanism proposed by Treichel and Hess is



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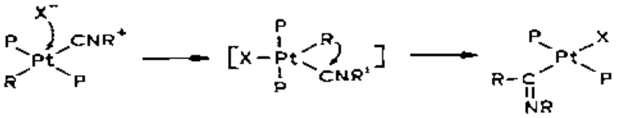


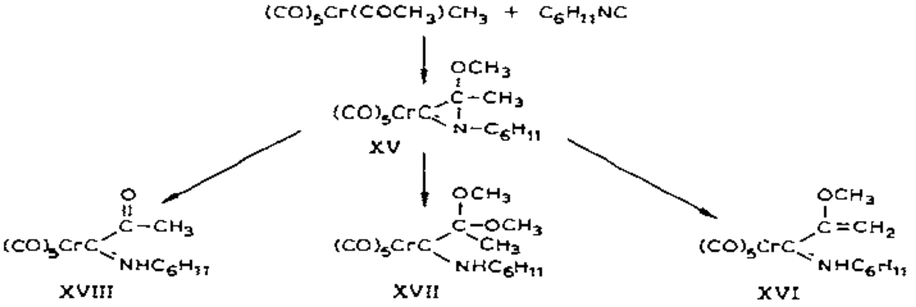
(19)

In the reaction of *cis*-$Pt(PPh_3)_2R_2$ ($R = CH_3$ or Ph) with CH_3NC, the only product isolated is *cis*-$Pt(PPh_3)(CNCH_3)R_2$; there is no evidence that an intermediate 1:1 adduct is produced.

Interestingly, the reaction of *trans*-$Pt(PPh_3)_2Br(C_6F_5)$ with CH_3CN in refluxing benzene involves[26] dealkylation to give $Pt(PPh_3)_2(C_6F_5)CN$ The dealkylation reaction also occurs, affording *trans*-$Pt(PPhMe_2)_2I(CN)$, when $[Pt(PPhMe_2)_2(CNC(CH_3)_3)CH_3]I$ is refluxed in toluene[27]. Although the detailed mechanism of the dealkylation is unknown, it probably involves the elimination of CH_3Br or tetramethylmethane, respectively.

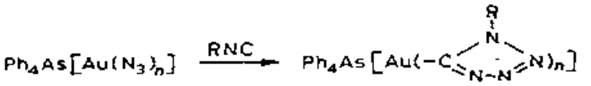
(ii) Reactions with carbene complexes[28]

An unusual insertion reaction occurs when isocyanide reacts with a metal carbene complex. Reaction of $Cr(CO)_5C(COCH_3)CH_3$ with an equivalent amount of cyclohexyl isocyanide gives a 1:1 adduct (XV) in high yield. It was suggested from spectral and chemical evidence that the structure has an aziridine ring. Complex XV reacts with benzoyl peroxide to give XVI, which can also be prepared from the reaction of XV with HCl and triethylamine. Treatment of XV with methanol results in an addition reaction, affording XVII. The complex XV reacts with acid in aqueous THF to yield XVIII. These reactions also suggest an aziridine structure for XV.

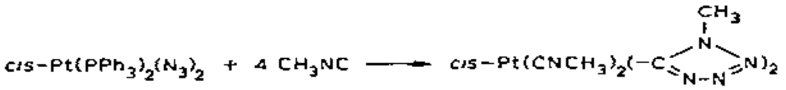


(iii) Reactions with metal azides

Recently, an insertion of isocyanide into a metal–nitrogen bond to give tetrazole complexes with a metal–carbon bond was reported by Beck et al.[29] Azide complexes of Au react with isocyanides in methylene chloride to produce stable tetrazole complexes (eqn. (20)). The tetrazole complexes of Pd or Pt can also be prepared (eqns. (21), (22)). These reactions are similar to those which give 1-substituted tetrazoles by α-addition reactions of organic azides to isocyanides[47].


(20)

$n = 2$ or 4, $R = CH_3$, $i\text{-}C_3H_5$, C_6H_{11}, $PhCH_2$, Ph or $p\text{-}CH_3OC_6H_4$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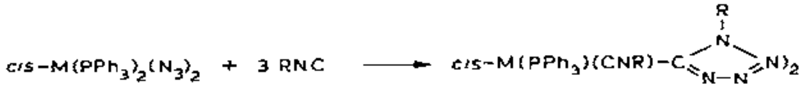
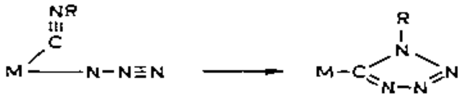
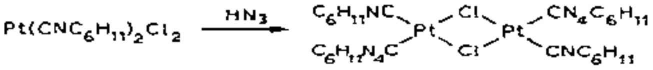

(22)

$R = C_6H_{11}$, $PhCH_2$ or Ph M = Pd or Pt

The pathway postulated involves initial coordination of the isocyanide to the metal, accompanied by the formation of a tetrazole ring derived from insertion of a coordinated isocyanide into a metal–azide bond and subsequent cyclization, as follows



A bridged tetrazole complex of Pt can be prepared from the reaction of dichlorobis(cyclohexyl isocyanide)platinum with hydrazoic acid.

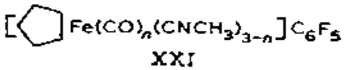

(23)

C. REACTIONS OF COORDINATED ISOCYANIDES

(i) Reactions of cationic isocyanide complexes with alkyllithium[30] and Grignard reagents[6,31]

$[\pi\text{-}C_5H_5Fe(CO)(CNCH_3)_2]PF_6$ reacts with C_6F_5Li to give $\pi\text{-}C_5H_5Fe(CNCH_3)_2C_6F_5$ (8.9%), $\pi\text{-}C_5H_5Fe(CO)(CNCH_3)[C(C_6F_5){=}NCH_3]$ (m.p. 93–94°C, 15.4%), XIX and $\pi\text{-}C_5H_5Fe(CO)(CNCH_3)[C(C_6F_5){=}NCH_3]$ (m.p. 90–91°C, 13.6%), XX. The structures were confirmed by spectroscopic studies. In the two isomers of the imino complexes, the methyl group can assume either a *cis* or a *trans* orientation to the iron group with respect to the C=N double bond.

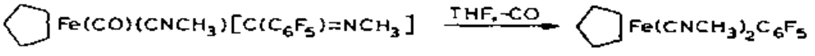
Reaction of $[\pi\text{-}C_5H_5Fe(CO)_2(CNCH_3)]PF_6$ with C_6F_5Li gives many products, among which $\pi\text{-}C_5H_5Fe(CO)(CNCH_3)C_6F_5$ and $\pi\text{-}C_5H_5Fe(CO)_2[C(C_6F_5)=NCH_3]$ were isolated. The reactions probably proceed via a cationic intermediate XXI.



XXI

n = 2 or 1

The attempted carbonylation of $\pi\text{-}C_5H_5Fe(CNCH_3)_2C_6F_5$ (60°C in n-hexane, 10 atm carbon monoxide pressure) is unsuccessful. Decarbonylation takes place, affording $\pi\text{-}C_5H_5Fe(CNCH_3)_2C_6F_5$, when complex XIX is refluxed in THF for 18 h Analogously, the complex gives $\pi\text{-}C_5H_5Fe(CNCH_3)_2C_6F_5$ and complex XIX.



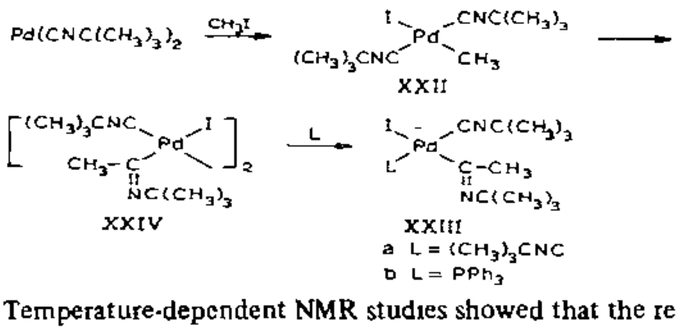
(24)

As mentioned briefly (see sect. B(i)(*c*)), $\pi\text{-}C_5H_5Ni(L)I$ (L = PPh_3 or PEt_3) reacts with isocyanide to afford the cationic complex $[\pi\text{-}C_5H_5Ni(L)(CNR)]I$ in high yield However, in the case of L = $P(OPh)_3$ or $AsPh_3$, the reaction produces $[\pi\text{-}C_5H_5Ni(CNR)_2]I$ The reactions of these cationic complexes with phenylmagnesium bromide give the corresponding imino complexes, $\pi\text{-}C_5H_5Ni(CNR)[C(Ph)=NR]$.

(ii) Oxidative addition reactions of alkyl halides to zero-valent isocyanide complexes

Many attempts have been made to prepare metal alkyls by means of oxidative addition reactions of low-valent transition metal complexes with alkyl halides Among them, the reaction of $\pi\text{-}C_5H_5Rh(CO)(PPhMe_2)$ with alkyl halides to yield the acyl complex $\pi\text{-}C_5H_5Ph(PPhMe_2)(COR)X$ is very interesting[32]. The reaction proceeds via an ionic intermediate $[\pi\text{-}C_5H_5Rh(CO)(PPhMe_2)R]X$

Attempts to prepare imino complexes by the oxidative addition of alkyl halides to isocyanide complexes of Ni^0 or Pd^0 have been conducted by Otsuka et al.[33]. The reaction of $Pd(CNC(CH_3)_3)_2$ with CH_3I in n-hexane at 0°C produces *trans*-$Pd(CNC(CH_3)_3)_2I(CH_3)$, XXII This complex reacts with *tert*-butyl isocyanide or triphenylphosphine to give the corresponding imino complex XXIII.



XXII

XXIV

XXIII

a L = $(CH_3)_3CNC$

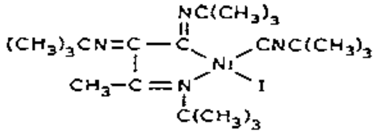
b L = PPh_3

(25)

Temperature-dependent NMR studies showed that the reactions proceed via an unstable intermediate XXIV. The phosphine analog of this dimer has been isolated (see sect. B(i)(*d*)).

Treatment of $Pd(CNC(CH_3)_3)_2$ with C_6H_5COCl in *n*-hexane at 0°C affords $Pd(CNC(CH_3)_3)_2Cl(COPh)$ in high yield.

An attempt to prepare a nickel analog of XXII from $Ni(CNC(CH_3)_3)_2$ was unsuccessful. On the other hand, reaction of $Ni(CNC(CH_3)_3)_4$ with alkyl halide leads to very interesting results. A multiple successive insertion of three isocyanide molecules takes place, affording a new imino complex XXV when $Ni(CNC(CH_3)_3)_4$ reacts with CH_3I. The



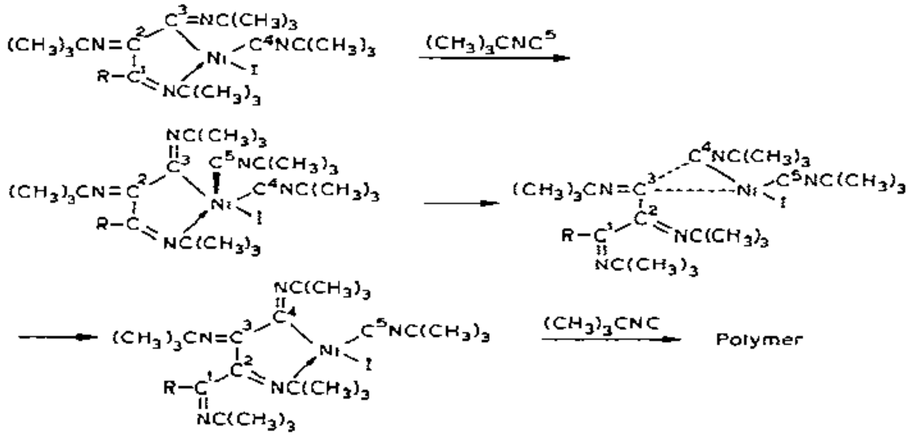
XXV

structure was supported by spectral data ($\nu_{N\equiv C} = 2172\ cm^{-1}$, $\nu_{C=N} = 1667$, 1634 and 1610 cm^{-1}) and physical properties The same compounds can also be prepared from $Ni(CNC(CH_3)_3)_4$ and RI ($R = C_2H_5$, *n*-C_3H_7, and i-C_3H_7) in high yield[34]. The mechanism of these multiple successive insertions remains undecided at present.

Treatment of isocyanide at 30–60°C in the presence of a catalytic amount of XXV produces poly-isocyanide with a repeating unit[35,36] suggesting that complex XXV is an intermediate in the catalytic polymerization of isocyanide.

$$\left(\begin{matrix} C - C \\ \| \quad \| \\ NR\ NR \end{matrix}\right)_n$$

The proposed polymerization is[34]



(26)

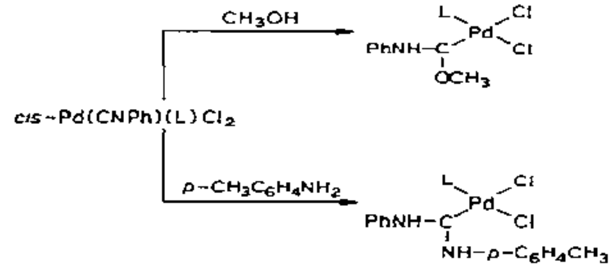
(iii) Reactions with amines and alcohols

Many attempts to prepare carbene complexes from metal carbonyl derivatives have been conducted[37]. Formation of analogous carbene complexes from isocyanide derivatives should also be possible.

cis-$Pt(CNR)(PEt_3)Cl_2$ reacts with alcohols or amines to give carbene complexes[38,39], viz.

$$cis\text{-}Pt(CNR)(PEt_3)Cl_2 + HQ \rightarrow cis\text{-}Pt[C(NHR)Q](PEt_3)Cl_2 \qquad (27)$$

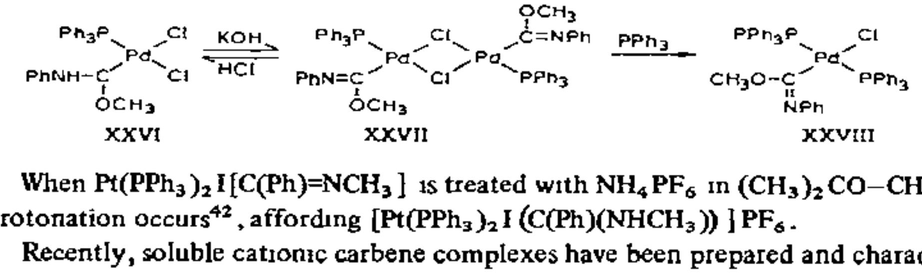
($R = CH_3$ or Ph, $Q = OCH_3$, OC_2H_5, O–i-Pr, NHPh, $NHCH_3$, NHC_2H_5 or $NHBu^{sec}$)
The structure is confirmed by IR spectroscopy and X-ray analysis. Similar carbene complexes of palladium can also be prepared from the reaction of *cis*-$Pd(CNPh)(L)Cl_2$ (L = PhNC or PPh_3) with methanol or *p*-toluidine[40], viz.



(28)

(29)

Reaction of a carbene complex with base leads to a very interesting result[41]. The complex XXVI reacts with a stoichiometric amount of alcoholic KOH at room temperature to afford bis[μ-chloro(triphenylphosphine)(phenyliminomethoxymethyl)palladium] (XXVII) in high yield. This reaction can be easily reversed. If the complex XXVII is refluxed with methanol containing HCl, XXVI is obtained in a 90% yield. The complex XXVII reacts smoothly with PPh_3 to give a quantitative yield of XXVIII.

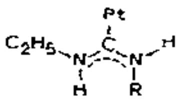


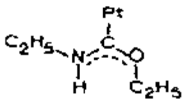
XXVI XXVII XXVIII

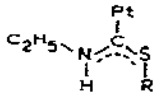
(30)

When $Pt(PPh_3)_2I[C(Ph)=NCH_3]$ is treated with NH_4PF_6 in $(CH_3)_2CO$–$CHCl_3$, protonation occurs[42], affording $[Pt(PPh_3)_2I(C(Ph)(NHCH_3))]PF_6$.

Recently, soluble cationic carbene complexes have been prepared and characterized by NMR. Treatment of *trans*-$[Pt(CNR)(PEt_3)_2X]ClO_4$ with alcohol or amines (QH) yields *trans*-$[Pt(C(NHR)Q)(PEt_3)_2X]ClO_4$, where[43] R = Ph or CH_3, Q = PhNH, C_2H_5NH or C_2H_5O, and X = Cl or Br. NMR studies show restricted rotation about the C–N or C–O bonds of the carbene ligand, similar to the carbene complexes of chromium[44,45]. Analogously, *trans*-$[Pt(CNC_2H_5)_2(PPhMe_2)_2](PF_6)_2$ reacts with QH ($Q = p\text{-}CH_3C_6H_4NH$, PhNH, C_2H_5O or $PhCH_2S$) under prolonged reflux conditions to give the corresponding carbene complexes[24,46], *trans*-$[Pt(C(NHC_2H_5)Q)(CNC_2H_5)(PPhMe_2)_2](PF_6)_2$. The ease of preparation decreases in the order $RNH_2 > RSH \gg ROH$. The NMR spectra indicate four non-equivalent phosphine methyls caused by the absence of a σ-plane of symmetry along the C–Pt–C axis and restricted rotation of the carbene about the Pt–C bond. The most likely structures are





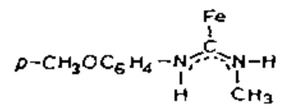


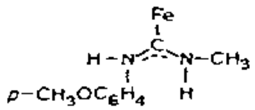
This results from a 1,2-*cis*-addition of the nucleophile across the C–N triple bond. Furthermore, the carbene plane is perpendicular to the plane of the complex.

Carbene complexes of iron can be prepared[4] from the reactions of $[\pi\text{-}C_5H_5Fe(p\text{-}CNC_6H_4OCH_3)_3]^+$ with CH_3NH_2, viz.

$$[\pi\text{-}C_5H_5Fe(p\text{-}CNC_6H_4OCH_3)_3]^+ + CH_3NH_2 \rightarrow [\pi\text{-}C_5H_5Fe(p\text{-}CNC_6H_4OCH_3)_2\text{-}(C(NHCH_3)NH\text{-}p\text{-}C_6H_4OCH_3)]^+ \quad (31)$$

These complexes are isolated as PF_6^- and BF_4^- salts. NMR studies show the presence of the two isomers The postulated structures are





It has been suggested that the mechanism for carbene formation from isocyanide complexes probably involves nucleophilic attack by alkoxy or alkylamino groups at the electron-deficient isocyanide carbon[24].

This review summarizes the fundamental reactions which have been reported recently concerning the insertion of isocyanide into transition metal–carbon sigma-bonds and the reactions of the transition metal isocyanide complexes so produced. Significant developments in their reactions and mechanisms can be expected in the future.

REFERENCES

1 L. Malatesta, *Progress in Inorganic Chemistry*, Vol. 1, Interscience, New York, 1959, p. 283, L. Malatesta and F. Bonati, *Isocyanide Complexes of Metal*, Wiley-Interscience, New York, 1969.
2 G.F. Van Hecke and W D. Horrocks, Jr., *Inorg. Chem.*, 5 (1966) 1960.
3 See for example, J.P. Candlin, K.A. Taylor and D.T. Thompson, *Reactions of Transition-Metal Complexes*, Elsevier, Amsterdam, 1968, p. 119.
4 R.J. Angelici and L.M. Charley, *J. Organometal. Chem.*, 24 (1970) 205.
5 M.D. Johnson, M.L. Tobe and L.Y. Wong, *J. Chem. Soc. A*, (1968) 923.
6 Y. Yamamoto, H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jap.*, 41 (1968) 532, *J. Organometal. Chem.*, 18 (1969) 189.
7 P.J. Craig and M. Green, *J. Chem. Soc. A*, (1969) 157.
8 J.A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1963) 4096.
9 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 43 (1970) 143.
10 Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, 24 (1970) 717.
11 R.F. Heck and D.S. Breslow, *J. Amer. Chem. Soc*, 84 (1962) 2499.
12 Y. Yamamoto and H. Yamazaki, unpublished results.
13 T.H. Coffield, J. Kozikowski and R.D. Closson, *Intern. Conf. Coord. Chem., Abstr., London, April 1959*, p. 126.

14 R.B. Bibler and A. Wojcicki, *Inorg. Chem.*, 5 (1966) 889.

15 P.M. Treichel, R.L. Shubkin, K.W. Barnett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.

16 S.R. Su and A. Wojcicki, *J. Organometal. Chem.*, 27 (1971) 231.

17 Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 11 (1972) 211.

18 Y. Yamamoto and H. Yamazaki, unpublished results.

19 R.B. King and M.B. Bisnette, *J. Organometal. Chem.*, 2 (1964) 15.

20 H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagihara, *J. Organometal. Chem.*, 6 (1966) 86.

21 G. Booth and J. Chatt, *J. Chem. Soc. A*, (1966) 634.

22 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 43 (1970) 2653.

23 Y. Yamamoto and H. Yamazaki, unpublished results.

24 H.C. Clark and L.E. Manzer, private communication.

25 T. Kajimoto, H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, 23 (1970) 275.

26 P.M. Treichel and R.W. Hess, *J. Amer. Chem. Soc.*, 92 (1970) 4731.

27 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 44 (1971) 1873.

28 R. Aumann and E.O. Fischer, *Chem. Ber.*, 101 (1968) 954.

29 W. Beck, K. Burger and W.P. Fehlhammer, *Chem. Ber.*, 104 (1971) 1816.

30 P.M. Treichel and J.P. Stenson, *Inorg. Chem.*, 8 (1969) 2563

31 Y. Yamamoto and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 26 (1969) 167.

32 A.J. Oliver and W.A. Graham, *Inorg. Chem.*, 9 (1970) 243.

33 S. Otsuka, A. Nakamura and T. Yoshida, *J. Amer Chem. Soc.*, 91 (1969) 7198.

34 S. Otsuka, A. Nakamura and T. Yoshida, *Symn. Organometal. Chem., Osaka, October 1969*, p. 181.

35 Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc. Jap.*, 39 (1966) 1084.

36 Y. Yamamoto, T. Takizawa and N. Hagihara, *Nippon Kagaku Zasshi*, 87 (1966) 1355, *Chem. Abstr.*, 67 (1967) 32995c.

37 E.O. Fischer, *Pure Appl. Chem.*, 24 (1971) 407.

38 E.M. Badley, J. Chatt and R.L. Richards, *J. Chem. Soc. A*, (1971) 21.

39 E.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, *Chem. Commun.*, (1969) 1322.

40 B. Crociani, T. Boschi and U. Belluco, *Inorg. Chem.*, 9 (1970) 2021.

41 B. Crociani and T. Boschi, *J. Organometal. Chem.*, 24 (1970) C1.

42 P.M. Treichel, J.J. Benedict, R.W. Hess and J.P. Stenson, *Chem. Commun.*, (1970) 1027

43 E.M. Badley, B.J.L. Killy and R.L. Richards, *J. Organometal. Chem.*, 27 (1971) C37.

44 E. Moser and E.O. Fischer, *J. Organometal. Chem.*, 13 (1968) 209.

45 J.A. Connor and E.O. Fischer, *J. Chem. Soc.* 4, (1969) 578.

46 H.C. Clark and L.E. Manzer, *J. Organometal. Chem.*, 30 (1971) C89.

47 I. Ugi and C. Steinbruckner, *Chem. Ber.*, 94 (1961) 734.