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# Aminocarbene complexes derived from nucleophilic addition to isocyanide ligands

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**Contents**



## Abstract

Isocyanides ligating medium to high-valent electron-poor metal centers can undergo activation toward α-nucleophilic addition to afford a variety of aminocarbene complexes

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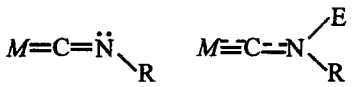
with either heterocyclic or acyclic aminocarbene ligands. These reactions as well as the structural and electronic properties of such products are reviewed. 

*Keywords:* Aminocarbene complexes; Heterocyclic aminocarbene complexes; Isocyanide complexes; Nucleophilic addition reactions; Cycloaddition reactions

## 1. Introduction

By coordination to a transition metal center, isocyanides (C≡NR) can be activated toward a variety of reactions which usually can be rationalized in terms of two contrasting basic modes of activation. The less common one involves coordination to an electron-rich metal site with a high π-electron releasing capacity, resulting in the development of a nucleophilic center at the N atom with localization therein of an electron pair. The isocyanide ligand can then be represented by the aminocarbene-type valence form $M$=C=N̈R (**1**) with a bending geometry at this atom which is thus susceptible to addition of an electrophile (E), typically by reaction with a protic acid or an alkylating agent, to form the aminocarbyne species $M \equiv C - NER$ (**2** E = H, alkyl). These reactions have been described in the preceding review [1]; the current review, of a complementary nature, deals with the opposing type of activation, i.e. toward nucleophilic attack.

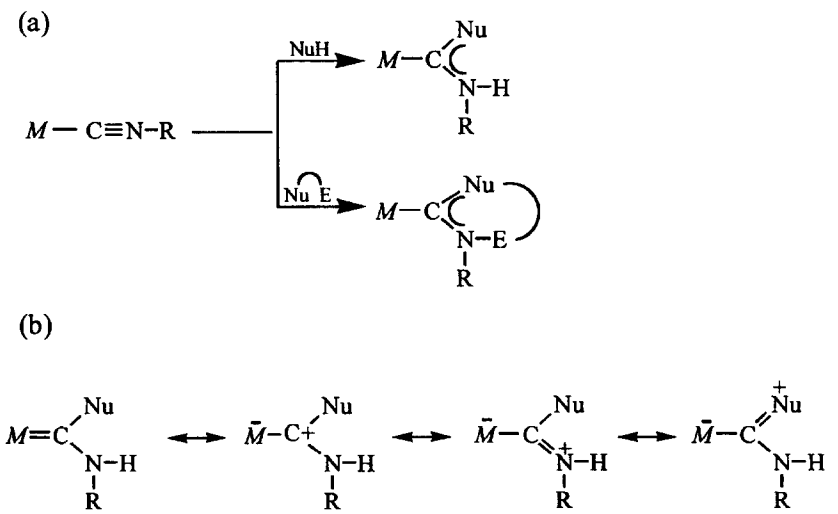


**1** **2**

The nucleophilic attack on coordination-activated isocyanide ligands has attracted worldwide interest in the past, following the discovery that metal–carbene complexes could be readily isolated from addition reactions of protic nucleophiles [2]. The great interest in this field has both theoretical and practical aspects, since the metal–carbene species involved a new type of metal–carbon bond possibly possessing novel reactivity and having implications for organic synthesis. In other words, new, otherwise inaccessible (until 10 years ago, see Section 4), highly reactive species such as carbenes might be trapped upon a complex metal center. However, such stabilization exceeded expectations since the resulting metal–carbene bond proved, in most cases, to be very stable toward further reactions. Typical metal–carbon bond reactions such as insertion and electrophilic cleavage are rather rare. Thus interest focused progressively on methods of preparation, bonding properties and mechanism of formation rather than on reactivity. Either acyclic or cyclic aminocarbene species can be obtained in the reactions of electrophilic CNR ligands with protic nucleophiles such as alcohols, amines and thiols (Scheme 1, NuH=ROH, $RNH_2$ or RSH; R = alkyl, aryl) or with other types of nucleophiles, in particular when bearing an electrophilic center [Nu⌒E, Scheme 1(a)].

The structure and bonding of aminocarbene complexes derived from isocyanide ligands have been already discussed in the past [2b]. In general, the electronic distribution along the M–C–N and M–C–Nu (considering Nu a π-donor atom), as illustrated in the canonical structures of Scheme 1(b) using the VB description, is influenced by several factors such as the type of ligands bound to the metal center, the oxidation state of M and the number and type of heteroatoms adjacent to the carbene carbon so that a single canonical form cannot be taken as representative of all possible metal–carbene situations. On the other hand, aminocarbenes, and particularly those where Nu is an heteroatom, as is the case of most of the carbenes reported in this review, have seen shown to be good σ-donors with little or no π-acceptor properties ([2b] see also Ref. [93a,b]). Thus, except of a few cases, we will generally use throughout this review the unified representation of Scheme 1(a).

The above type of isocyanide reactivity leading to aminocarbene species appears to be facilitated when the RNC ligand is coordinated to an "electron-poor" metal center, e.g. with reduced electron density (usually, metal ions in the higher oxidation state) so as to enhance the σ/π ratio in the M–CNR bond and hence the donor/acceptor properties of the CNR ligand. These are also affected by the nature of the other ligands L coordinated to the metal and the R group of the isocyanide. Thus, good π-accepting ligands L will reduce the electron density on the metal and correspondingly increase the σ/π ratio in the M–CNR bond, while aryl isocyanides (or isocyanides in which R contains electron-withdrawing groups) are better π-acceptors than the alkyl analogues. Steric factors of the ancillary ligands and/or the R group of the isocyanide may also influence the reactivity of metal-coordinated isocyanides as will be discussed further on. In many instances this type of reactivity corresponds to an increase of $\Delta\nu$(N≡C) on going from the unbound




Scheme 1. (a) Activation of isocyanide toward nucleophilic addition (NuH — protic nucleophile; Nu E — nucleophile that also bears an electrophilic center) and (b) valence-bond representation of the derived aminocarbene ligand (exemplified for the case of the NuH nucleophiles).

isocyanide to the isocyanide coordinated in different environments as observed in the values of $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$, which reflects the electrophilic character of the isocyanide carbon and therefore its ability to undergo nucleophilic attack [2b,c]. A positive value of $\Delta\nu \geq 40$ cm$^{-1}$ was observed to indicate CNR ligand susceptibility to nucleophilic attack [2b].

In the last 15 years cyclization reactions of coordinated isocyanide ligands to give N-heterocyclic aminocarbene derivatives have attracted much synthetic interest, possibly because they relate to the formation of heterocyclic organic compounds promoted by transition metal centers [3], and they will be discussed first in the following sections. A review on the coordination chemistry of β-functional phenyl isocyanides has recently appeared [2a] and therefore this subject will not be covered here in detail.

## 2. Synthesis of heterocyclic aminocarbene complexes

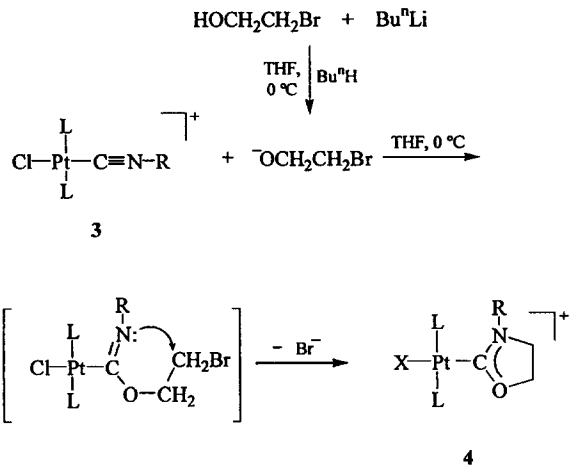
The cyclization reactions of electrophilic metal-coordinated isocyanide ligands leading to heterocyclic aminocarbene complexes have been accomplished by different synthetic strategies which will be described in the following sections.

While the basic mechanistic features of the nucleophilic addition reactions to isocyanides to give acyclic aminocarbenes are understood (see below), reactions resulting in the formation of cyclic carbenes have not been examined in detail, although they are of interest as they relate to the formation of heterocyclic organic compounds [3]. Within this research area, interest has focused on the cyclization reactions of electrophilic CNR ligands leading to heterocyclic carbene complexes, which have been accomplished by several strategies as reported below.

### *2.1. Cycloaddition reactions of isocyanide complexes with haloalcohols and haloamines*

The homologous series of Pt(II) and Pd(II) cationic complexes of the type *trans*-[M(X)(CNR)$L_2$][$BF_4$] (X = halide, alkyl; R = alkyl, aryl; L = monodentate tertiary phosphine), in which both the R groups of the isocyanide ligand as well as the other metal substituents were varied over a wide range, and a few neutral bis(isocyanide) Pt(II) and Pd(II) complexes of the type *cis*-[$MCl_2$(CNR)$_2$] were investigated in the reactions with 2-bromoethanol $HOCH_2CH_2Br$ [4] and 2-bromoethylamine, $H_2NCH_2CH_2Br$ [5], which have an easily displaced $Br^-$ at the β carbon atom.

All the isocyanide complexes display high positive $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$ values, e.g. in the range 54–108 cm$^{-1}$ for M = Pt and 79–108 cm$^{-1}$ for M = Pd, thus indicating that the isocyanide carbon is a potentially reactive electrophilic center [4]. As expected, the lowest $\Delta\nu$ value is observed for *trans*-[Pt(Me)($CNC_6H_4$-OMe-4)($PMePh_2$)$_2$][$BF_4$], where the strongly σ-electron-donating Me group is *trans* to the isocyanide ligand.




Scheme 2. Formation of cyclic mono-aminooxycarbene complexes of Pt(II) from nucleophilic addition of haloalcohols to isocyanides [4].

The electrophilic isocyanide ligands in the cationic Pt(II) complexes *trans*-$[Pt(Cl)(CNR)L_2][BF_4]$ (**3**) (Scheme 2) react in THF with a slight molar excess of 2-bromoethoxide, $^-OCH_2CH_2Br$, generated by reaction of the corresponding bromoalcohol with Bu$^n$Li, to afford the corresponding five-membered cyclic aminooxycarbene derivatives **4** [4].

The less sterically hindered CNMe and aryl isocyanide ligands in **3** are converted in a few minutes into the final products **4** in ca. 70–90% yield, while the more bulky $CNC_6H_{11}$ derivative gave only a 25% yield. The CNBu$^t$ ligand in *trans*-$[Pt(Cl)(CNBu^t)(PPh_3)_2][BF_4]$ does not react at all, nor does $CNC_6H_4OMe$-4 in *trans*-$[Pt(Cl)(CNC_6H_4OMe\text{-}4)(PCy_3)_2][BF_4]$ with bulky $PCy_3$ ligands or in *trans*-$[Pt(Me)(CNC_6H_4OMe\text{-}4)(PMePh_2)_2][BF_4]$ where the isocyanide is *trans* to the strongly σ electron-donating methyl group. It is also observed that the bromide ion that is liberated upon ring closure displaces the chloride ion to various extents depending on reaction times.

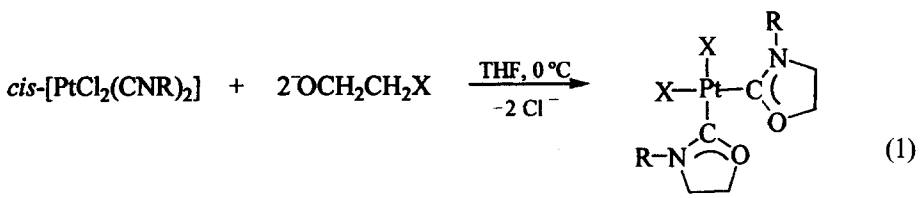
No Pd(II)–carbene complexes were isolated from the analogous reactions of Pd(II)–isocyanide complexes of the type *trans*-$[Pd(Cl)(CNR)(PPh_3)_2][BF_4]$ (R = $C_6H_4OMe$-4, $C_6H_4Me$-4, Me, $C_6H_{11}$) with 2-bromoethoxide, even at −50°C. In all cases, red solutions were obtained in which no $\nu(C{\equiv}N)$ of the starting isocyanide or $\nu(C=N)$ of the carbene product were present, thereby suggesting the formation of Pd(0) species.

A reasonable mechanism for the isocyanide to cyclic aminocarbene transformation reported in Scheme 2 entails initial deprotonation of the haloalcohol by Bu$^n$Li,

followed by nucleophilic attack on the isocyanide carbon atom to give an imidoyl intermediate, which then undergoes intramolecular cyclization by imino nitrogen displacement of $Br^-$ to give the final carbene product. Although stable imidoyl complexes M–C(OR)=NR [e.g. M = Pt(II), Au(I), Ag(I)] are known to be formed by nucleophilic attack of alkoxide ions $RO^-$ on coordinated isocyanides [2e] or by insertion of isocyanides on a M–OR bond [6], no evidence was observed for the generation of the intermediate imidoyl species in Scheme 2, even when R is an efficient electron-withdrawing group such as *p*-nitrophenyl, which would make the imino N atom less nucleophilic for $Br^-$ displacement.

The isocyanide cyclization reaction reported in this scheme is closely related to the conversion of CO ligands in several metal carbonyl complexes to cyclic dioxycarbene derivatives by $^-OCH_2CH_2Br$ [7]. These latter reactions are also presumed to proceed via an alkoxycarbonyl intermediate, which was not detected since it cyclizes rapidly to the carbene ligand.

Treatment of *cis*-$[PtCl_2(CNC_6H_4OMe\text{-}4)_2]$ with 2 equiv. of 2-haloethoxide under reaction conditions analogous to those used for the cationic derivatives rapidly gives the bisaminooxycarbene derivatives **5**, in high yield (Eq. (1)) [4,8].




(1)

R = $C_6H_4OMe$-4; X = Cl, Br

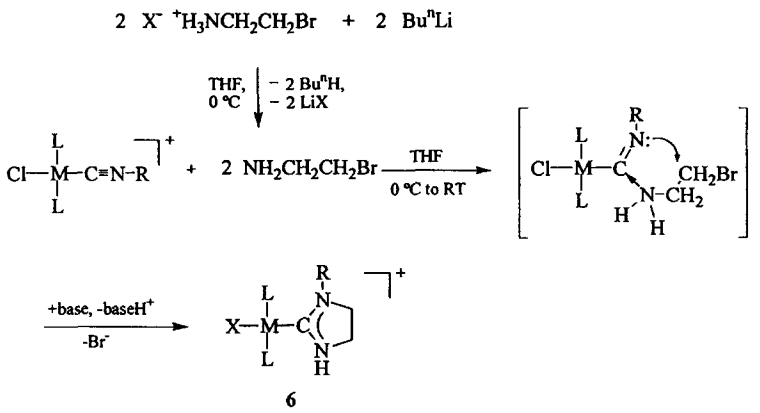
**5**

Also in this case, chloride–bromide exchange takes place at the metal center and no carbene complexes were obtained from neutral bis(isocyanide) palladium(II) complexes, since reductive elimination to Pd(0) occurs in the presence of alkoxide ions.

Five-membered cationic diaminocarbene complexes of Pt(II) and Pd(II) of type **6** were obtained [5] from the corresponding isocyanide derivatives (Scheme 3) by reaction with 2 mol of 2-bromoethylamine, generated by treatment of the ammonium salt $[BrCH_2CH_2NH_3]Br$ with $Bu^nLi$ in THF at 0°C. The reactions were completed in 1 h and the yields were higher for the Pt(II) products compared to those of Pd(II).

The carbene complex *trans*-$[Pt(Me)\{\overline{CN(C_6H_4OMe\text{-}4)CH_2CH_2N}\}(PMePh_2)_2][BF_4]$ was produced in good yield, but the reaction required prolonged stirring of the isocyanide complex (24 h) with excess 2-bromoethylamine(4 mol) to go to completion. The slowness of this reaction is explained by the less electrophilic character of the isocyanide carbon in *trans*-$[Pt(Me)(CNC_6H_4OMe\text{-}4)(PMePh_2)_2][BF_4]$ being *trans* to a methyl group, which is a stronger σ-electron donor ligand compared to chloride.

The formation of the cyclic diaminocarbene complexes outlined in Scheme 3 has been suggested to occur by initial nucleophilic attack of the bromoethylamine on



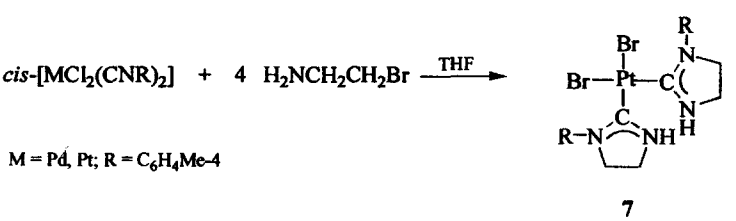

M = Pd, Pt; R = $C_6H_4OMe$-4, $C_6H_4Me$-4, Me; L = $PPh_3$, $PMePh_2$; X = Cl, Br; Base = $NH_2CH_2CH_2Br$

Scheme 3. Formation of cyclic mono-diaminocarbene complexes of Pt(II) and Pd(II) from nucleophilic addition of an haloamine to an isocyanide [5].

the isocyanide carbon to afford an imino intermediate which then undergoes ring closure to the final product in the presence of a further molecule of 2-bromoethylamine. Although no intermediates were detected, a similar mechanism has been proposed [9] on the basis of kinetic investigations for the reactions of Pd(II)-coordi nated isocyanides with various amines and for the cyclization reactions of CO groups in metal carbonyl complexes with 2-bromoethylamine or aziridine [7,10].

The N–H group in the Pt(II)- and Pd(II)-cyclic diaminocarbene complexes **6** (X = Br) is deprotonated at low temperature by $Bu^nLi$ to give the intermediate imino species $[MBr(\overline{C{=}NCH_2CH_2NR})L_2]$ (M = Pd, Pt) (M = Pd, Pt) which could not be isolated and rapidly reacts with allyl bromide ($BrCH_2CH{=}CH_2$) or propargyl bromide ($BrCH_2C{\equiv}CH$) to give the corresponding *N*-alkyl products *trans*-$[MBr\{\overline{CN(R')CH_2CH_2NR}\}L_2]$ (R′ = $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$) [5].

The cyclization process shown in Scheme 3 may involve one or even two isocyanide ligands in neutral Pt(II) and Pd(II) complexes, affording, in the latter case, bis(diaminocarbene) derivatives **7** (Eq. (2)) [8]. The reaction proceeds stepwise through the rapid formation of a carbene–isocyanide intermediate complex, detected by IR spectroscopy, which slowly converts to the final dicarbene product.

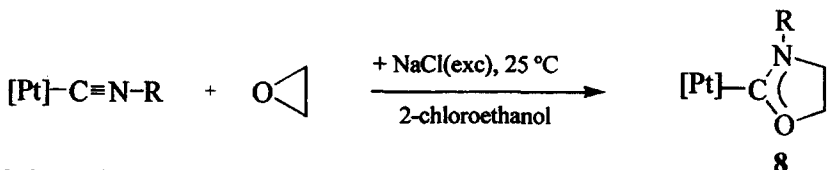



(2)

Structural investigations of *trans*-[PtBr{$\overline{CN(C_6H_4Me\text{-}4)CH_2CH_2O}$}$(PPh_3)_2$]-[$BF_4$] containing a five-membered aminooxycarbene ligand, and *cis*-[$PtBr_2$-{$\overline{CN(C_6H_4Me\text{-}4)CH_2CH_2N(H)}$}$(PPh_3)$] containing a five-membered diaminocarbene ligand, show that both cyclic carbenes are strictly planar. Bond lengths within the five-membered ring for the diaminocarbene ligand indicate a significant π-bonding between the carbene carbon and the two adjacent heteroatoms. The Pt(II)–carbene bond distance of 1.98(1) and 1.93(1) Å found for the aminooxy- and diaminocarbene complexes, respectively, is in good agreement with other Pt(II)–C(carbene) distances of square planar Pt(II) systems, which usually occur in the range 1.82–2.01 Å when a halide is *trans* to the carbene ligand [11]. The aminooxycarbene ligand is almost perpendicular (93.4°) to the Pt(II) square plane, as observed in several other Pt(II)–carbene complexes [11], while the dihedral angle formed by the diaminocarbene ring with the platinum square plane is larger (102.1°). This feature can be explained by the dissymmetry of the steric pressure exerted by the two different *cis* ligands (Br and $PPh_3$, for the diaminocarbene, and two $PPh_3$, for the aminooxycarbene complex).

### 2.2. Cycloaddition reactions of isocyanide complexes with three-membered heterocycles

Five-membered cyclic aminooxy-, diamino- and aminothiocarbene complexes can be formed from isocyanide ligands coordinated to Pd(II) and Pt(II) metal centers [12] by taking advantage of the tendency of highly strained three-membered heterocycles $\overline{YCH_2CH_2}$, where Y = O (oxirane), NH (aziridine) and S (thiirane), to undergo ring opening reactions summarized in Eq. (3).




(3)

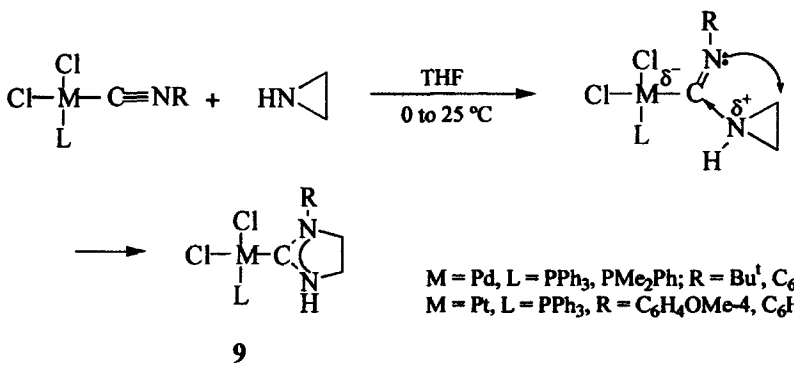
**8**

[Pt] = *cis*-[$PtCl_2(PPh_3)_2$], *trans*-[$PtCl(PPh_3)_2$][$BF_4$], *cis*-[$PtCl_2$(CNR)]
R = $C_6H_4OMe$-4

The conversion of an isocyanide to a cyclic carbene (**8**) by oxirane proceeds only in the presence of $Cl^-$ ion (ca. fivefold excess with respect to the metal complex), which likely attacks an oxirane carbon to give ring opening and formation of $^-OCH_2CH_2Cl$. The latter then adds to the electrophilic isocyanide carbon yielding the aminooxycarbene by a mechanism similar to that reported in Scheme 2. The ring opening of oxirane by $Cl^-$ attack to produce the haloalkoxide ion is supported by other studies in which the halide ion acts as catalyst to produce ring opening in certain organic reactions [13]. The mechanism proposed for an isocyanide to aminoxycarbene conversion is also similar to that previously proposed for the related conversion of ligated CO to a dioxycarbene ligand by oxirane and halide ion

[10b]. It is observed that the formation of **8** is slow (ca. 3 days) and, as previously observed for similar $HOCH_2CH_2Cl/Bu^nLi$ reactions, Pd(II)–isocyanide complexes failed to give the corresponding carbene derivatives.

In contrast with the oxirane/$Cl^-$ reactions with coordinated isocyanide ligands, aziridine reacts spontaneously with the CNR ligand in Pt(II) and Pd(II) complexes affording five-membered cyclic diaminocarbene derivatives **9** in good yield [12] (Eq. (4)). The aryl isocyanide ligands react faster than the bulky $CNBu^t$ ligand and this trend in reactivity parallels that found for the reactions of coordinated CNR ligands with $^-OCH_2CH_2Br$ and $H_2NCH_2CH_2Br$ [4,5]. It was found that the reaction of the $CNBu^t$ ligand, which does not react with aziridine alone when coordinated to Pt(II) does, however, proceed when in the presence of $ClCH_2CH_2NH_3^+Cl^-$ [8].



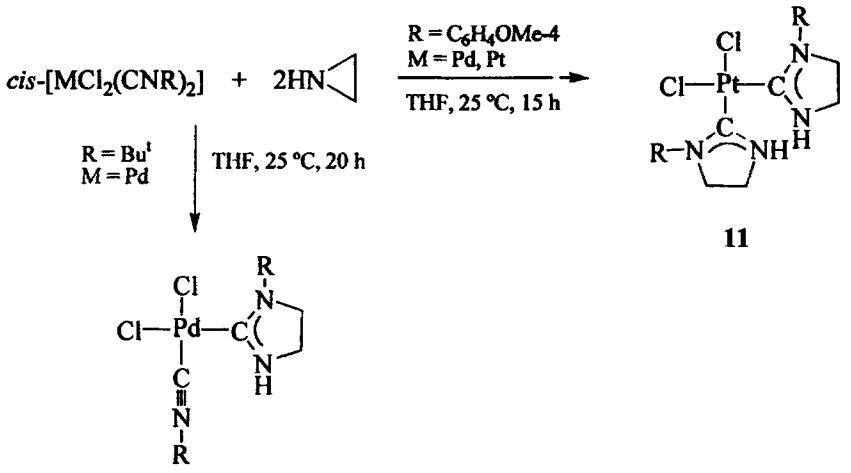

(4)

**9**

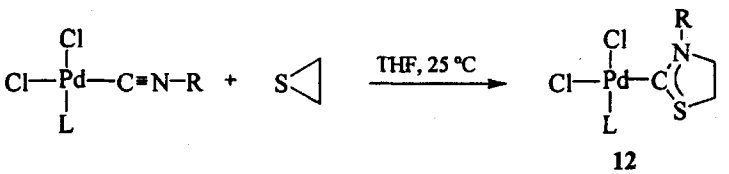
The possible mechanism for the isocyanide-cyclic carbene conversion by aziridine could proceed by an initial attack of the entering amine on the electrophilic isocyanide carbon atom to give an intermediate imino-metal(II) species. The subsequent step to give the final complex could involve C–N ring opening of the coordinated aziridine, which may occur by intramolecular attack of the nucleophilic imino nitrogen on the adjacent methylene group of aziridine.

Bisisocyanide complexes of Pd(II) of the type $[MCl_2(CNR)_2]$ (M = Pd, Pt) are found to react with 2 equiv. of aziridine to give mono- or dicarbene complexes (**10** or **11**, respectively) depending on the nature of the CNR ligand [8,12] (Eq. (5)). When R = $Bu^t$ only one isocyanide ligand is converted to a carbene group as in **9**, but when R = $C_6H_4OMe$-4 the reaction proceeds stepwise through the rapid formation of a carbene–isocyanide complex, which slowly converts to the final dicarbene product **11**.

Thiirane was found to react [12] only with some isocyanide ligands in Pd(II), but not Pt(II), complexes to afford the corresponding five-membered cyclic aminothiocarbene derivatives **12** (Eq. (6)), and a reaction intermediate similar to that proposed for the aziridine reactions may be suggested.




(5)

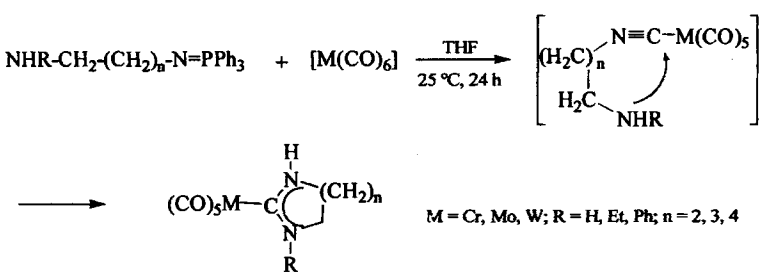



(6)

L = $PPh_3$, $PMe_2Ph$, R = $C_6H_4OMe$-4; L = $C_6H_{11}NC$, R = $C_6H_{11}$

## 2.3. Cycloaddition reactions with other nucleophiles

Following previous studies on the reactions of the phosphinimine phosphine ligand $Ph_3P{=}N(CH_2)_3PPh_2$ with metal carbonyls to form isocyanide complexes [14], a series of heterocyclic metal carbene complexes **13** were prepared (Eq. (7)) by reaction of $[M(CO)_6]$ (M = Cr, Mo, W) with amino-phosphinimines of the type $RNH(CH_2)_nN{=}PPh_3$ (R = H, Et, Ph; $n = 2$–4), which were obtained in high yield by reaction of the corresponding azido compounds $RNH(CH_2)_nN_3$ with $PPh_3$ [15].




(7)

The reaction proceeds by deoxygenation of one carbonyl of the metal complex by the amino-phosphinimine (1 equiv.) with elimination of $PPh_3P{=}O$ and formation of the corresponding isocyanide intermediate, which, in most cases, was not isolated, cyclizing rapidly by intramolecular attack of the dangling amino moiety on the isocyanide carbon atom to produce five-, six- or even seven-membered diaminocarbene complexes. The only exception to this synthetic route was due to the reaction of $H_2N(CH_2)_4N{=}PPh_3$ with $[W(CO)_6]$, which under the same experimental conditions gave exclusively the isocyanide complex $[W(CO)_5\{C{\equiv}N(CH_2)_4NH_2\}]$ that could be isolated and characterized. This outcome is quite similar to the species $[Cr(CO)_5\{C{\equiv}N(CH_2)_4NH_2\}]$ obtained from the reaction of the trichloromethyl isocyanide complex $[Cr(CO)_5(C{\equiv}NCl_3)]$ with $H_2N(CH_2)_4NH_2$, which also did not undergo intramolecular cyclization to form the cyclic diaminocarbene species [16]. However, the isocyanide–amine complex $[W(CO)_5\{C{\equiv}N(CH_2)_4NH_2\}]$ was slowly converted into the corresponding cyclic diaminocarbene complex in the presence of diethylamine.

Treatment of the diaminocarbene complexes **13** (M = Cr, Mo, W; R = H, $n = 1$ or 2) with acylating agents R′COX (R′ = Ph, Me) results in their conversion into the corresponding isocyanide complexes $[M(CO)_5\{C{\equiv}N(CH_2)_nNR_{2-m}(COR')_m\}]$ ($n = 2$, 3; $m = 1$, 2; R′ = Ph, Me) [17]. The acylation of the amino group appears to destabilize the ring causing the cleavage of the C–N bond to form the isocyanide product [17].

It is interesting to note that other amino-functionalized phenylisocyanides coordinated to $\{M(CO)_5\}$ (M = Cr, W) moieties were not observed to undergo intramolecular cyclization to produce six-membered diaminocarbene derivatives [18]. In fact, the *o*-(aminomethyl)phenyl isocyanide complexes $[M(CO)_5(C{\equiv}NC_6H_4\text{-}CH_2NHAr\text{-}2)]$ (M = Cr, W; Ar = $C_6H_4$Me-4), which were obtained from the corresponding *o*-iodomethyl derivatives by reaction with an aromatic amine such as *p*-toluidine, could be isolated and spectroscopically characterized.

The X-ray structure [16] of $[Mo(CO)_5\{{=}\overline{CN(H)CH_2CH_2CH_2N(H)}\}]$ containing a six-membered diaminocarbene ligand, shows the Mo–C(carbene) bond distance of 2.262(6) Å and carbon–nitrogen bond distances of 1.31(1) Å, typical for C=N bond. The carbene ligand shows a half-chair-like conformation and it is staggered with the $\{Mo(CO)_5\}$ unit.

No dicarbene complexes were obtained [16] from the reactions of $[M(CO)_6]$ with 2 equiv. of amino-phosphinimine. This was explained by the fact that the monocarbene complexes $[M(CO)_5(carbene)]$ (**13**) display carbonyl stretching frequencies shifted to lower wavenumbers compared to $[M(CO)_6]$, thus indicating a lower electrophilic character of CO toward nucleophilic attack by the amino-phosphinimine. Thus, such reactions proceed only with highly electrophilic carbonyl ligands and this is confirmed by the reaction of $[ReBr(CO)_5]$ with 1 equiv. of $H_2N(CH_2)_2N{=}PPh_3$ to afford the monocarbene complex $[ReBr(CO)_4\text{-}\{{=}\overline{CN(H)CH_2CH_2N(H)}\}]$ which displays $\nu$(CO) at 2105, 2003 and 1916 $cm^{-1}$. The latter complex further reacts with another equivalent of $H_2N(CH_2)_2N{=}PPh_3$ to give the dicarbene derivative *fac*-$[ReBr(CO)_3\{{=}\overline{CN(H)CH_2CH_2N(H)}\}_2]$ which was also structurally characterized [16].

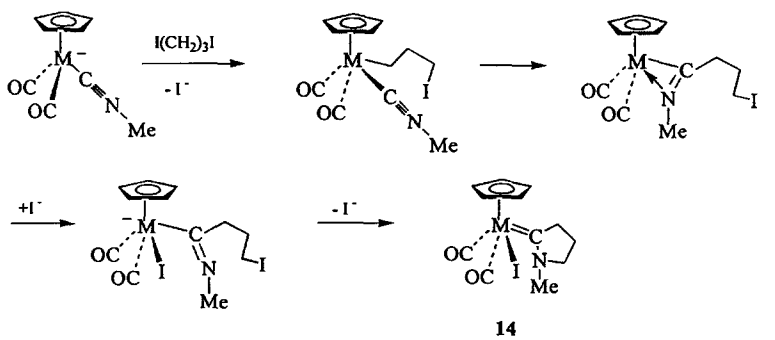
The reactions of the isocyanide metal anions $[(Cp)M(CNMe)(CO)_2]^-$ (M = Mo, W) with $I(CH_2)_3I$ in THF solution have been reported to give in good yield cyclic aminocarbene complexes as shown in Scheme 4 [19]. The reaction of the metal anion with 1,3-diiodopropane affords the alkylated product which then undergoes migration of the alkyl group $(CH_2)_3I$ to the isocyanide carbon to give an azacyclopropane-type structure. Addition of iodide ion to remove the M–N interaction, followed by intramolecular ring closure at the imino nitrogen with displacement of $I^-$ ion, leads to the formation of a five-membered aminocarbene species **14**. The structure of the Mo compound was studied by X-ray crystallography.

Similarly, the six-membered carbene ring complex *cis*-$[(Cp)MoI\{=\overline{C(CH_2)_4N}(Me)\}(CO)_2]$ is formed in the analogous reaction of $[(Cp)Mo(CNMe)(CO)_2]^-$ with $I(CH_2)_4I$ [19].

The isocyanide insertion reactions of some manganese(I) alkyl and iminoacyl complexes have been reported [20] to afford in some instances carbene complexes (Scheme 5). Manganese(I) alkyl complexes undergo PdO-catalyzed CO replacement by $CNR^1$ to give $[Mn(CH_2R)(CNR^1)(CO)_4]$ which react with a further molecule of isocyanide to afford the corresponding iminoacyl intermediate **15**. At this point, two possible pathways (a and b) are available. In the minor one (a), an isocyanide is attacked intramolecularly by the iminoacyl N atom to produce the carbene species **16**. The major pathway (b) is insertion of a second isocyanide to afford the bis(iminoacyl) complexes **17** having a 1-mangana-2-azacyclobutene ring. These latter complexes may react further with a molecule of isocyanide $CNR^2$ to give carbene complexes of type **18**, whose structure has been also confirmed by X-ray crystallography.

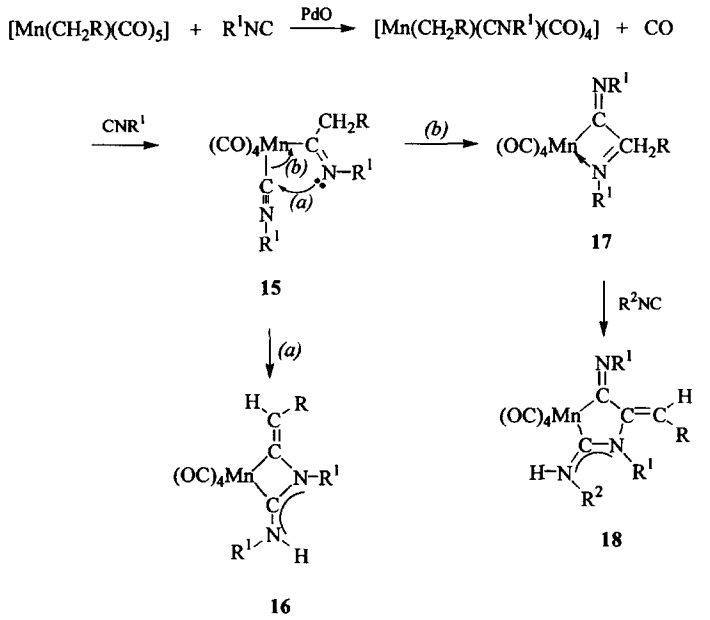
A carbene complex similar to **16**, i.e. $[\overline{Fe\{=C(=CH_2)N(R)C(NHR)\}}(CO)(CNR)(PMe_3)_2]^+$ (R = $C_6H_{11}$) was previously prepared [21] by rearrangement of the product of double isocyanide insertion $[FeI(CNR)\{C(=NRC(=NR)CH_3\}(CO)(PMe_3)_2]$.

A luminescent hexanuclear platinum(II) complex containing chelating dicarbenes and bridging cyanide ligands, $[\{Pt(CN)(C_{10}H_{21}N_4)\}_6]$, was obtained by reaction of $K_2[PtCl_4]$ with $CNBu^t$ and hydrazine hydrate [22]. Each of the chelating dicarbene




14

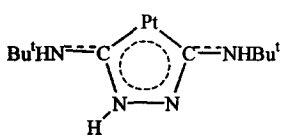
Scheme 4. Formation of cyclic aminocarbene complexes of Group 6 metals from cycloaddition reactions of isocyanide complexes with 1,3-diiodopropane [19].




R = $C_6H_4Cl$-4, $C_6H_4OMe$-4; $R_1$ = $C_6H_4Me$-4; $R_2$ = $C_6H_4Me$-4, $C_6H_{11}$

Scheme 5. Formation of aminocarbene complexes of Mn(I) from isocyanide insertion reactions [20].

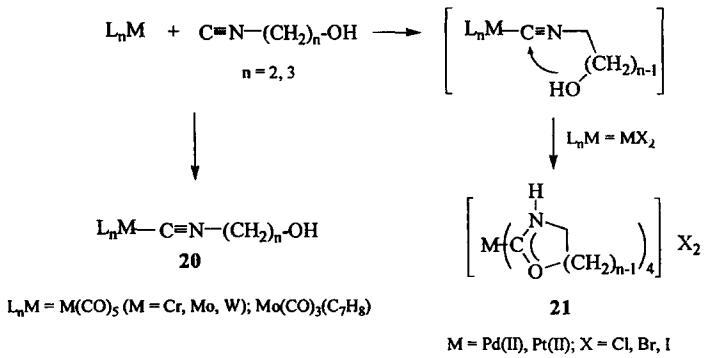
species is represented by the planar five-membered metallacycle motif $PtC_{10}H_{21}N_4$ (**19**) which was formed by nucleophilic addition of hydrazine to two CNBu$^t$ ligands (a type of reaction known since long for CNMe but leading then to a mononuclear complex [23]) whereas the bridging cyanide was derived from dialkylation of the isocyanide.




**19**

## 2.4. Reactions of functionalized isocyanide complexes

The interest in the transition-metal coordination chemistry of functionalized isocyanides stems from the role of the function that can (i) interact directly with the isocyanide; (ii) activate the C–H bond of an adjacent methylene group to produce α-metalated isocyanides or metal–carbon bonds; or (iii) react independently to form new functional isocyanides. The more relevant examples of these ligands



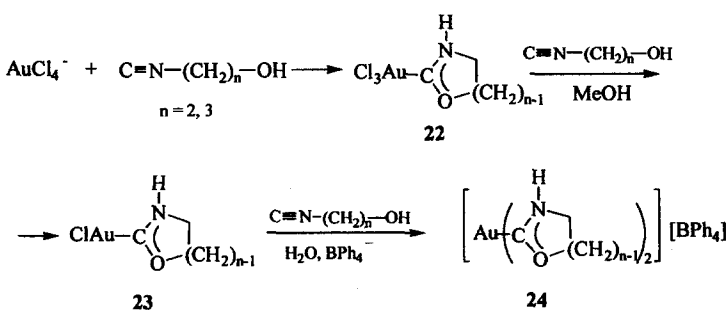
Scheme 6. Formation of cyclic aminooxycarbene complexes from cyclization of hydroxyalkyl isocyanides [24,25].

whose reaction chemistry leads to the formation of transition metal carbene complexes are described in the following sections.

*2.4.1. Hydroxyalkyl- and hydroxyarylisocyanides*

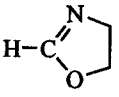
Pioneering work in the area of functionalized isocyanide chemistry has been done by Fehlhammer and co-workers who initially synthesized 2- and 3-hydroxyalkyl isocyanides such as 2-hydroxyethyl isocyanide, $HOCH_2CH_2N{\equiv}C$, and 3-hydroxypropyl isocyanide, $HOCH_2CH_2CH_2N{\equiv}C$ [24] and showed that these ligands, with an appropriate choice of the metal substrate, may undergo coordination through the isocyano group to give **20** or eventually even form the corresponding N,O-cyclic carbene oxazolidin-2-ylidene via intramolecular attack of the dangling OH group on the coordinated isocyanide carbon atom to afford **21**, as illustrated in Scheme 6. With transition metal ions such as $Pd^{2+}$ and $Pt^{2+}$ the spontaneous cyclization of 2-hydroxyethyl and 3-hydroxypropyl isocyanides led exclusively to the synthesis of homoleptic heterocyclic aminocarbene metal complexes **21** [24,25].

Similar reactions of $HO(CH_2)_nN{\equiv}C$ ($n = 2$, 3) with $Na[AuCl_4]$ in methanol or water yield initially a gold(III)–carbene complex **22**, which is then reduced in the presence of excess isocyanide to the corresponding gold(I) derivative **23** and eventually to the cationic dicarbene complex **24** (Eq. (8)) [24].



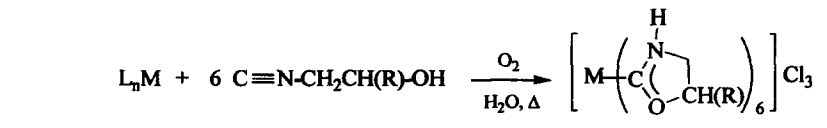
(8)

These cyclization reactions proceed with a stoichiometric ratio of $L_nM$ to isocyanide, while a catalytic amount of metal leads quantitatively under mild conditions to the formation of the organic-free heterocycles, as illustrated for the synthesis of 2-oxazoline **25** from $C{\equiv}N(CH_2)_2OH$ in the presence of $ZnSO_4$ or $PdCl_2$.



**25**

Homoleptic hexacarbene complexes of the type **26** (Eq. (9)) were also obtained by reaction of the 2-hydroxyalkyl isocyanides $CNCH_2CH(R)OH$ (R = H, Me) with the metal chlorides $CoCl_2$ and $RhCl_3$ in warm ethanol or water in air [26]. The presence of dioxygen was necessary to oxidize Co(II) to Co(III) and to prevent Rh(III) reduction by the isocyanide. A Co(III)–hexacarbene (R = H) complex was also structurally characterized.

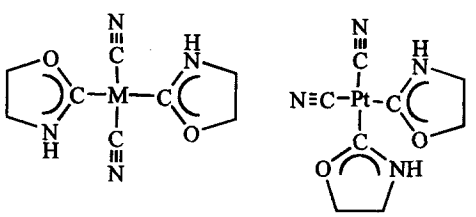


(9)

**26**

$L_nM = CoCl_2, RhCl_3{\cdot}3H_2O$; R = H, Me

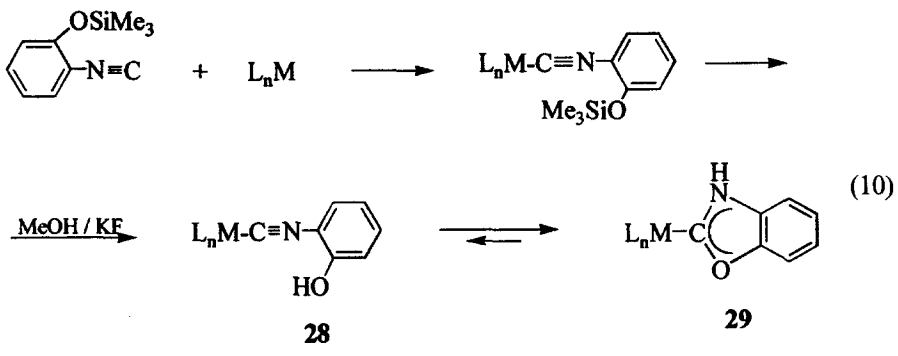
Contrary to chloride, the cyano ligands in the $[M(CN)_2]$ (M = Pd, Pt) compounds are not displaced even in the presence of an excess of the hydroxyalkyl isocyanide, thus making possible the preparation of heteroleptic N,O–carbene complexes [27a] from their reactions with 2-(trimethylsiloxy)ethyl isocyanide, $C{\equiv}NCH_2CH_2OSiMe_3$, in methanol and in the presence of fluoride [27b]. Methanolysis of the trimethylsiloxy function in the presence of $F^-$ ions affords the hydroxy moiety, which then intramolecularly attacks the isocyanide carbon to form the cyclic carbene. Both the *trans*- and *cis*-isomers of **27** thus obtained have been characterized by crystal structure determinations. In the *cis*-Pt(II) compound the carbene ligands are linked by NH···O hydrogen bonds in a quasi-chelating arrangement. The Pt···Pt distance of 3.2828(6) Å observed in this crystal structure indicates a weak metal–metal interaction [27a].



**27**

Hahn and co-workers reported the coordination properties of 2-hydroxyphenyl isocyanide and its trimethylsiloxy derivative, as well as those of 2,6-(dihydroxy)phenyl and 2,6-bis(trimethylsyloxy)phenyl isocyanides. Typical reactions leading to N,O-cyclic carbene (1,2-dihydrobenzoxazol-2-ylidene) derivatives **29**

[28,29] and **31** [30] (via intramolecular nucleophilic attack of the hydroxy function at the isocyanide carbon atom) or to an equilibrium mixture with the corresponding isocyanide complexes **28** or **30**, respectively, according to the electronic properties of the metal substrate $L_nM$ are given in Eq. (10) and (11), but they will not be discussed further since they have already been reviewed [2a]. Nevertheless, it is noteworthy to mention that with electron-poor metal centers such as $L_nM$ = $\{Fe(CO)_4\}$ [28] or the Re(V) site *fac*-$\{Re(O)Cl_3\}$ [31] there is a weak $(d \rightarrow p)\pi$ backbonding from the metal center and the isocyanide is activated toward nucleophilic attack by OH. Changes of the electronic properties of the metal center may change the reactivity pattern as observed for $L_nM$ = *cis*-$\{W(CO)_4(PPh_3)\}$ [32]. In this case, substitution of the π-acceptor CO in $\{W(CO)_5\}$ by the σ-donor $PPh_3$ enhances the backbonding and stabilizes the coordinated isocyanide of type **28**. The latter species is also observed in certain electron-rich Re(I) and Re(III) complexes [31] of the type $L_nM$ = *trans*-$\{ReCl(dppe)_2\}$ and *mer*-$\{ReCl_3(PPh_3)_2\}$. In several other examples in which $L_nM$ = $\{M(CO)_5\}$ (M = W, Cr, Mo) [28] an equilibrium is observed between **28** and **29**, which is shifted toward the carbene species. In most of the investigated cases, the ν(CN) stretching frequencies or the calculated values of the force constants for the CN bond of the coordinated 2-trimethylsyloxy isocyanide allows the prediction of the course of the reaction after Si–O bond cleavage [32].

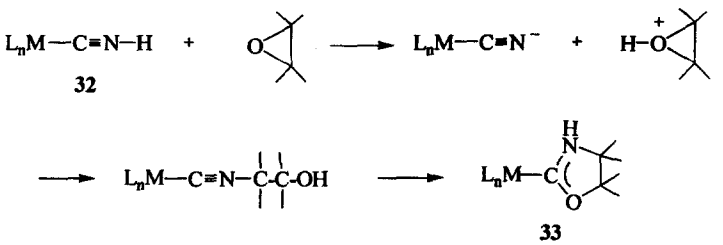



*2.4.2. Hydrogen isocyanide and α-perchloroalkyl isocyanides*

A wide range of functional isocyanides can be prepared from cyano metal complexes; their syntheses and organometallic chemistry has been reviewed by Fehlhammer and Fritz [33] and only a short description of their reactions to give carbene complexes will be reported here. Hydrogen isocyanide metal complexes,

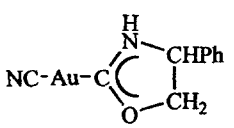
$L_nM$–C≡N–H, can be usually generated in situ by N-protonation of the corresponding metal-coordinated cyanide (although other routes are known [1]). Only in a few cases the former route led to the isolation of discrete hydrogen isocyanide metal complexes such as $[M(CNH)(CO)_5]$ (M = Cr, Mo, W) [34a,b], $[W(OEt)(Cp)_2(CNH)][PF_6]$ [34c], $[Ru(Cp)(CNH)(dppe)][BF_4]$ [34d] and $[Fe(Cp)(CNH)(dppe)][BF_4]$ [34e]. None of these complexes has been characterized by X-ray or neutron diffraction and only fragmentary IR data are available. In some cases, a drop in the $\nu$(NC) frequency on protonation has been observed as in $[Ru(Cp)(CNH)(dppe)][BF_4]$ [$\nu$(NC) = 2024 s cm$^{-1}$, nujol mull] versus $[Ru(Cp)(CN)(dppe)]$ [$\nu$(NC) = 2070 s cm$^{-1}$, nujol mull], while other hydrogen isocyanide complexes experience a slight shift to higher wavenumbers as in $[W(OEt)(Cp)_2(CNH)][PF_6]$ [$\nu$(NC) = 2133 s cm$^{-1}$, KBr] versus $[W(OEt)(Cp)_2(CN)]$ [$\nu$(NC) = 2105 s cm$^{-1}$, KBr] [33].

$L_nM$–C≡N–H complexes **32** undergo hydrosocyanation reactions, e.g. addition to several unsaturated substrates such as alkenes, alkynes an α,β-unsaturated carbonyl compounds to afford new alkyl, vinyl and γ-oxoalkyl isocyanide complexes, respectively [33]. They can also undergo cycloaddition reactions with oxiranes [33] to give the oxazolidin-2-ylidene complexes **33** by a mechanism illustrated in Eq. (12).




(12)

Protonation of oxirane by hydrogen isocyanide affords the protonated oxirane which then undergoes ring opening upon nucleophilic attack of the cyano-N atom to yield an open chain hydroxyalkyl isocyanide. The latter then spontaneously rearranges to the N,O-cyclic carbene **33** through an intramolecular 1,2-addition of the hydroxy function across the CN triple bond as previously described for other hydroxyalkyl and aryl isocyanides. Depending on the nature of the metal substrate and the type of epoxide, the reaction may stop at the isocyanide step or proceed to the ylidene derivative. Thus, for instance, reactions of [Au(CN)(CNH)] [35] and $[W(CO)_5(CNH)]$ [36] with styrene oxide lead to the formation of compounds **34** and **35**, respectively:

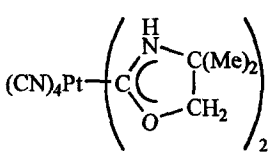



34

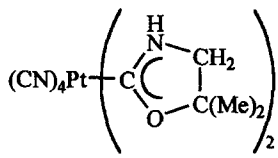
$(CO)_5W$–C≡N-CHPhCH$_2$OH

35

These ring opening reactions are regiospecific occurring at the higher-substituted carbon. However, in general this type of reactivity is reversed with other monoalkylated epoxides $\overline{OCH_2CH}(R)$ (R = Me, Et, $CH_2OPh$, $CH_2Cl$) since the preferential entry of the CN is at the less-substituted carbon [33]. The reactions of cyano metal acids such as $[HAu(CN)_2]$ and $[H_2Pt(CN)_6]$ with 1,1-dimethyl-substituted oxiranes lead to a mixture of isomers containing the oxazolidin-2-ylidene ligand. In the case of the Pt(IV) complex, the situation is more complicated since in addition to the regioisomers (for instance **36** and **37**), *cis–trans* isomers and even *RR*(*SS*)/*RS*(*SR*) diastereoisomers have to be taken into account in the reactions of other oxiranes such as $\overline{OC(Me)_2CH}(COMe)$. The X-ray structure of **36** has been reported [37].

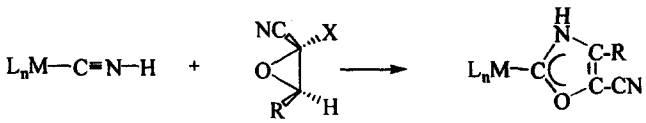


**36**



**37**

The reactions of hydrogen isocyanide complexes with *gem*-dicyano and cyanocarbethoxy epoxides **38** (Eq. (13)) lead to the synthesis of oxazolin-2-ylidene complexes **39** [33,38].

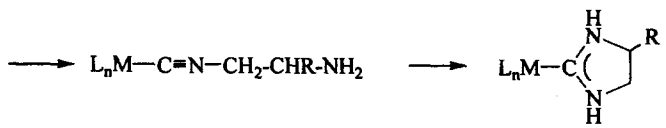


**38** **39**

(13)

$L_nM$ = $Cr(CO)_5$, $[Fe(Cp)(dppe)]^+Br^-$; X = CN, $CO_2Et$; R = $C_6H_4Me$-4, $C_6H_4Cl$-4

Similar to the reactions of oxiranes, aziridines react with hydrogen isocyanide complexes to give cyclic diaminocarbene derivatives **40** (Eq. (14)) [33,39].



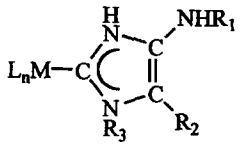
**40**

(14)

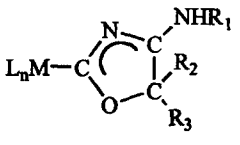
$L_nM$ = $M(CO)_5$ (M = Cr, Mo, W); R = H, Me

It is finally worth mentioning that hydrogen isocyanide complexes (or cyano metal acids) undergo multicomponent one-pot reactions such as four-component

condensation reactions (hydrogen isocyanide complex, isocyanide, aldehyde and primary amine) [33,40] and three-component cycloaddition (hydrogen isocyanide complex, isocyanide and ketone) [33,41] to give imidazolin-2-ylidene **41** and oxazolin-2-ylidene **42** species, respectively.



**41**

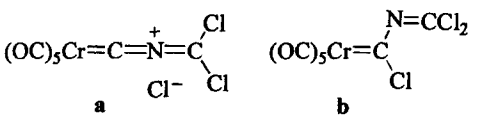


**42**

Fehlhammer et al. reported also the synthesis and reactivity of other functional isocyanides such as C≡N–$NH_2$ [42], C≡N–$NR_2$ [43], C≡N–C≡N [33,44], chlorovinyl isocyanides of the type C≡N–C(Cl)=CHCl, C≡N–C(Cl)=$CH_2$ and C≡NCH=CHCl [33,45], alkynyl isocyanides C≡N–C≡CR [46] and poly- and perchloroalkyl isocyanides of the type C≡N–$CCl_2$–$CCl_2R$ and C≡N–$CCl_3$ [33,47]. Some of these isocyanides were prepared from other isocyanide precursors or by protonation or alkylation of cyano complexes. Some of these ligands were found to be stable only when coordinated to a transition metal and they could be converted to carbene derivatives. For instance, the radical alkylation of the cyano complex $[Cr(CN)(CO)_5]^-$, by reaction with $ArN_2^+$ and $CHCl_2R$, led to the synthesis of the complex-stabilized σ-haloalkyl isocyanides $[Cr(CO)_5(C{\equiv}NCCl_2R)]$ (R = H, Cl) [47b].

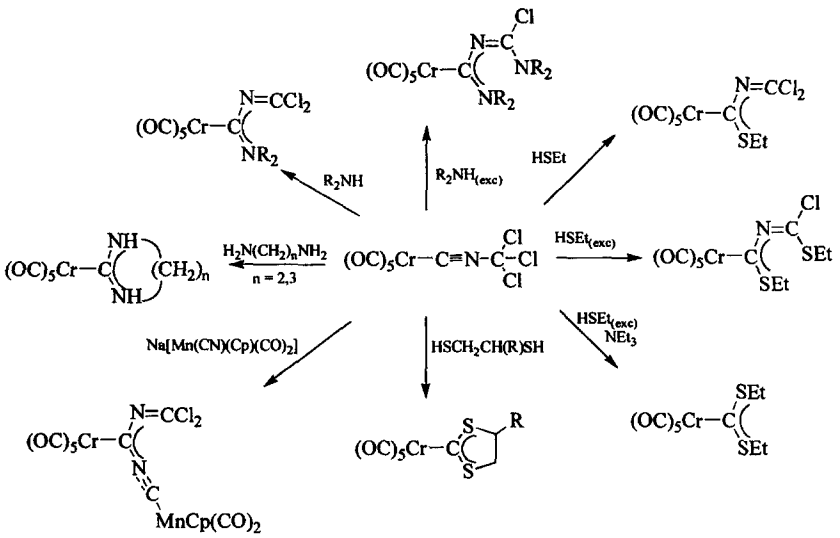
The trichloromethyl isocyanide ligand in $[Cr(CO)_5(C{\equiv}N{-}CCl_3)]$ revealed an unusual and wide reactivity [47c] due to the presence of two electrophilic centers, i.e. the isocyanide carbon and the trichloromethyl carbon atom. Although it was shown that it is possible to address the reactivity to each group (for instance, reactions with reducing agents or organometallic bases and phosphanes proceed at the $CCl_3$ function to yield new functionalized isocyanides), most reactions have been observed to occur at the two electrophilic centers jointly. Thus, N and S nucleophiles such as amines and thiols attack the isocyanide carbon atom and simultaneously cause the departure of a chloride ion from the trichloromethyl group. A few examples of such reactivity are reported in Scheme 7.

The formation of such products has been explained as arising from one of the two isomeric forms **a** (azaallenium chloride) and **b** (chlorocarbene) of the trichloromethyl isocyanide starting complex.



**a** **b**

The analogy between $[Cr(CO)_5(C^1{\equiv}N{-}C^3Cl_3)]$ and complexes of the allenylidene type $[L_nM{=}C^1{=}C^2{=}C^3R_2]$ stems from the identical reactivity of the corresponding electrophilic centers $C^1$ (for O and N nucleophiles) and $C^3$ (for P nucleophiles) [48].

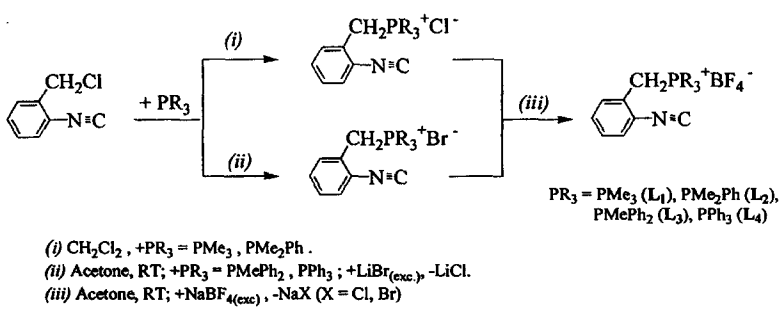


Scheme 7. Formation of amino- and thio-carbene complexes from nucleophilic addition reactions to a trichloromethyl isocyanide complex [47].

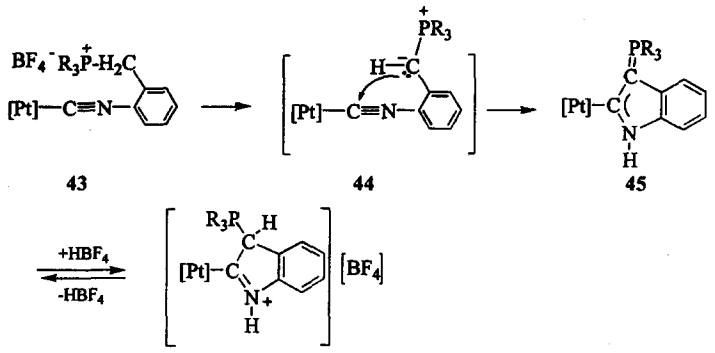
### 2.4.3. *Phosphonium-substituted isocyanides*

The synthesis and coordination properties of functionalized isocyanides of the type *o*-$(CH_2X)C_6H_4N{\equiv}C$ (X = Cl, I), which contain a halomethyl moiety *ortho* to the isocyano group, have been reported [49]. These ligands show the coordination ability to metal substrates of each one of the two functionalities, thus giving rise either to mono- or dinuclear complexes. In particular, these isocyanides react with a slight molar excess of tertiary phosphines $PR_3$ to form in nearly quantitative yield a new series of *o*-(phosphoniomethyl)phenyl isocyanides [50] (Scheme 8). The coordinating ability of the isocyanide ligands $L_1$–$L_4$ (Scheme 8) has been tested with some cationic Pt(II) complexes as illustrated in Scheme 9.

All the complexes, except that involving the two highly sterically demanding $PCy_3$ in *trans*-$[Pt(Me)(L_1)(PCy_3)_2]^+$ for which $\nu(N{\equiv}C)$ increases only by 7 $cm^{-1}$ with respect to the free ligand, display a large shift of the N≡C stretching to higher



Scheme 8. Preparation of *o*-(phosphoniomethyl)phenyl isocyanides [50].




[Pt] = *trans*-[(PR'$_3$)$_2$PtX]$^+$; PR'$_3$ = $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$, $PCy_3$; X = Cl, Me
[Pt] = *cis*-[($Ph_2PCH$=$CHPPh_2$)PtCl]$^+$

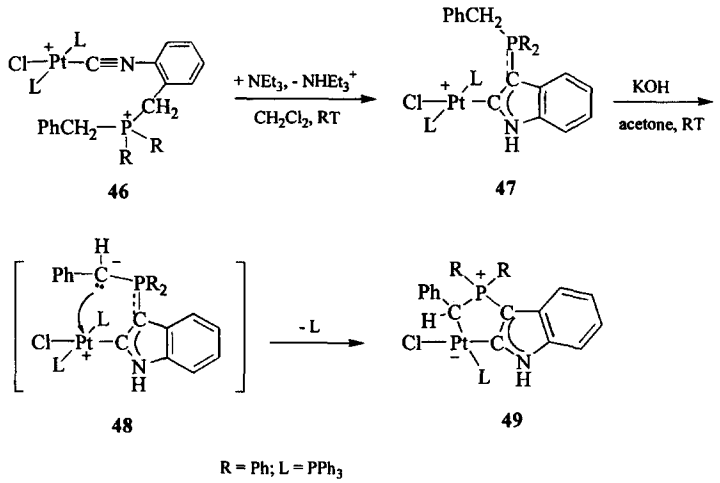
Scheme 9. Formation of cyclic aminocarbene Pt(II) complexes from cyclization of *o*-(phosphoniomethyl)phenyl isocyanides [50,51].

wavenumbers (ca. 45–80 cm$^{-1}$) upon coordination to Pt(II). These complexes are found to react with an excess of $NEt_3$ to afford in good yield (ca. 70%) the C-2 metal-bonded indole derivatives. A possible mechanism for this transformation (Scheme 9) entails initial attack of $NEt_3$ to the activated methylene group of the phosphonium moiety of **43** to form the highly reactive ylide intermediate **44**, which subsequently adds intramolecularly to the adjacent coordinated isocyanide carbon atom to form the final carbene product **45**.

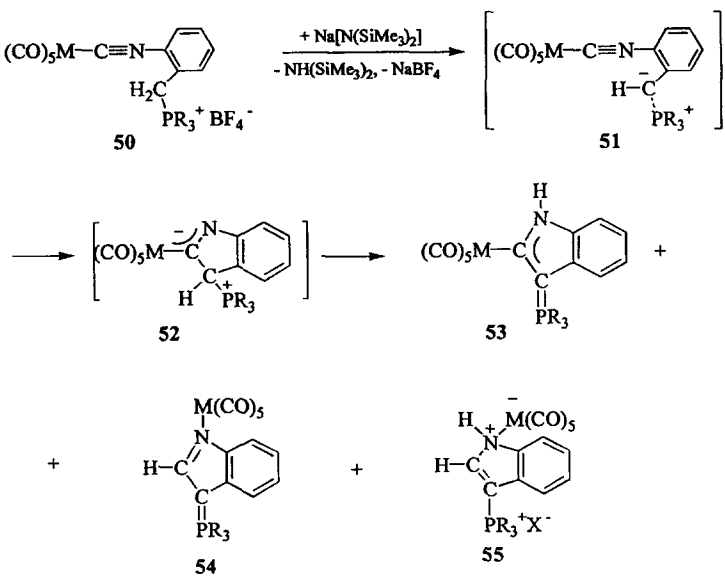
Qualitative observations, based on IR data, of the reaction times for these cyclizations show that the reactivity parallels that of $\Delta\nu$ of the N≡C stretching, so that the larger is the variation of $\Delta\nu$ the faster is the corresponding reaction, thus reflecting the electrophilic character the isocyanide carbon. Furthermore, it is observed that the reactivity of the phosphonium–isocyanide ligands is $L_1 > L_2 > L_3 > L_4$ (Scheme 8), according to an increasing nucleophilic character of the corresponding ylide intermediate **44** paralelling that of the $PR_3$ groups (Scheme 9).

A structural investigation of *trans*-[PtCl{ = $\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}$}$(PPh_3)_2$]-[$BF_4$] shows that there is an extensive electronic delocalization within the indole system [50a]. As a consequence, the carbenoid ligand in this complex exhibits the typical reactivity of indoles [51] reacting with electrophiles such as $HBF_4$ to give addition at the π-position of the indole ring.

A further development of the reaction chemistry reported in Scheme 9 is given by benzylphosphonium-substituted isocyanides complexes **46** (Scheme 10) [52]. Initial reaction of **46** with $NEt_3$ affords the 3-(benzylphosphonio)indolin-2-ylidene complexes **47**. These then react with KOH to give the platinaheterocycles **49** likely via the formation of an ylide intermediate **48** which intramolecularly attacks the metal center with displacement of a $PPh_3$ ligand. The chemistry of 2-(methylphosphonio)phenyl isocyanides was also extended to Group 6 transition-metal carbonyls [53] (Scheme 11).




Scheme 10. Formation of aminocarbene platinaheterocycles from cyclization of benzylphosphonium-substituted isocyanides [52].

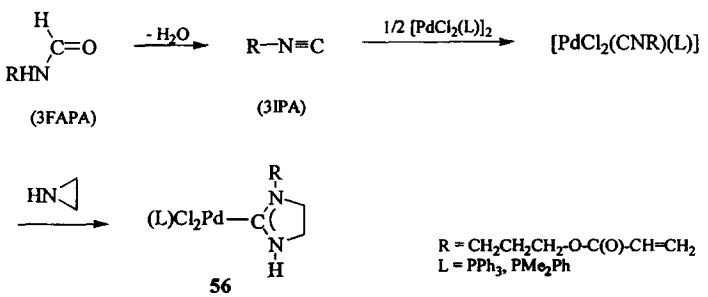



Scheme 11. Formation of cyclic aminocarbene and indole-type Group VI metal complexes from cyclization of *o*-(phosphoniomethyl)phenyl isocyanides [53].

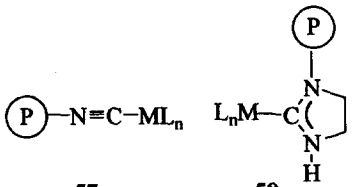
The coordinated phosphonio-substituted ligands in complexes of the type **50** do not react with a weak base such as $NEt_3$ as previously described for the Pt(II) reactions, but with a stronger base such as $Na[N(SiMe_3)_2]$ to give in most cases a mixture of different cyclization products whose structures have been assigned, on the basis of spectroscopic and electrochemical data, as the carbene-type **53**, indole-type **54** or protonated indole-type **55** species. The relative abundance of the final products is strictly related to the nature of the metal and the type of R group in the phosphonium moiety: as a general trend the $[W(CO)_5L]$ complexes yield mostly type **53** derivatives, while those of Cr and Mo give primarily types **54** and **55**. The higher stability of the M–C bond in intermediate **52**, derived by intramolecular cyclization of **51**, when M = W than with Cr or Mo could likely favour the 1,3-proton shift from the ylide carbon to the nitrogen atom with the formation of the type **53** carbene, the primary product obtained with tungsten isocyanides.

As a further example of the potential role of certain functionalized isocyanides and carbene ligands in the development of polymer supported coordination chemistry, the synthesis and coordination ability toward Pd(II) metal centers of 3-isocyanopropylacrylate (3IPA) [54] and the derived cyclic aminocarbene complex [55] have been reported (Scheme 12).

3IPA, which can be obtained by dehydration of 3-formamidopropylacrylate (3FAPA), reacts with stoichiometric amounts of $[PdCl_2(L)]_2$ to give the corresponding coordinated isocyano complexes, one of which was structurally characterized [54a]. These latter react further with aziridine to yield cyclic diaminocarbene complexes **56** and the X-ray analysis of the $PPh_3$ derivative has been reported [55]. These types of complexes represent an interesting prototype of a novel class of metal–isocyano or metal–carbene acrylic monomers suitable to be copolymerized to prepare highly dispersed metal-containing supported catalysts of the general types **57** and **58** which are potentially useful for diverse catalytic applications. To this regard a Pd(II) complex with 3IPA has been reported to be successfully copolymerized with dimethylacrylamide by γ-ray initiation [56].



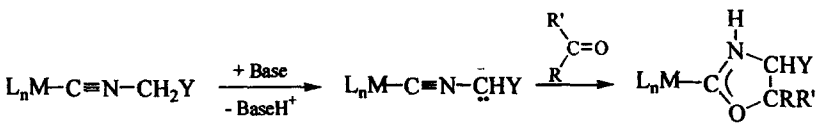

Scheme 12. Formation of cyclic diaminocarbene complexes of Pd(II) from 3-isocyanopropylacrilate complexes [54,55].



57 58

*2.5. Reactions of α-deprotonated isocyanide complexes*

Several heterocyclic carbene complexes can be prepared from metal-coordinated α-CH-acidic isocyanides of the general type $L_nM–C{\equiv}N–CH_2Y$ ($Y = CO_2Et$, $SO_2R$ ($R = p$-tolyl), $PPh_3^+$). These latter, upon treating with a base, afford metal-coordinated α-deprotonated isocyanides of the type $L_nM–C{\equiv}N–\overset{(-)}{C}HY$, which are 1,3-dipoles and they have been shown to react with different dipolarophiles such as aldehydes and ketones by [3 + 2] cycloadditions to afford C(2)-bonded heterocyclic ylidenes **59** [57] (Eq. (15)).

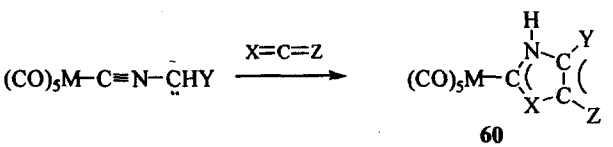


(15)

**59**

$L_nM$ = [OsH(Cl)(CO)($PPh_3$)$_2$], *trans*-[PtCl($PPh_3$)$_2$][$BF_4$]; Y = $CO_2Et$, $SO_2$-*p*-tolyl; Base = $NEt_3$, NaOMe; R, R' = H, alkyl, aryl

Similarly, the reactions of α-metalated isocyanides with heteroallenes X=C=Z such as carbon disulphide, methyl isocyanate and phenyl isothiocyanate regio- and site-selectively lead to five-membered cyclic carbenes **60** [58] (Eq. (16)). Cycloaddition of the α-deprotonated isocyanide (or metallo-nitrile ylide) [$M(CO)_5$–C≡N–$\overset{(-)}{C}H(\overset{(+)}{P}Ph_3)$] with the keteneimine $Ph_2C{=}C{=}NPh$ has been also reported [59].

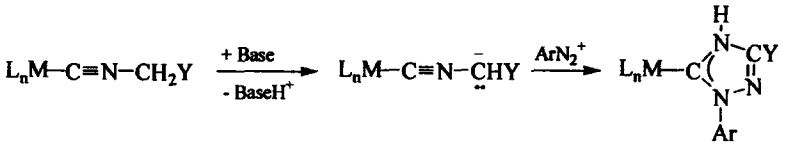


(16)

**60**

M = Cr, W; Y = $PPh_3$, $CO_2Et$; X=C=Z = $CS_2$, RNCO, RNCS; X = S, RN; Z = O, S

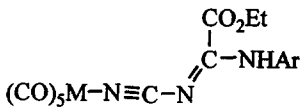
The metallo nitrile ylides [$L_nM–C{\equiv}N–\overset{(-)}{C}HY$] ($L_nM = W(CO)_5$, Y = tosyl; $L_nM$ = *trans*-[Pt(Cl($PPh_3$)$_2$]$^+$, $Y = CO_2Et$), generated by deprotonation with Bu$^n$Li or $NEt_3$ of the corresponding tosylmethyl isocyanide and ethyl isocyanoacetate, respectively, react regiospecifically with aryldiazonium salts to give 1,2,4-triazoles isolated as the triazolin-5-ylidene complexes **61** [60] as shown in Eq. (17).



$L_nM = W(CO)_5$, Y = tosyl, Base = $Bu^nLi$, -78 °C
$L_nM$ = *trans*-$[PtCl(PPh_3)_2]^+$, Y = $CO_2Et$, RT
Ar = Ph, $C_6H_4Cl$-4, $C_6H_4Me$-4, $C_6H_4NO_2$-4, $C_6H_4NMe_2$-4

**61** (17)

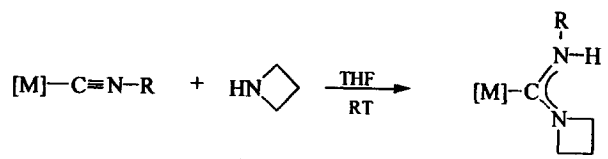
Analogous reactions of $[(CO)_5M{-}C{\equiv}N{-}CH_2CO_2Et]$ (M = Cr, W) complexes with the coordinated ethyl isocyanoacetate ligand afford a mixture of triazolin-5-ylidene (**61**) [$L_n = (CO)_5$, Y = $CO_2Et$] and *N*-cyanamidine species **62** [60]. The formation of the carbene and the nitrile ligands has been proposed to occur according to the different site of attack of the diazonium salt at the α-deprotonated isocyanide.



**62**

## 3. Other reactions of isocyanide complexes

Closely related to the three-membered organic nucleophiles described previously, the four-membered ring of azetidine, $HNCH_2CH_2CH_2$, is known to be less strained than aziridine and, consequently, the ring opening of azetidine occurs much less easily than that of aziridine. On the other hand, azetidine is a stronger nucleophile ($pK_a = 11.2$) compared to aziridine ($pK_a = 8.4$) suggesting that it would react faster than aziridine with metal-activated isocyanide ligands. The reactions of a series of Pt(II)– and Pd(II)–isocyanide complexes (**23**) with azetidine have been reported to yield acyclic diaminocarbene complexes **63** with no evidence of the formation of six-membered diaminocarbenes derived from the ring opening of azetidine [61] (Eq. (18)).



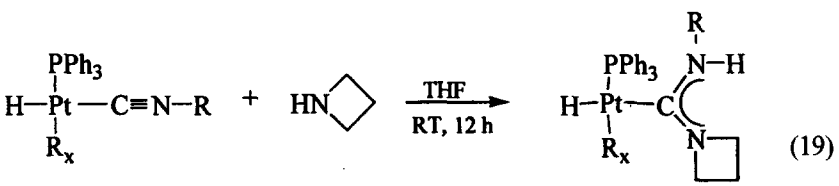
[M] = *cis*-$[MCl_2(PPh_3)]$, M = Pd, Pt; R = $C_6H_4OMe$-4, $Bu^t$
[M] = *trans*-$[MCl(PPh_3)_2]^+$, M = Pd, Pt; R = $C_6H_4OMe$-4
[M] = *cis*-$[PdCl_2(L)]$, L = $Bu^tNC$, R = $Bu^t$

**63** (18)

In the case of di-isocyanide complexes of the type *cis*-$[MCl_2(CNR)_2]$ (M = Pd, Pt), the reactions with azetidine lead to the conversion of one (R = $Bu^t$) or both (R = $C_6H_4OMe$-4) isocyanides to the corresponding acyclic diaminocarbenes. The

reactions of monoisocyanide complexes of the type *cis*-[$MCl_2(PMe_2Ph)$-($CNC_6H_4OMe$-4)] (M = Pd, Pt) with 2 equiv. of azetidine afford cationic diaminocarbene complexes containing a metal coordinated azetidine ligand via displacement of a coordinated chloride. One of these complexes (M = Pd, R = $C_6H_4OMe$-4) has been also characterized by X-ray crystallography. The Pd–C(carbene) bond distance is 1.990(6) Å and the bond lengths within the diaminocarbene indicate extensive electronic delocalization involving the carbene carbon and the two adjacent nitrogen atoms.

Azetidine, but not aziridine, was also found [62a] to react with less metal activated isocyanides as in the hydrido-alkyl complexes [$Pt(H)(R_x)(PPh_3)(CNR)$] ($R_x$ = $CF_3$, $CH_2CN$, $CH_2CF_3$; R = $C_6H_4OMe$-4), having *cis*-Pt–H and Pt–$R_x$ bonds with the RNC ligand *trans* to hydride. These complexes were prepared by reaction in *n*-heptane at room temperature for 12 h of hydrido-alkyls of the type *trans*-[$PtH(R_x)(PPh_3)_2$] ($R_x$ = $CH_2CN$, $CF_3$) or *cis*-[$PtH(CH_2CF_3)(PPh_3)_2$] with a slight excess of the RNC ligand. The $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$ values found in [$Pt(H)(R_x)(PPh_3)(CNR)$] complexes are in the range 48–51 $cm^{-1}$, indicating that the isocyanide is less electrophilic than that having chloride as a *trans* ligand. These complexes are found [62a] to react with azetidine to give stable hydrido-alkyl-carbene complexes **64** as outlined in Eq. (19).



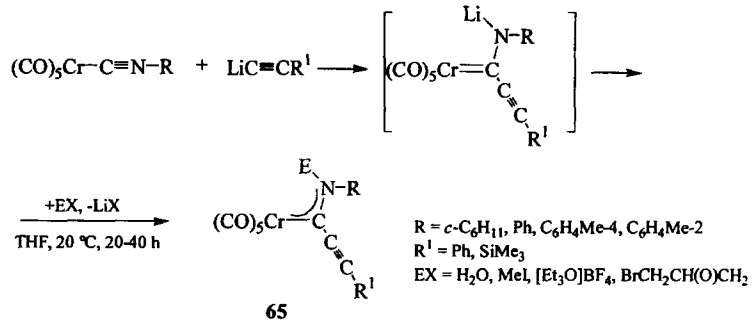

(19)

**64**

$R_x$ = $CF_3$, $CH_2CN$, $CH_2CF_3$; R = $C_6H_4OMe$-4

These Pt(II) complexes together with those previously reported of the type *trans*-[$Pt(H)(carbene)(PPh_3)_2$]$^+$ (carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$, $\overline{CSCH_2CH_2S}$) [62b] represent one of the few examples of hydrido carbene complexes of transition metals, which have been shown to undergo unusual reactivity. The X-ray structure of [$Pt(H)(CH_2CN)\{C(\overline{NCH_2CH_2CH_2})NH(C_6H_4OMe\text{-}4)\}(PPh_3)$] [62a] shows that the plane of the carbene ligand intersects the platinum square plane at an angle of 73.7(2)°. An intermolecular contact of the amino nitrogen of the carbene ligand with the nitrogen atom of the $CH_2CN$ group of an adjacent molecule [N–H···$NCCH_2$ = 2.36(5) Å] is also observed and this feature is possibly related to the observed reactivity of this complex with P-ligands.

Acyclic (aminoalkynylcarbene)chromium complexes have been prepared by addition of (1-alkynyl)lithium compounds to isocyanide ligands [63] (Scheme 13). Isocyano pentacarbonylchromium complexes react with 1-lithioalkynes, $LiC{\equiv}CR^1$, to give *N*-lithio iminoacylates, [$Cr\{{=}C(NRLi)C{\equiv}CR^1\}(CO)_5$], which were not isolated but were converted to the corresponding aminocarbenes **65** by protonation or alkylation with different electrophiles EX. This reaction proceeds with high regio-



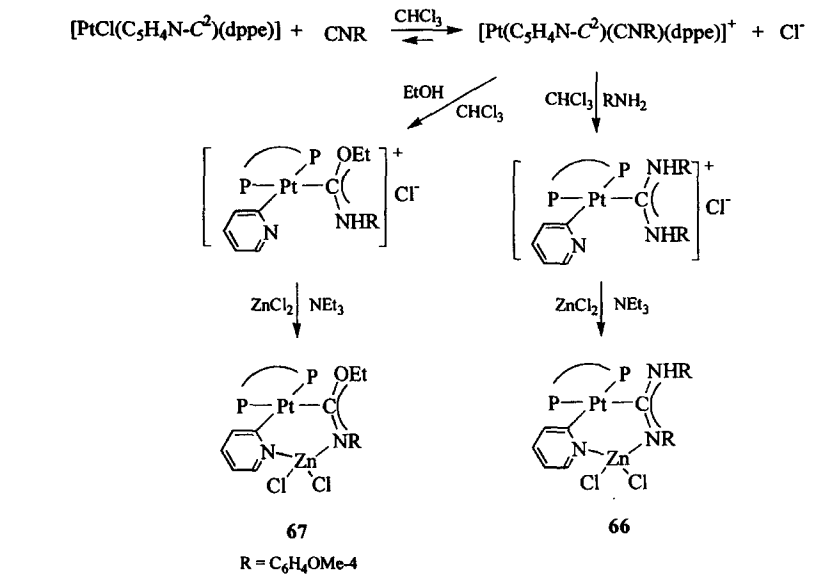

65

Scheme 13. Formation of acyclic aminocarbene complexes from nucleophilic addition of alkynyls to isocyanides [63].

selectivity since $LiC{\equiv}CR^1$ adds exclusively to the isocyanide carbon atom, while attack at a CO ligand to yield an *O*-lithio acylate was not observed. Protonation and alkylation, respectively, of the *N*-cyclohexyl compound $[Cr\{=C(NRLi)\text{-}C{\equiv}CR^1\}(CO)_5]$ ($R = c\text{-}C_6H_{11}$) with EX produces the aminocarbene complexes $[Cr\{=C(NRE)C{\equiv}CR^1\}(CO)_5]$ (**65**) in high yield, which are generated stereoselectively in (*E*) configuration either by kinetic reaction control via *anti* addition of the 1-lithioalkyne to the isocyano group and, possibly, also by the stabilization of the (*E*) configuration by an interaction of the lithium atom with the nitrogen atom as well as an oxygen atom of the (negatively polarized) $\{Cr(CO)_5\}$ moiety. Complexes **65** are isomerized at 80°C to give the corresponding (*Z*) stereoisomers as main products. It was observed that the stereochemical course of alkylation of the $[Cr\{=C(NRLi)C{\equiv}CR^1\}(CO)_5]$ derivatives is strongly influenced by the substituents at the nitrogen atom as well as by the type of electrophile EX involved. Alkylation of the *N*-aryl compounds $[Cr\{=C(NArLi)C{\equiv}CR^1\}(CO)_5]$ (Ar = Ph, $C_6H_4Me$-4, $C_6H_4Me$-2) yields the corresponding aminocarbenes mainly in (*Z*) configuration.

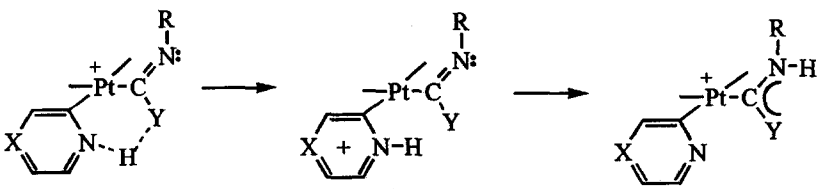
It has been reported that the reactions of Pt(II) isocyanide complexes with alcohols and amines proceed at considerably reduced rates which prevent a kinetic investigation by conventional spectrophotometric techniques [64]. However, in the course of the study on the chemistry of 2-pyridyl $d^8$ metal complexes [65] it was noted that in the cationic 2-pyridyl complex $[Pt(C_5H_4N\text{–}C^2)(CNR)(dppe)]^+$ (Scheme 14), the isocyanide group is readily attacked by protic nucleophiles such as alcohols, primary amines and water [66].

When the 2-pyridyl-Pt(II) chloro complex is treated in $CHCl_3$ at room temperature with 1 equiv. of CNR it generates the cationic isocyanide intermediate which reacts with a twofold excess of *p*-anisidine (piperazine reacts similarly) to give the diaminocarbene complex. This reaction occurs readily (ca. 1 h for completion). $[Pt(C_5H_4N\text{–}C^2)(CNR)(dppe)]^+$ reacts also with oxygen nucleophiles such as EtOH present in small amount (0.75%) as a stabilizer in $CHCl_3$ (Scheme 14). This reaction takes ca. 1 day at room temperature to give the (ethoxy)aminocarbene compound. Both carbenes have been isolated as their $ZnCl_2$ compounds, **66** and **67**, respectively.



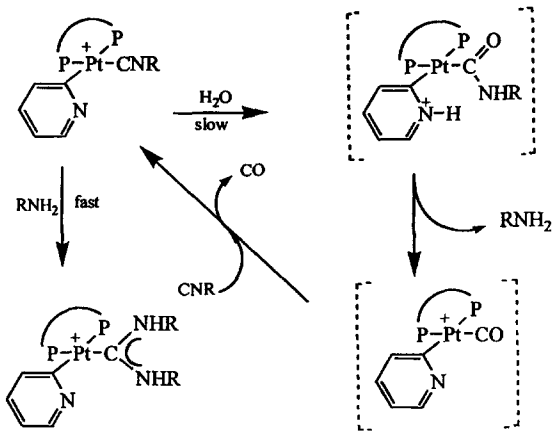

Scheme 14. Formation of aminocarbene complexes from nucleophilic addition of amines and alcohol to an isocyanide complex [65,66].

The enhanced reactivity of the isocyanide ligand in this complex is ascribed to the highly basic 2-pyridyl group in *cis* position, which assists the nucleophilic attack at the isocyanide carbon by hydrogen bonding with the incoming protic nucleophile (see **68**) and possibly takes part in the subsequent proton transfer to form the carbene derivative (**69** → **70**).




**68** **69** **70**

Similar reactivity is observed when the *cis* C-bonded heterocyclic ligand is 2-pyrazyl ($C_4H_3N_2$–$C^2$) or 1-methyl-2-pyridylium ($C_5H_4NMe$–$C^2$), but the observed reactivity trend is: $[Pt(C_5H_4N\text{-}C^2)(CNR)(dppe)]^+ > [Pt(C_4H_3N_2\text{-}C^2)(CNR)\text{-}(dppe)]^+ > [Pt(C_5H_4NMe\text{-}C^2)(CNR)(dppe)]^{2+}$, which agrees with the decreasing basic properties of the heterocyclic ligands. Interestingly, the CNR ligand in $[Pt(C_5H_4N\text{-}C^2)(CNR)(dppe)]^+$ is hydrolyzed to CO and $RNH_2$ by trace amounts of water present in commercial benzene or acetone. The proposed [66] mechanism of the hydrolysis of the coordinated isocyanide is reported in Scheme 15.




71

Scheme 15. Proposed mechanism for hydrolysis of an isocyanide complex to form an aminocarbene derivative [66].

The initial isocyanide complex undergoes a slow nucleophilic attack by $H_2O$ to produce a reactive intermediate containing a 2-pyridylium and carbamoyl ligand, which then rearranges to a carbonyl derivative with concomitant formation of the amine $RNH_2$, according to a well-documented [67] reaction of carbamoyl groups with protic acids. Displacement of CO by a second molecule of CNR regenerates the starting compound, which is readily attacked by $RNH_2$ to yield the final diaminocarbene product **71**.

Kinetic studies of the mechanisms of the nucleophilic attack of aliphatic amines ($HNR^1R^2$) (in 1,2-dichloroethane) [68] or of the methoxide ion (in acid-base equilibrium with triethylamine in anhydrous methanol) [69] on the isocyanide complexes $[Pt(R)(CHC_6H_{11})(dppe)][ClO_4]$ (R = 4-pyridyl or 2-pyrazyl), leading to the corresponding diaminocarbene or (methoxy)aminocarbene derivatives, $[Pt(R)\{C(NHC_6H_{11})(NR^1R^2)\}(dppe)][ClO_4]$ or $[Pt(R)\{C(NHC_6H_{11})OMe\}(dppe)][ClO_4]$, respectively, have been reported. The mechanisms were shown to proceed via a direct bimolecular attack of the nucleophile on the ligated isocyanide carbon, involving, in the case of the amines, a multi-center transition state with concomitant proton transfer from the amine to the isocyanide nitrogen atom assisted by the heterocyclic nitrogen in position 1 of the 2-pyrazyl ligand [68]. When the reaction with methoxide was performed in the presence of a primary or secondary amine instead of triethylamine, concomitant formation of (methoxy)amino- and diamino-carbene products was observed via competitive, second-order paths involving nucleophilic attack by either methoxide or amine on the ligated isocyanide. However, the methoxide ion behaves as a much better nucleophile than the amines and moreover the interconversion of the (methoxy)amino- and diamino-carbene species via methoxy-amine exchange is a very slow process [69].

*N*-Isocyanides can also be activated toward nucleophilic addition and in particular the *N*-isocyanoimine ligand ($C{\equiv}N{-}N{=}CMe_2$) was found to be more reactive

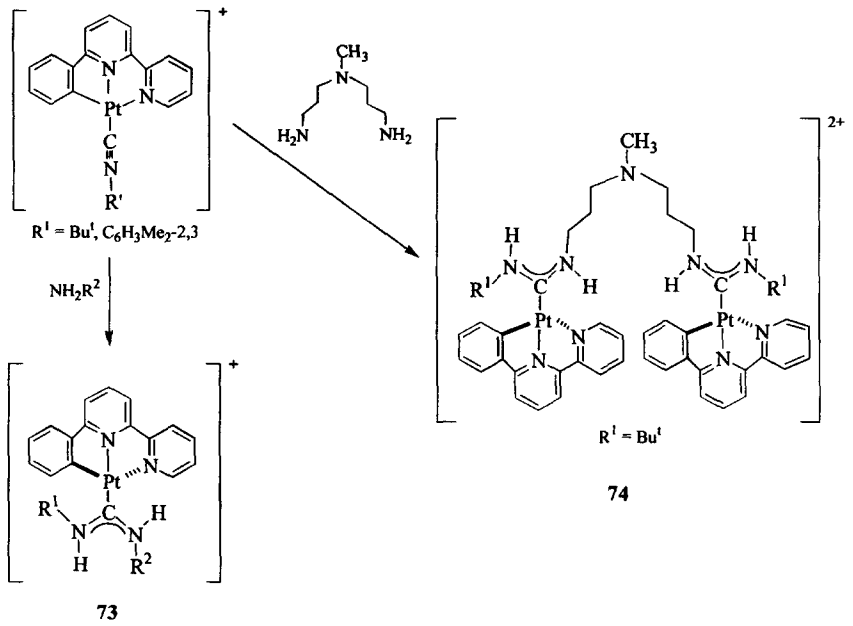
toward amines than organoisocyanides (C≡NR), on account of the stronger electron-withdrawing ability of the imine group in comparison with the organic R moiety [70]. In fact, $[ReBr(CO)_3(CNR)(CNN{=}CMe_2)]$ (R = Pr or Ph), derived from treatment of the corresponding *N*-isocyanoiminetriphenylphosphorane ($C{\equiv}NNPPh_3$) with acetone (Wittig-type reaction) in the presence of a catalytic amount of $HBF_4$, reacts with isopropylamine ($H_2NPr^i$) to give first the amino-(hydrazono)carbene complexes $[ReBr(CO)_3(CNR)\{C(NHPr^i)(NHN{=}CMe_2)\}]$ which (R = Ph), on further reaction with the amine, convert into the dicarbene species $[ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}]$ [70].

The related diaminocarbene complexes $[ReBr(CO)_4\{C(NHPh)(NHR)\}]$ (R = Pr or $Pr^i$) were also obtained by nucleophilic addition of the appropriate amine ($H_2NR$) to the ligated CNPh in $[ReBr(CO)_4(CNPh)]$ [71] and were shown [72] to undergo facile, reversible *ortho*-metalation reactions induced by further reaction with amine (with formation of HBr) leading to the cyclometallated aminocarbene species [Re(CO)4{C(NHC6H4)(NHR)}] (**72**) with a carbon as the donor atom. The Re–C σ bond of the cyclometallated ring in **72** is labile and can be cleaved by electrophilic attack of $I_2$ [71].


**72**

The formation of aminocarbene ligands with *ortho*-metalated phenyl rings has also been quoted in other cases such as in the reaction of the bis(diaminocarbene) complex *trans*-$[PtI_2\{C(NHPr)(NHC_6H_4R\text{-}4)_2\}]$ (R = *n*-octyl) (obtained by reaction of $H_2NPr$ with the corresponding diisocyanide complex) with an amine (liberation of HI) [73], and on treatment of the phenylisocyanide complex $[(Cp^*)OsCl_2(CNPh)]$ with MeLi/LiI followed by chromatography on $Al_2O_3$ to give $[(Cp^*)OsCl_2\{C(Me)(NHC_6H_4)\}]$ [74].

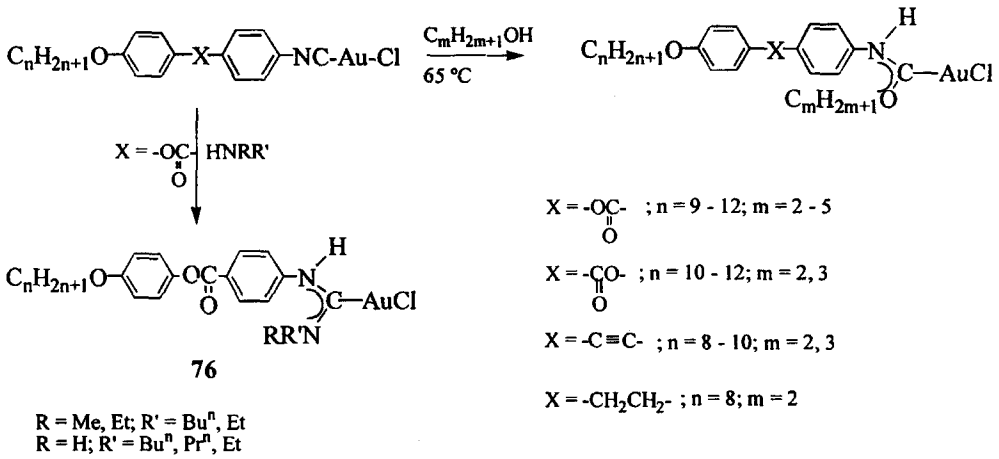
A series of luminescent cyclometalated platinum(II) diaminocarbene complexes, $[(CNN)Pt\{C(NHR^1)(NHR^2)\}]^+$ (**73**) (HCNN = 6-phenyl-2,2′-bipyridine. $R^1 = Bu^t$; $R^2$ = Me, $NH_2$, $CH_2Ph$. $R^1$ = 2,6-$Me_2C_6H_3$; $R^2$ = Me, $NH_2$, $CH_2Ph$) has been prepared (Scheme 16), by nucleophilic addition of amines or hydrazine, $NH_2R^2$, to the ligated isocyanides in the corresponding $[(CNN)Pt(CNR^1)]^+$ complexes [75]. By using 3,3′-diamino-*N*-methyldipropylamine, $N(Me)(CH_2CH_2CH_2NH_2)_2$, with two isolated amine functionalities, as the protic nucleophile, the binuclear species $[\{(CNN)Pt\}_2\mu\text{-}\{C(NHBu^t)(NHCH_2CH_2CH_2)\}_2NMe]^{2+}$ ($R^1 = Bu^t$) (**74**), with a bidentate bis(diaminocarbene) moiety acting as a bridging ligand, was the obtained product [75]. All the complexes exhibit photoluminescence in solution at room temperature and, in the carbene compounds, the short N–C(carbene) bond lengths (mean 1.332 Å) are indicative of substantial $p_\pi$–$p_\pi$ interactions within the N–C(carbene)–N fragment and conceivable minimal π-character in the




Scheme 16. Formation of acyclic diaminocarbene complexes with cyclometalated 6-phenyl-2,2′-bipyridine from nucleophilic addition of amines or hydrazine to isocyanides [75].

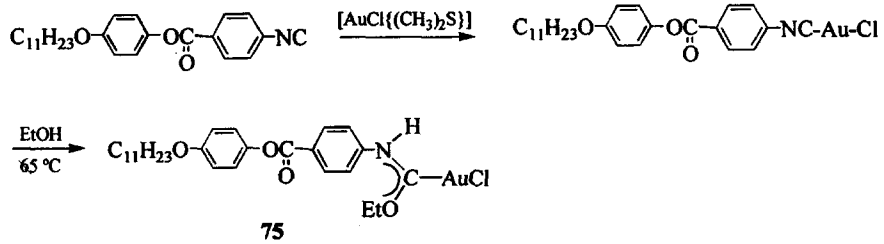
Pt–C(carbene) bond [75]. The reaction of iodomethane with one of the mononuclear diaminocarbene complexes (**73**; $R^1 = Bu^t$, $R^2 = Me$) in NCMe was studied under photolytic conditions (UV–vis light) and shown to lead to decomposition of the carbene ligand with formation of the platinum(IV) diiodide cyanide derivative *trans*-[(CNN)$PtI_2$(CN)] [75].

In a study of metallomesogens, e.g. liquid crystals incorporating transition metals, Takahashi and co-workers [76] developed liquid crystalline platinum-alkynyls and new families of organometallic liquid crystals including isocyanide complexes of platinum [77] and gold [78]. While platinum–isocyanide can display stable mesomorphic properties over a high and wide temperature range without any decomposition, bis(diaminocarbene) platinum(II) complexes obtained by treatment of the corresponding bis(isocyanide) derivatives with amines, were not found to exhibit mesomorphic properties [73,79]. However, some of the unsymmetrically substituted bis(carbene) Pt(II) complexes, *trans*-[$PtI_2${C($OR^1$)(NHR){C($NHR^2$)-NHR}] [R = $C_6H_4$Y-4 (Y = alkyl or alkoxide); $R^1$, $R^2$ = alkyl] bearing long alkyl substituents on the carbene ligands and derived from consecutive nucleophilic attack by an alcohol ($R^1OH$) and an amine ($H_2NR^2$) to the corresponding diisocyanide complexes *trans*-[$PtI_2(CNR)_2$], appear to exhibit a liquid crystalline property [80].




Scheme 17. Formation of liquid-crystalline Au(I)–aminocarbene complexes from nucleophilic addition of alcohols or amines to isocyanides [82].

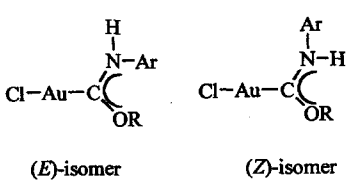
On the other hand, while most gold–isocyanide complexes undergo considerable decomposition due to high phase-transition temperatures caused by strong intermolecular interactions [81], certain isocyanide-derived gold(I)–carbene complexes have been reported [82] to show mesomorphic properties. Gold(I)–(alkoxy)-aminocarbene complexes **75** were initially prepared from the corresponding isocyanide derivatives by reaction at 65°C with EtOH (Eq. (20)) and have been shown to exhibit smectic phases with lower clearing temperatures.




(20)

A further development of the synthesis of a variety of liquid-crystalline gold(I)–carbene complexes was achieved by using branched alcohols instead of linear alcohols as nucleophiles and also using amines to produce Au(I)–diaminocarbene complexes **76** (Scheme 17). Both gold(I)–(alkoxy)aminocarbene and –diaminocarbene complexes show mesogenic behaviors.

The gold(I)–carbene complexes are formed as a mixture of (*E*) and (*Z*) isomers in ca. 3:1 molar ratio, which could be separated by fractional recrystallization:



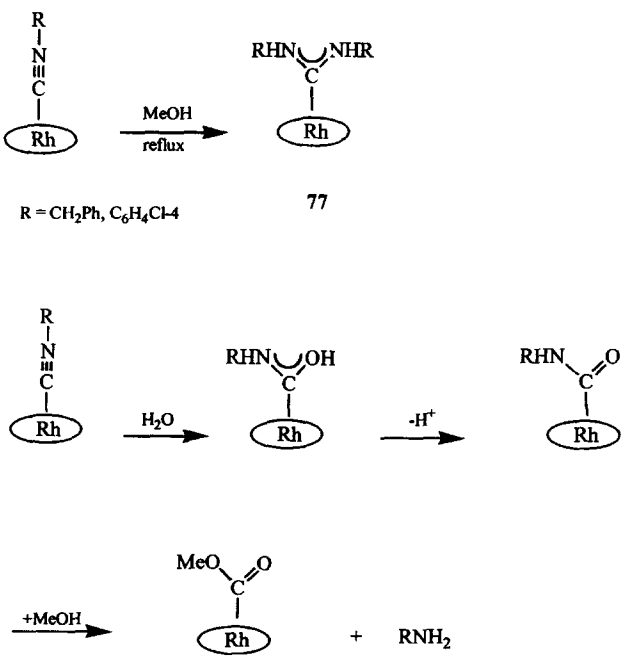

(*E*)-isomer (*Z*)-isomer

The (*E*) isomers exhibit almost the same thermal behavior of the (*Z*) isomers with the exception of their melting points. The X-ray crystal structure of (*E*)-[AuCl{=C($OC_2H_5$)($NHC_6H_4CO_2C_6H_4OC_2H_5$}] shows the Au–C(carbene) distance of 1.985(7) Å similar to those reported [83] for other Au(I)–(alkoxy)-aminocarbene derivatives. The C(carbene)–Au–Cl angle is 176.2(2)° showing a linear dicoordinate geometry. The shortest Au···Au distance is > 4 Å, indicating that there are no Au···Au interactions (which should be in the range 2.75–3.40 Å).

The synthesis and reactivity toward nucleophiles of some bis(isocyanide)-(porphyrinato)rhodium(III) complexes of the general formula [Rh($CNR)_2$(P)][$PF_6$] (P = octaethylporhyrin or *meso*-tetraphenylporphyrin) have been reported [84]. These complexes have been found to react with MeOH to give a series of products including cationic mono- and bis(diaminocarbene) (**77**) derivatives together with neutral carboxylate and carbamoyl species. The formation of the diaminocarbene complex **77** has been suggested to occur through a series of steps as outlined in Scheme 18, involving the conversion of an isocyanide ligand to the corresponding amine, which eventually attacks another coordinated isocyanide to give the final product.

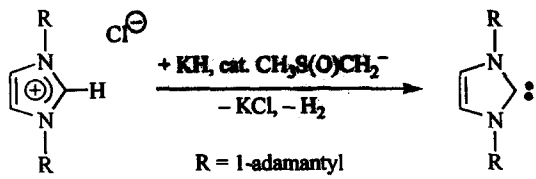
## 4. Outlook and prospects

The activation of isocyanides by medium to high-valent electron-poor metal centers toward α-nucleophilic addition has found, in the last 15 years, application in the




Scheme 18. Formation of diaminocarbene complexes of Rh(III) from reaction of methanol with isocyanides and proposed pathway [84].

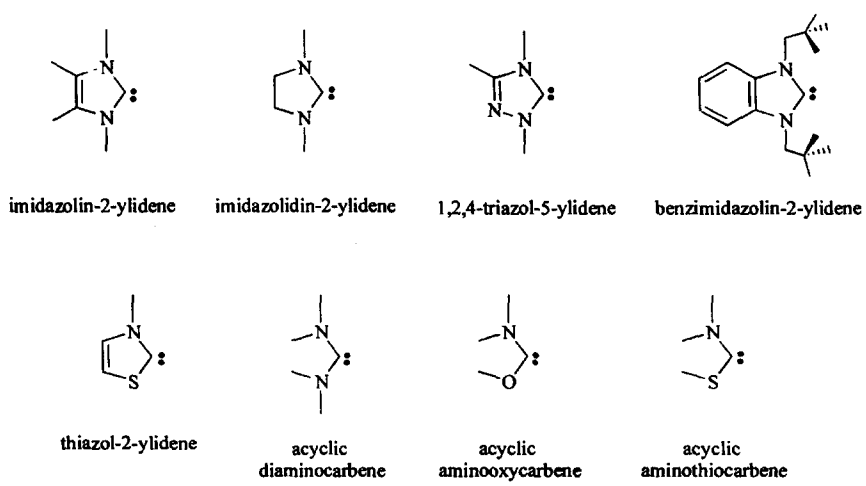
synthesis of a large variety of heterocyclic aminocarbene transition metal complexes. It must be noted, however, that other important synthetic strategies to N-heterocyclic carbenes are known. In fact, the first structures and preparations of metal complexes containing N-heterocyclic carbenes (NHCs) were reported more than 30 years ago independently by Öfele [85] and Wanzlick [86], who deprotonated an imidazolium salt by a basic metal precursor to form the imidazolin-2-ylidene metal derivatives. Lappert [87] subsequently extended the methodology to complexes containing imidazolidin-2-ylidene ligands derived by cleavage of electron-rich olefins. In 1991, Arduengo et al., following the early studies of Wanzlick [86c,d], succeeded in the preparation of the first, stable, crystalline carbene [88], the 1,3-diadamantylimidazolin-2-ylidene, obtained in near quantitative yield by deprotonation of the corresponding imidazolium chloride with potassium hydride in the presence of catalytic amounts of dimethyl sulfoxide anion or *t*-BuOK (Eq. (21)).




(21)

Other synthetic routes were subsequently developed by Herrmann [89], Kuhn [90], Enders [91], Hahn [92] and other researchers so that a number of stable cyclic and acyclic aminocarbenes have been isolated [93], some of which are reported in Scheme 19.

The availability of metal-free NHCs allowed the direct preparation of a large number of metal–NHC complexes [93]. The latter have been receiving increased




Scheme 19. Isolated cyclic and acyclic aminocarbenes [93].

attention in the literature since the aminocarbene ligands have been found to constitute promising alternative ligands to the commonly used phosphines and phosphites and also for their favorable application in homogeneous catalysis [93a,e]. The NHCs are, in fact, strong σ-donor and weak π-acceptor ligands and they afford a remarkable chemically and thermally stable metal–carbon bond. Finally, one can note that many of the stable carbenes reported in Scheme 19 may be obtained from nucleophilic attack on coordination-activated isocyanide ligands. Extension of this work could be related, for instance, to the synthesis from transition-metal coordinated isocyanides of chiral N-heterocyclic as well as acyclic aminocarbene complexes to be used in asymmetric catalysis.

A further prospect of the chemistry of aminocarbene complexes derived from nucleophilic addition to coordinated isocyanides is the application to materials science. This area appears still to be at an early stage, but the preliminary reported results on the photophysical and mesogenic properties of some aminocarbene complexes of gold(I) are promising for future developments into a broadly useful method.

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