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Synthesis of heterocyclic systems by activation of isocyanide, carbonyl, trifluoromethyl and nitrile ligands in platinum(II) and palladium(II) complexes

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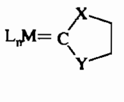
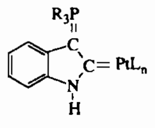
Abstract

Pd(II)- and Pt(II)-coordinated isocyanide, carbonyl and trifluoromethyl ligands are converted to heterocyclic carbenes (type **I–III** structures), while nitrile ligands are converted to oxazolines (type **IV** structure) using different synthetic strategies. Thus, RNC ligands in Pt(II) complexes react with $HOCH_2CH_2X$/base (X = Cl, Br; base = n-BuLi) to afford five-membered cyclic aminooxycarbenes of the general formula $Pt{=}\overline{CN(R)CH_2CH_2O}$ (R = alkyl, aryl) (type **I** structure). The corresponding reactions with Pd(II) isocyanides lead to Pd(0) species. Similar reactions of Pd(II)- and Pt(II)-metal bound isocyanides with $NH_2CH_2CH_2Br$ lead to five-membered cyclic diaminocarbenes of the general formula $M{=}\overline{CN(R)CH_2CH_2N(H)}$ (type **I** structure). Cyclic five-membered diamino-, aminothio- and aminooxycarbenes of the general type $M{=}\overline{CN(R)CH_2CH_2X}$ (X = NH, S, O) (type **I** structure) are obtained from metal coordinated RNC ligands by reaction with the three-membered heterocycles $\overline{YCH_2CH_2}$ (Y = NH, aziridine; S, thiirane; O, oxirane), respectively. Among the four-membered heterocycles $\overline{YCH_2CH_2CH_2}$ (Y = NH, S, O) only azetidine was found to react with some Pd(II)– and Pt(II)–isocyanides to afford acyclic diaminocarbenes. Pt(II)-coordinated phosphonium-functionalized isocyanides of the type o-$(BF_4{}^-R_3P^+\text{-}CH_2)C_6H_4NC$ (R = alkyl, aryl) react with NEt_3 to give indole derivatives (type **II** structure). When R is a benzyl group, the reaction with KOH produces heterometallacycles (type **III** structure). Pt(II)-bound CO ligands are converted to cyclic aminooxycarbenes of the type $Pt{=}\overline{COCH_2CH_2N}(H)$ (type **I** structure). The C–F bonds α to Pt in *trans*-$L_2PtX(CF_3)$ (X = H, L = PPh_3; X = Cl, L = PMe_2Ph) are susceptible to electrophilic attack. The reaction with HBF_4 leads to the formation of the highly reactive difluorocarbene intermediate $Pt{=}CF_2{}^+$, which reacts with diols and thiols to give five- and six-membered heterocycles of the type $Pt{=}\overline{CX(CH_2)_nX}$ (n = 2, X = O, S; n = 3, X = O) (type **I** structure). Nitrile ligands coordinated to Pt(II) in complexes of the type *cis-* and *trans*-$Cl_2Pt(NCR)_2$ react with $HOCH_2CH_2Cl$/base or oxirane/Cl^- to afford N-coordinated oxazolines $Pt\text{–}\overline{NC(R)OCH_2CH_2}$ (type **IV** structure). Mechanistic and structural aspects as well as some significant reactions and electrochemical behaviour of the metal-coordinated heterocycles are reported.



I



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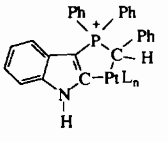

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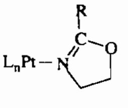
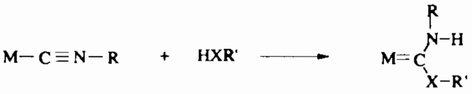


IV

M = Pd, Pt; X, Y = NR (R = H, alkyl, aryl), O, S; R = alkyl, aryl

Introduction

The reactivity of a large number of ligands promoted by Pt(II) and Pd(II) metal centers is well documented [1] and it often leads to several important stoichiometric and catalytic processes [2]. Among these ligands, considerable research efforts have been pursued with isocyanides, R–N≡C, which have been shown to add alcohols and amines to form stable metal–carbene complexes (eqn. (1)) [3].



$$M{-}C{\equiv}N{-}R \;+\; HXR' \longrightarrow M{=}C\begin{matrix}{}^{\diagup N(R)-H}\\{}_{\diagdown X-R'}\end{matrix} \qquad (1)$$

M = Pd(II), Pt(II); X = O, NH; R, R' = alkyl, aryl

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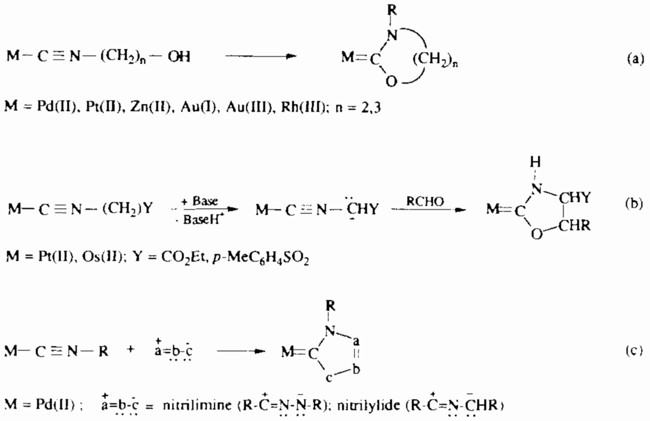
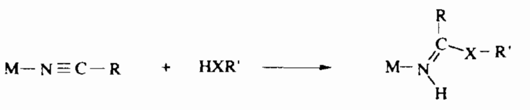
Mechanistic information on the reactions with amines indicate that these reactions proceed by initial attack of the amine on the isonitrile carbon followed by the involvement of a second molecule of amine which facilitates proton transfer to the N atom via a cyclic intermediate [4]. While the basic mechanistic features of these reactions are understood, reactions resulting in the formation of cyclic carbenes have not been examined and are of particular interest as they relate to the formation of organic compounds. Within this research area, interest has focused on the cyclization reactions of electrophilic metal coordinated RNC ligands leading to heterocyclic carbene complexes, which have been accomplished by several strategies as shown in Scheme 1. For instance, suitably functionalized isocyanides such as some hydroxyalkyl isocyanides (reaction (a)) undergo spontaneous intramolecular ring closure upon metal coordination [5]. Isocyanides with acidic C—H bonds in the α-position can be anionized with an appropriate base. The resulting α-metalated compounds can add to polar double bonds to form heterocycles [6] (path (b)). Finally, cyclic carbene complexes have been produced by reactions of RNC ligands with 1,3-dipoles such as nitrilimines and nitrilylides [7] (path (c)).



Scheme 1.

Nitrile, R—C≡N, complexes of transition metals are important reagents in many stoichiometric and catalytic processes [8]. The electrophilicity of the nitrile carbon on Pt(II) and Pd(II) complexes has been exploited in addition reactions of protic nucleophiles [9] such as alcohols, thiols, water and amines as reported in eqn. (2). Reactions with aprotic nucleophiles such as carbanions [10] and azide ion [11], mechanistic studies of amination [12] and metal-catalyzed hydration [13], and catalytic hydration to amides have been reported [8, 13, 14].



$$M-N\equiv C-R \quad + \quad HXR' \longrightarrow M-N(H)=C(R)-X-R' \qquad (2)$$

M = Pd(II), Pt(II); X = O, NH, S; R, R' = alkyl, aryl

Herein we report further development of isocyanide cyclization processes and novel reactions of carbonyl, trifluoromethyl and nitrile ligands, promoted by Pt(II) and Pd(II) metal ions, to yield a variety of coordinated heterocyclic systems such as oxazolines, imidazolines, thiazolines, indoles, or other polycyclic systems.

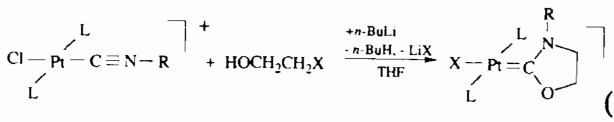
Results and discussion

Reactions of isocyanide ligands

With 2-haloalcohols/base

The homologous series of Pt(II) cationic complexes of the general formula *trans*-$[L_2Pt(CNR)X]BF_4$ (L = monodentate tertiary phosphine; R = alkyl, aryl; X = halide, alkyl; see also eqn. (3)), in which both the R group of the isocyanide ligand as well as the other metal substituents were varied over a wide range, were first investigated [15] in the reactions with the 2-haloalcohols $HOCH_2CH_2X$ (X = Cl, Br), which have an easily displaced X^- at the β-carbon atom. A remarkable feature of this series of complexes is the increase of $\nu(N\equiv C)$ on passing from the unbound isonitrile to the isonitrile coordinated in different environments as observed in the values of $\Delta\nu = \nu(N\equiv C)_{coord} - \nu(N\equiv C)_{free}$ [16], which reflect the electrophilic character [17] of the isocyanide carbon and therefore its ability to react with nucleophiles to form carbene complexes [4]. A positive value of $\Delta\nu \geqslant 40$ cm^{-1} was previously observed to indicate CNR ligand susceptibility to nucleophilic attack [16]. All the cationic Pt(II) complexes display positive Δν values in the range 54–108 cm^{-1}, thus indicating that the isocyanide carbon is a potentially reactive electrophilic center. As expected, the lowest Δν value is observed for the complex *trans*-$[(PMePh_2)_2Pt(CNC_6H_4$-*p*-$OMe)Me]BF_4$, where the strongly σ-electron-donating methyl group is *trans* to the isocyanide ligand [18].

When the cationic Pt(II) isocyanide complexes are added to a THF solution containing a slight molar excess of 2-haloalcohol in the presence of n-BuLi at 0 °C, the isocyanide groups are converted to the corresponding five-membered cyclic aminooxycarbene derivatives (eqn. (3)) [15]. When 2-bromoethanol is



(3)

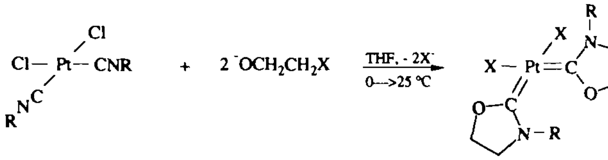
R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-$NO_2C_6H_4$, Me, C_6H_{11}

L = PPh_3 , $PMePh_2$, PMe_2Ph

X = Cl, Br

used instead of 2-chloroethanol, the bromide ion that is liberated upon ring closure (see also Scheme 2) displaces the chloride ion from the starting isocyanide complexes to various extents (*c.* 60–100%) depending on the reaction times. However, the isocyanide ligand in complex *trans*-$[(PMePh_2)_2Pt(CNC_6H_4$-*p*-OMe)-Me]BF_4 does not react with $^-OCH_2CH_2Br$. It is likely that the haloalkoxide undergoes intramolecular cyclization to oxirane [19] faster than it attacks the weakly activated isocyanide ligand.

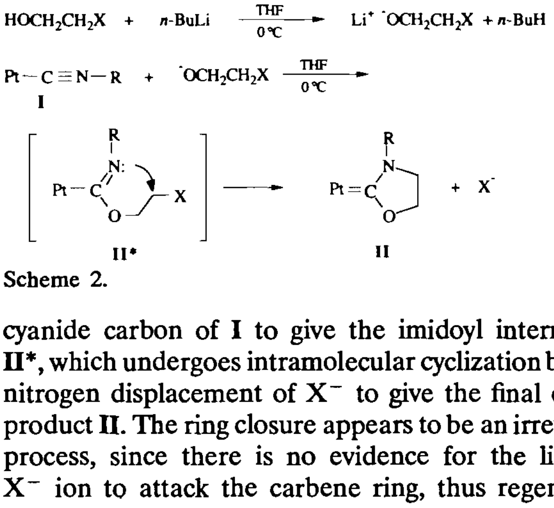
In addition to the isocyanide cationic complexes, the bis(isocyanide) complex *cis*-$Cl_2Pt(CNC_6H_4$-*p*-$OMe)_2$ ($\Delta\nu = 108$ and 79 cm^{-1}) reacts with 2 equiv. of 2-haloalkoxide to give the corresponding bis-(aminooxycarbene) derivative in high yield [15, 20] (eqn. (4)).



(4)

R = *p*-$MeOC_6H_4$; X = Cl, Br

A reasonable mechanism (Scheme 2) for the isocyanide to cyclic carbene conversion described in eqns. (3) and (4) entails initial 2-haloalcohol deprotonation by n-BuLi, followed by nucleophilic attack on the isocyanide carbon of **I** to give the imidoyl intermediate **II***, which undergoes intramolecular cyclization by imino nitrogen displacement of X^- to give the final carbene product **II**. The ring closure appears to be an irreversible process, since there is no evidence for the liberated X^- ion to attack the carbene ring, thus regenerating the imidoyl intermediate **II***. However, this reactivity has been observed in some hydrido-carbene complexes (see trifluoromethyl section).



Scheme 2.

Although stable imidoyl complexes M–C(OR)=NR (M = Pt(II), Au(I), Ag(I)) are known to be formed by nucleophilic attack of alkoxide ions RO^- on coordinated isocyanides [21], no evidence was observed for the intermediate imidoyl species **II***, even when R is an efficient electron-withdrawing group such as *p*-nitrophenyl, which would make the imino N atom less nucleophilic for X^- displacement. The present isocyanide cyclization is closely related to the conversion of CO ligands in several metal carbonyl complexes to cyclic carbene derivatives by $BrCH_2CH_2O^-$ [22] and indicates that the correlation of $\Delta\nu$ versus the susceptibility to nucleophilic attack of the CNR groups appears to parallel that of C–O stretching force constants (k_{CO}) with the electrophilicities of CO ligands in metal carbonyl complexes [23]. However, in contrast to the reactions of carbonyl ligands where k_{CO} is useful for predicting the reactivity of CO ligands with 2-bromoethanol or oxirane in the presence of a halide [19], a high $\Delta\nu$ (> 60 cm^{-1}) appears to be a necessary but not sufficient condition for facilitating reactions of isocyanide ligands with nucleophiles. Thus the aryl isocyanides (eqn. (3), $\Delta\nu = 76$–79 cm^{-1}) and the methyl isocyanide ($\Delta\nu = 91$ cm^{-1}) are converted in a few minutes to the final carbenes with yields of *c.* 70–90%. However, the more bulky $C_6H_{11}NC$ ligand ($\Delta\nu = 82$ cm^{-1}) in *trans*-$[(PPh_3)_2Pt(CNC_6H_{11})Cl]BF_4$ is only partially transformed to the carbene product after 1 h of reaction and gives after 24 h only a 24% yield of isolated product and the t-BuNC ligand in *trans*-$[(PPh_3)_2Pt(CNBu$-t$)Cl]BF_4$ ($\Delta\nu = 81$ cm^{-1}) is not reactive at all under the same reaction conditions. It thus appears that the isocyanide cyclization reactions shown in Scheme 2 parallel those with alcohols and amines in which aryl isocyanides (higher electron-withdrawing properties of the substituent R) react faster than alkyl analogues [4, 24]. Steric effects of the phosphine ligands *cis* to the electrophilic isocyanide carbon are also apparent. Nucleophilic attack is favored by decreasing steric hindrance and increasing the π-accepting capability of the ancillary ligands L as noted for the series *cis*-$Cl_2Pd(CNC_6H_4$-*p*-Me)(L) (L = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3) [25]. When L = PCy_3 as in the complex *trans*-$[(PCy_3)_2Pt(CNC_6H_4$-*p*-$OMe)Cl]BF_4$, the conditions are so unfavorable that no reaction occurs. On the other hand for the complex *cis*-$Cl_2Pt(CNR)_2$ (R = *p*-$MeOC_6H_4$) (eqn. (4)), i.e. with ligands less sterically demanding and better π-accepting, the reaction of one isocyanide ligand with $^-OCH_2CH_2Br$ is very fast.

A structural investigation of *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$ [15] reveals that the cyclic aminooxycarbene is strictly planar and is almost perpendicular (93.4°) to the Pt(II) square plane as observed in several other Pt(II)–carbene complexes [26]. The Pt(II)–carbene bond length of 1.98(1) Å is also in good agreement with other Pt–C(carbene) distances of square planar Pt(II) systems, which generally occur in the range 1.82–2.01 Å when a halide is *trans* to the carbene ligand [26]. Bond lengths within the five-membered ring indicate significant π-bonding between the nitrogen, oxygen and carbene carbon.

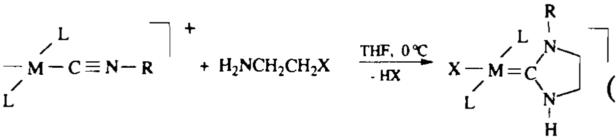
The electrochemical behaviour of the aminooxycarbene complexes *cis*-$Cl_2Pt(PPh_3)[\overline{CN(R)CH_2CH_2O}]$ and *cis*-$Cl_2Pt[\overline{CN(R)CH_2CH_2O}]_2$ (R = *p*-$MeOC_6H_4$) has been studied by cyclic voltammetry (CV, at a Pt wire electrode) and controlled potential electrolysis (CPE, at a gauze electrode) in aprotic media (NCMe/0.2 mol dm^3 $[Bu_4N][BF_4]$) [20, 27]. The monocarbene complex undergoes an irreversible oxidation at $E_p{}^{ox} = 1.78$ V versus SCE, which involves, by CPE, *c*. 2 electrons with extrusion of *c*. $2H^+$ as measured by acid–base titration. The dicarbene complex exhibits two anodic processes, the first one occurring at lower potential ($E_p{}^{ox} = 1.46$ V) than that observed for the monocarbene complex and involving, by CPE, *c*. 2 electrons and a similar number of protons extruded. The second anodic wave ($E_p{}^{ox} = 1.78$ V) corresponds to a multielectron and multiproton loss process (*c*. 4 electrons and 4 protons). The observed proton evolution, which is featured also by the diaminocarbene complexes (*vide infra*), should involve anodically induced C–H (from a methylene group of the carbene ring) heterolytic bond cleavage. It is also suggested that the initial electron removal can be metal centred for the monocarbene complex, since the oxidation potential lies in the known range [28] for the oxidation of related Pt(II) complexes without the carbene ligand, whereas for the dicarbene it can be based on the aminocarbene ligand, since the oxidation potential values are in the range [29] for those of the oxidation of free aliphatic secondary amines. No cathodic reduction has been detected, above the potential of the electrolyte solution reduction, for the neutral dicarbene complex. However, the cationic aminooxycarbene complex *trans*-$[(PPh_3)_2Pt(X)(\overline{COCH_2CH_2N}(R)]^+$ (X = Cl or Br; R = allyl), with a single anionic halide ligand, undergoes, by CV, an irreversible cathodic process ($E_p{}^{red} = -1.75$ V) which, by CPE, involves a single electron transfer, possibly leading to low valent carbene compounds (see further eqn. (9)) [30].

Palladium(II)-isocyanide complexes of the type *trans*-$[(PPh_3)_2Pd(CNR)Cl]BF_4$ (R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me, C_6H_{11}) and *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$ display $\Delta\nu$ values similar to those observed for the parent Pt(II) complexes, but no Pd(II)–carbene derivatives were isolated from the analogous reactions with equivalent amounts of the haloalkoxides even operating at −50 °C (eqn. (5)) [15]. In all cases red solutions were obtained in which no $\nu(C{\equiv}N)$ of the starting isocyanide and $\nu(C{=}N)$ of the final carbene product were present, thereby suggesting the formation of Pd(0) species. It is likely that, for the Pd systems, the alkoxide preferentially attacks the metal center with the formation of Pd–alkoxo species, which decompose by β-hydrogen abstraction and subsequent reductive elimination as reported for the reaction of *trans*-$(PPh_3)_2Pd(R)Cl$ (R = Ph, $CH{=}CCl_2$) with NaOMe [31] to give $[Pd(PPh_3)_2]_n$.

$$L_nPd-C\equiv N-R \quad + \quad OCH_2CH_2X \longrightarrow \text{"unidentified Pd(0) species"} \tag{5}$$

With 2-bromoethylamine

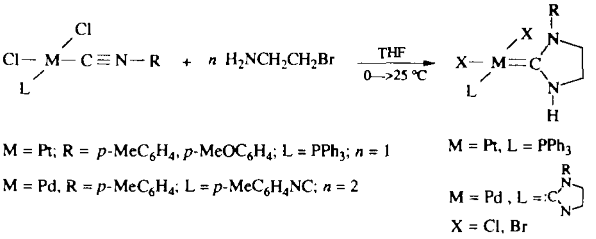
Similarly to the reactions of the 2-haloalcohols, 2-bromoethylamine reacts in THF at 0 °C with aryl and alkyl isocyanide ligands in cationic Pt(II) and Pd(II) complexes to form the corresponding air-stable five-membered cyclic diaminocarbene complexes (eqn. (6)) [32]. The Pt(II) cyclic diaminocarbene complexes of the type *trans*-$\{(PPh_3)_2Pt[\overline{CN(R)CH_2CH_2N}(H)]Br\}BF_4$ (R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4, Me) were isolated in high yield (up to 85%) from the reaction of the precursors isocyanide derivatives with 2 mol of 2-bromoethylamine for *c*. 1 h. The Me complex *trans*-$\{(PMePh_2)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}(H)]Me\}BF_4$ was produced in 68% 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 the starting complex, being *trans* to the strong σ-donor methyl group. The Pd(II)–carbene derivatives *trans*-$\{(PPh_3)_2Pd[\overline{CN(R)CH_2CH_2N}(H)]Br\}BF_4$ (R = *p*-Me-OC_6H_4, *p*-MeC_6H_4, Me) were obtained similarly, but in lower yields (37–52%) compared to the corresponding Pt(II) complexes.



(6)

M = Pd, Pt; R = aryl, alkyl; X = Cl, Br, Me; L = PPh_3, $PMePh_2$

The cyclization process shown in eqn. (6) may involve even two isocyanide ligands in neutral Pd(II) and Pt(II) complexes (eqn. (7)). In the case of the bis(isocyanide) complex *cis*-$Cl_2Pd(CNC_6H_4$-*p*-$Me)_2$, the reaction proceeds stepwise through the rapid formation



(7)

M = Pt; R = *p*-MeC_6H_4, *p*-$MeOC_6H_4$; L = PPh_3; *n* = 1

M = Pd, R = *p*-MeC_6H_4; L = *p*-MeC_6H_4NC; *n* = 2

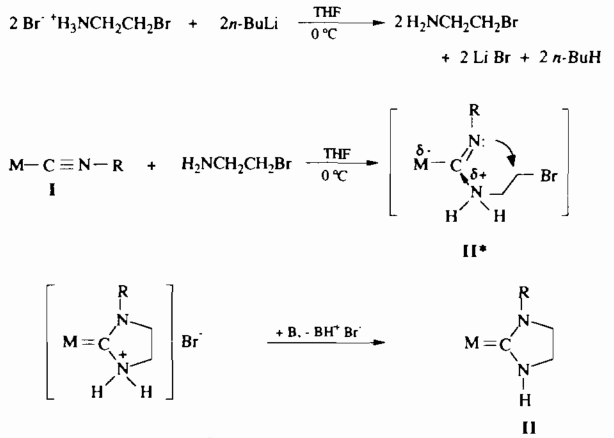
M = Pt, L = PPh_3

M = Pd, L = :C

X = Cl, Br

of a carbene–isocyanide complex, which was not isolated but was detected by IR spectroscopy in solution. This intermediate slowly converts to the final dicarbene product [32].

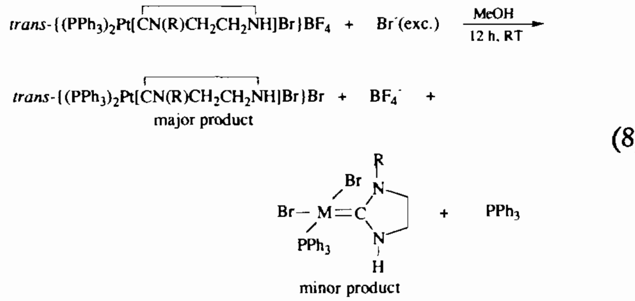
The proposed mechanism for the isocyanide to imidazolil-2-ylidene conversion (Scheme 3) involves



M = Pd, Pt; B = $H_2NCH_2CH_2Br$

Scheme 3.

nucleophilic attack of the haloamine, generated by reaction of $[BrCH_2CH_2NH_3]Br$ and n-BuLi in THF at 0 °C, on the carbon of the coordinated isocyanide to give the intermediate imino–metal(II) species **II***. The subsequent step to give the final carbene complex **II** may involve intramolecular cyclization of the imino intermediate **II*** and subsequent deprotonation of the cyclic carbene by an additional 2-bromoethylamine molecule. As noted earlier for the haloalcohols reactions (Scheme 2), also for the 2-bromoethylamine reactions there is no evidence that the Br^- ions would attack the carbene ring to regenerate the imino intermediate **II*** (Scheme 3). However, it has been observed [32] that the presence of Br^- promotes the exchange of tetrafluoroborate by bromide ion and also, but to a lesser extent, the displacement of a PPh_3 ligand by Br^- as described in eqn. (8).



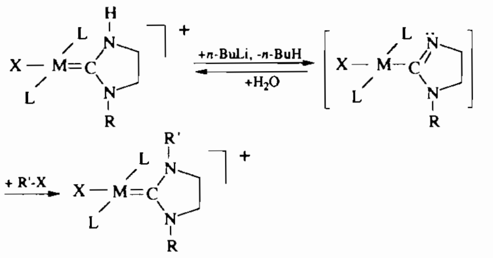
(8)

The X-ray structure [32] of the *cis*-dibromo(diaminocarbene)(PPh_3)Pt(II) derivative (eqn. (8)) shows that the whole set of bond distances from the Pt-atom center shows some significant differences from the values observed in the closely related aminooxycarbene complex discussed earlier. For instance, the slight lengthening of the Pt–Br *trans* to the diaminocarbene is accompanied by an appreciable shortening of the Pt–C(carbene) bond length (1.93(1) Å). Furthermore, although the diaminocarbene ring is strictly planar, the angle formed with the platinum square plane is larger (102.1°) than that observed in the related aminooxycarbene species, thus reflecting the dissymmetry of the steric pressure exerted by the two different *cis* ligands on the carbene ligand. The C–N bond lengths of 1.35(1) Å (average) indicate that also for the diaminocarbene there is extensive π-bonding within the N–C(carbene)–N system.

The electrochemical behaviour of some diaminocarbene complexes of the type *cis*-$Cl_2M(L)[\overline{CN(R)CH_2CH_2N}(H)]$ and *cis*-$Cl_2M[\overline{CN(R)CH_2CH_2N}(H)]_2$ (M = Pd, Pt; L = PPh_3, PMe_2Ph or t-BuNC; R = *p*-$MeOC_6H_4$, *o*-$(CH_2Cl)C_6H_4$ or t-Bu) has been studied by CV and CPE in acetonitrile [20, 27, 30]. The anodic behaviour of the mono- and bis(diaminocarbene) complexes is similar to that found for the aminooxycarbene derivatives (see above) exhibiting one or several irreversible oxidation waves, respectively ($E_p^{ox} = 1.5$–1.9 V versus SCE for the mono(diaminocarbene) and $E_p^{ox} = 1.0$–1.5 V for the bis(diaminocarbene) species), with a multielectron character and involving liberation of a similar number of protons, likely to result from N–H or C–H bond cleavage of the carbene ring. The mono(diaminocarbene) complexes undergo, by CV, an irreversible cathodic process (at $E_p^{red} = -1.5$ to -1.8 V), which, by CPE, involves *c.* 2 electrons and appears to generate zerovalent species, possibly of the type $Cl_2ML(diaminocarbene)^{2-}$ or $ClML(diaminocarbene)^-$ or derived species, which, in a simplified way, can be denoted as ‘Pd^0L(diaminocarbene)’ [27, 30] formed according to the overall process (eqn. (9))

$$Cl_2M^{II}L(\text{diaminocarbene}) \xrightarrow[-x\,Cl^-\ (x = 0,\,1,\,2)]{+2e} \text{"}M^0L(\text{diaminocarbene})\text{"} \qquad (9)$$

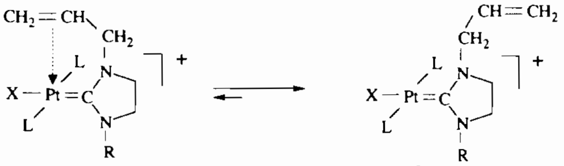
The chemical reactivity of the diaminocarbene complexes involves the N–H group, which can be readily deprotonated by a strong base to give the intermediate imino complex. This latter, which could not be isolated, being rapidly hydrolyzed by traces of H_2O to restore the starting aminocarbene complex, may give further reactions. When generated from cationic complexes, the imino intermediate reacts with haloalkyls R′–X, such as allyl bromide and propargyl bromide, to give novel functionalized N–R′ diaminocarbenes (eqn. (10)).



(10)

M = Pd, Pt; X = Cl, Br; L = PPh_3; R = aryl; R' = $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$

With the carbene ring likely to be oriented perpendicular to the metal square plane, the olefinic or the acetylenic group in the final complexes could be in a favorable position to interact with the metal center as shown for the allyl–diaminocarbene derivative I_a (eqn. (11)).

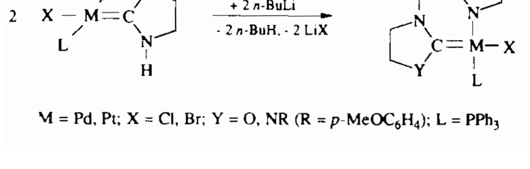


I_a I_b

(11)

Complexes of this type, with *cis* carbene and olefin ligands are of particular interest since such species have been proposed as key intermediates in catalytic processes such as olefin metathesis, cyclopropanation of alkenes and the Ziegler–Natta polymerization of alkenes and considerable effort has been spent in the isolation, characterization and reactivity of such complexes [33]. Although it has been suggested on the basis of IR and ^{1}H NMR data that in a related allyl-substituted aminothiocarbene complex *trans*-$\{(PPh_3)_2Pt[C(SCH_2CH{=}CH_2)NMe_2]Br\}BF_4$ [34], Pt(II) coordination of the olefin double bond occurs, we have no unequivocal spectroscopic evidence for allyl or propargyl group coordination to Pt(II) in the above-mentioned aminocarbene complexes [32]. On the other hand, an X-ray structure of the Pd(II) complex *trans*-$Cl_2Pd[\overline{CN(CH_2CH{=}CH_2)CH_2CH_2}N(CH_2CH{=}CH_2)]_2$ containing N-allyl diaminocarbene ligands shows that the allyl substituents at nitrogen are not implicated in bonding to palladium [35].

In contrast to the reactions of cationic aminocarbene complexes (eqn. (10)), the deprotonation reactions involving neutral aminocarbene complexes [20, 36] do not yield any N–R′ derivatives when carried in the presence of an excess of electrophiles R′–X (X = allyl, propargyl), but instead give dimeric derivatives as reported in eqn. (12). One of these (M = Pt; Y = O; X = Cl; L = PPh_3) has been also structurally characterized [20]. The two Pt coordination planes are orthogonally oriented. The hexaatomic ring formed by two Pt atoms and the nitrogen and carbon atoms of the carbene ligand has a boat conformation with the metal ions being in the apices and the two carbenes oriented in opposite directions with respect to the boat apices in order to minimize molecular strains. All the distances from the Pt atoms are in the normal range for carbene complexes.

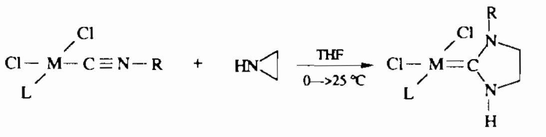


(12)

M = Pd, Pt; X = Cl, Br; Y = O, NR (R = *p*-$MeOC_6H_4$); L = PPh_3

With aziridine, thiirane and oxirane

Five-membered cyclic diamino-, aminothio- and aminooxycarbene complexes can be obtained from RNC ligands coordinated to Pd(II) and Pt(II) metal centers [37] by taking advantage of the tendency of highly strained three-membered heterocycles $\overline{YCH_2CH_2}$, where Y = NH (aziridine), S (thiirane) and O (oxirane), to undergo ring opening reactions. The reactions of aziridine with some Pd(II)– and Pt(II)–isocyanide complexes are summarized in eqn. (13).



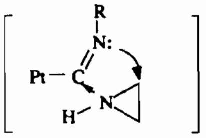
(13)

M = Pd, Pt; R = *t*-Bu, *p*-$MeOC_6H_4$, *p*-MeC_6H_4; L = PPh_3, PMe_2Ph

In contrast with similar reactions previously reported by Angelici and Singh with sufficiently electropositive CO and CS ligands in several metal carbonyl and thiocarbonyl complexes, which react with the heterocycles only in the presence of a halide ion as catalyst to afford cyclic carbene complexes [19], it is observed that aziridine reacts spontaneously with the RNC ligand in the above reported isocyanide complexes. It is also observed that the aryl isocyanides react faster than the bulky t-BuNC ligand. This trend in reactivity parallels that mentioned earlier for reactions of coordinated RNC ligands with $^-OCH_2CH_2X$ and $H_2NCH_2CH_2Br$ and it is also in order with the generally observed reactivity of aryl isocyanides with respect to alkyl analogues [4, 15, 32].

The bis(isocyanide) complexes *cis*-$Cl_2M(CNR)_2$ (M = Pd, R = t-Bu, *p*-$MeOC_6H_4$; M = Pt, R = *p*-$MeOC_6H_4$) react with 2 equiv. of aziridine under experimental conditions analogous to those used for the mono(isocyanide) derivatives. The reaction proceeds differently depending on the nature of the RNC ligand: when R = t-Bu, only one isocyanide ligand is converted to a carbene group, but when R = *p*-$MeOC_6H_4$, both isocyanides are transformed to the final diaminocarbene ligands [20, 37].

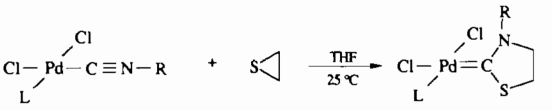
A possible mechanism for the isocyanide–cyclic carbene conversion by aziridine could proceed by nucleophilic attack of the entering amine on the electrophilic carbon of the coordinated RNC ligand to give the intermediate imino–metal(II) species **I*** as reported below.



I*

The subsequent step to give the final complex could involve the C–N ring opening of the coordinate heterocycle, which may occur by intramolecular attack of the nucleophilic imino nitrogen on the adjacent methylene group of aziridine in a four-membered cyclic transition state. We have no evidence for the proposed intermediate **I***, which has been proposed for the reactions of Pd(II)-coordinated isocyanides with various amines and for the cyclization reactions of RNC ligands in metal isocyanides complexes with 2-bromoethylamine [32].

Also thiirane is observed [37] to react spontaneously with some RNC ligands in Pd(II), but not Pt(II), complexes in THF at room temperature to yield five-membered cyclic aminothiocarbene derivatives (eqn. (14)). The reaction of the bis(isocyanide) complex

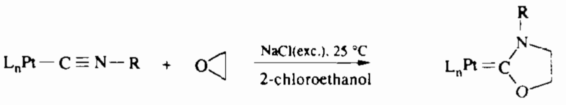


(14)

L = PPh_3, PMe_2Ph, $C_6H_{11}NC$; R = p-$MeOC_6H_4$, C_6H_{11}

cis-$Cl_2Pd(CNC_6H_{11})_2$ leads to the conversion of only one cyclohexyl isocyanide ligand even in the presence of a three-fold excess of thiirane. A reaction intermediate similar to that reported above for the aziridine reaction may be suggested for the reactions of thiirane with the coordinated RNC ligands.

In contrast to the reactions of aziridine and thiirane, oxirane alone fails to convert the isocyanide group in Pd(II) and Pt(II) complexes such as *cis*-$Cl_2(Ph_3P)M(CNC_6H_4$-p-OMe) (M = Pd, Pt) to the corresponding cyclic aminooxycarbene ligand. However, treatment of the isocyanide complexes reported in eqn. (15), with excess oxirane in the presence of NaCl leads to the slow conversion (3 days) of one isocyanide ligand to afford the cyclic aminoooxycarbene compounds [37].



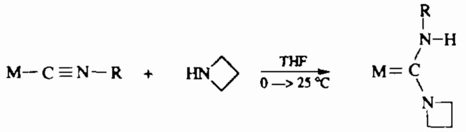
(15)

L_nPt = *cis*-$(Ph_3P)PtCl_2$, *cis*-$PtCl_2(CNC_6H_4$-p-OMe), *trans*-$[(PPh_3)_2PtCl]^+$
R = p-$MeOC_6H_4$

Similar reactions with Pd(II)–isocyanide complexes lead to the formation of Pd(0) species as noted earlier for the reactions with 2-haloalkoxides [15]. Although a reaction intermediate similar to that proposed for the aziridine and thiirane reactions might be suggested also for the oxirane reactions, it does not explain the failure to obtain aminooxycarbene products with oxirane alone or with Pd isocyanides. It is likely that a different mechanism may be involved through an initial Cl^- attack on oxirane to give ring opening and forming the $^-OCH_2CH_2Cl$ ion, which subsequently attacks the RNC ligand as described previously (Scheme 2). The ring opening of oxirane by Cl^- attack is supported by other studies in which the halide ion acts as a catalyst to produce ring opening in certain organic reactions [38].

With azetidine

Closely related to the above reported reactions, are those with the four-membered rings $\overline{YCH_2CH_2CH_2}$, where Y = NH (azetidine), S (thietane) and O (oxetane), which are known to be less strained than the corresponding three-membered heterocycles. No reactions with Pd(II) and Pt(II) isocyanide complexes are observed with thietane and oxetane either alone or in the presence of Cl^- ions [39]. However, 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. In fact azetidine reacts with isocyanide ligands in Pd(II) and Pt(II) compounds to give acyclic diaminocarbene complexes [39] without ring opening and subsequent formation of six-membered cyclic carbene complexes as summarized in the general eqn. (16). The bis(isocyanide) complexes *cis*-$Cl_2Pd(CNR)_2$ react with 2 equiv. of azetidine giving the mono- and the dicarbene derivatives for R = t-Bu and R = p-$MeOC_6H_4NC$, respectively.

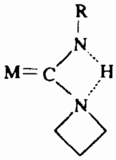


(16)

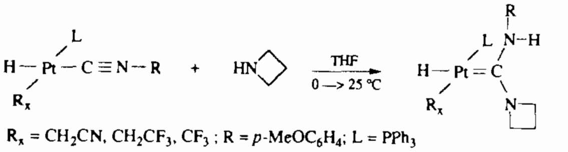
M = *cis*-$(Ph_3P)MCl_2$, M = Pd, Pt; R = p-$MeOC_6H_4$, t-Bu

M = *trans*-$[(PPh_3)_2MCl]^+$, M = Pd, Pt; R = p-$MeOC_6H_4$

As for the mechanism of azetidine reactions, it is likely that they proceed by nucleophilic attack of azetidine on the isocyanide carbon and subsequent proton transfer of the NH group of azetidine to the imino nitrogen as proposed in several mechanistic studies of nucleophilic attack of anilines on coordinated isocyanides [4].



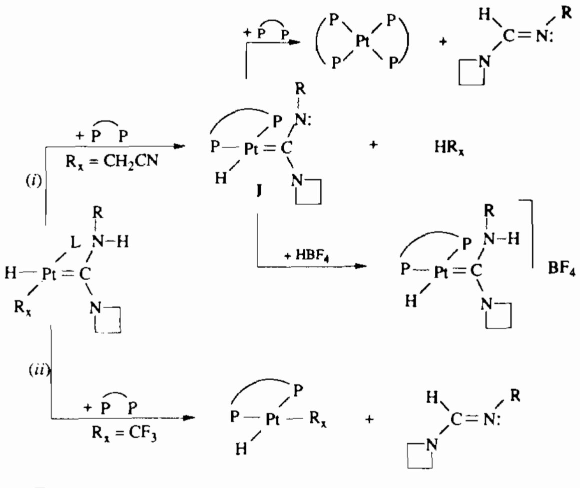
Azetidine, but not aziridine, reacts similarly with hydrido–alkyl–isocyanide complexes, which display low $\Delta\nu$ values (48–51 cm^{-1}) indicating that the isocyanide is less electrophilic than that having halide as *trans* ligand [15, 32, 37], to give the corresponding stable acyclic diaminocarbene derivatives (eqn. (17)) [40].



(17)

$R_x = CH_2CN, CH_2CF_3, CF_3$; $R = p\text{-}MeOC_6H_4$; $L = PPh_3$

It is worthwhile noting that most previous investigations on Pt(II) hydrido alkyls of the type $PtH(R)L_2$ have featured organophosphines as ancillary ligands. These metal species are of special interest since they can be regarded as models of higher reactive intermediates, which are involved in catalytic processes such as the hydrogenation of olefins [41] and the activation of the C–H bond [42]. The stabilities and reactivities of Pt(II) hydrido alkyls depend markedly on the metal complex geometry and the natures of the R and L ligands [43]. In this regard the investigation about how the physical and chemical properties of Pt(II) hydrido alkyls can be affected by the presence of carbene ligands in the metal coordination sphere appears to be an unexplored field [2a]. It is observed [40] that the hydridoalkyl Pt(II) species (eqn. (17)) having *cis* Pt–H and Pt–C bonds are stabilized toward thermal reductive elimination by the presence of a metal-coordinated diaminocarbene ligand. However, these complexes react with P-donors and these reactions appear to be strongly dependent on the nature of the metal-bound alkyl (R_x) group, as shown in Scheme 4, where are reported the reactions with chelating diphosphines. Thus, for $R_x = CH_2CN$, these reactions lead to the selective cleavage of the $Pt\text{–}CH_2CN$ bond and formation of CH_3CN and the *cis* hydrido imino derivative **I**. Analogous reactions occur also with PPh_3, for which isotopic experiments with N–D and Pt–D derivatives indicate that this reaction proceeds through the protonolysis of the metal–alkyl bond by the aminocarbene proton. The observed selective cleavage of the Pt–R_x bond suggests that a possible mechanistic pathway for these reactions is a concerted process promoted by P ligands involving rupture of both Pt–R_x and N–H bonds. It is also remarkable that an X-ray structure of one of these hydrido–alkyl–diaminocarbene complexes (eqn. (17), $R_x = CH_2CN$, $L = PPh_3$, $R = p\text{-}MeOC_6H_4$) shows that also in the solid state there is a short intermolecular interaction (2.32 Å) between the hydrogen atom of the NH group with the nitrogen atom of a CH_2CN group of an adjacent molecule [40]. The imino species **I** (Scheme 4) may react further with one equivalent of the diphosphine to give a Pt(0) species and liberation of the formamidine or may react with HBF_4 to yield the first isolated *cis* hydrido carbene complexes of a transition metal. These latter complexes are important in that they are involved in some stoichiometric and catalytic processes [2a]. For $R = CF_3$, the reactions with diphosphines lead instead to the selective cleavage of the metal–carbene bond with formation of formamidines and *cis* hydrido–trifluoromethyl complexes. This latter process is unprecedented in Pt(II) carbene chemistry.

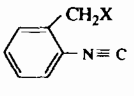


P P = $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$

Scheme 4.

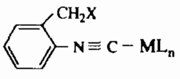
Functionalized isocyanide ligands

Isocyanides with a variety of different functional substituents have been reported in the literature; several of these are stable enough to be isolated as such, while others are stable only upon coordination to a metal center [44]. Our interest in the chemistry of this type of ligand led us to prepare isocyanides of the following structure.

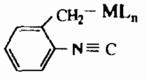


X = Cl, I

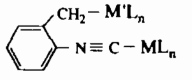
These ligands, which contain the isocyanide and the alkyl halide functions, show the coordination ability of each group, giving rise to mono- or binuclear complexes of the types shown below.



A



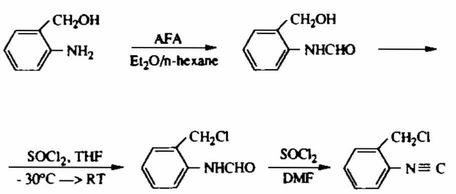
B



C

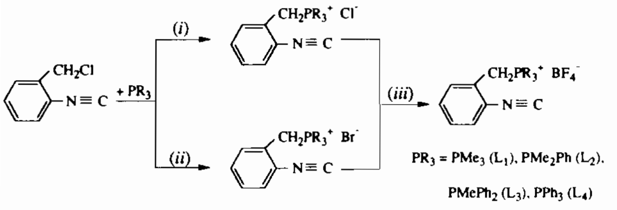
For example, species of type **A** involve simple coordination of the isocyanide end [44], whereas species of type **B** derive from halide displacement by metal carbonyl anions or oxidative addition to metal complexes in low oxidation state [45]. With an appropriate choice of the metal substrate, we have investigated the ability of these ligands to act as bifunctional entities to give homo- and heterobinuclear species of type **C** [44, 45].

The isocyanide ligands have been prepared [46a] as shown in Scheme 5. The *o*-(chloromethyl)-phenylisocyanide is obtained starting from the *o*-aminobenzyl alcohol, which is converted to the corresponding formamide with acetic formic anhydride (AFA). Reaction with $SOCl_2$ in THF at low temperature transforms the *o*-CH_2OH of the formamide to the corresponding *o*-CH_2Cl group and, finally, reaction with $SOCl_2$ in dimethylformamide (DMF) affords the isocyanide with an overall 30% yield.



Scheme 5.

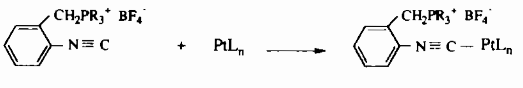
The phosphonium-substituted isocyanides *o*-(X^- R_3P^+ $-CH_2)C_6H_4NC$ (X = Cl, Br; $PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3) are obtained [46] in nearly quantitative yield by reacting the halomethyl function of the isocyanide with a slight molar excess of the tertiary phosphine as depicted in Scheme 6.



(*i*) CH_2Cl_2, + PR_3 = PMe_3, PMe_2Ph. (*ii*) Acetone, RT; +PR_3 = $PMePh_2$ PPh_3 + LiBr(exc), - LiCl. (*iii*) Acetone, RT; +$NaBF_4$ (exc.), -NaX (X = Cl, Br)

Scheme 6.

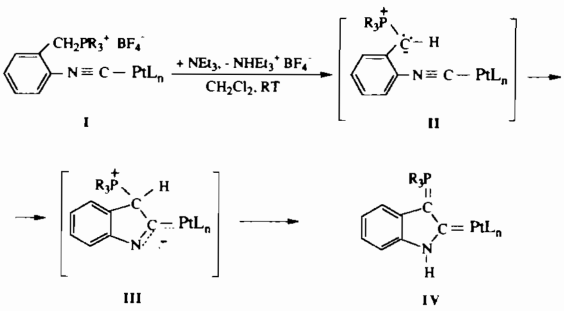
The coordinating ability of the isocyanide ligands L_1–L_4 (Scheme 6) has been tested with some cationic Pt(II) complexes, which have been appropriately chosen in order to investigate the subsequent reaction chemistry of these ligands (eqn. (18)). All the complexes, except that involving the two highly sterically demanding PCy_3 in the complex *trans*-$[(PCy_3)_2Pt(Me)(L_1)]^+$ for which $\nu(N{\equiv}C)$ increases only by 7 cm^{-1}, display a larger shift of the N≡C stretching to higher wavenumbers (*c*. 45–80 cm^{-1}) upon isocyanide coordination to Pt(II). These complexes are found to react with an excess of the mild base NEt_3 to afford in good yield (*c*. 70%) the C-2 metal-bonded indole derivatives [46] according to the mechanism proposed in Scheme 7. It involves initial attack of NEt_3 on the activated methylene group of the phosphonium moiety of **I** to form the highly reactive ylide–isocyanide–metal intermediate **II**, which subsequently intramolecularly adds to the adjacent coordinated isocyanide giving **III**. This latter species eventually converts to the final stable indole derivative **IV** by proton shift, which may occur either intramolecularly or by the assistance of the $NEt_3/NHEt_3{}^+$ couple acting as a proton transfer agent.



(18)

PtL_n = *trans*-$[(PR'_3)_2PtX]^+$; PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, PCy_3; X = Cl, Me

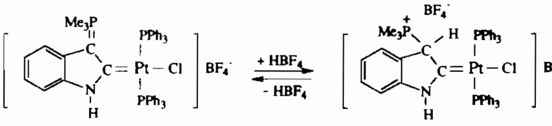
PtL_n = *cis*-$[(Ph_2PCH{=}CHPPh_2)PtCl]^+$



Scheme 7.

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 of 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 6), according to the nucleophilic character of the corresponding ylide intermediate **II** (Scheme 7).

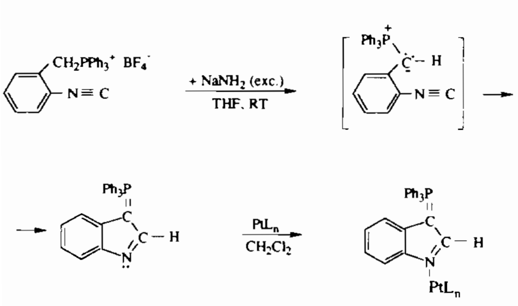
A structural investigation of *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C}(PMe_3)]Cl\}BF_4$ shows that there is an extensive electronic delocalization within the indole system [46]. As a consequence, the carbenoid ligand in this complex exhibits the typical reactivity of indoles [47] reacting with electrophiles such as HBF_4 to give addition at the β-position of the indole ring (eqn. (19)). The resulting cation is stable in solution in the presence of excess acid, but regenerates the



(19)

starting indole ring in an attempted isolation by addition of Et_2O.

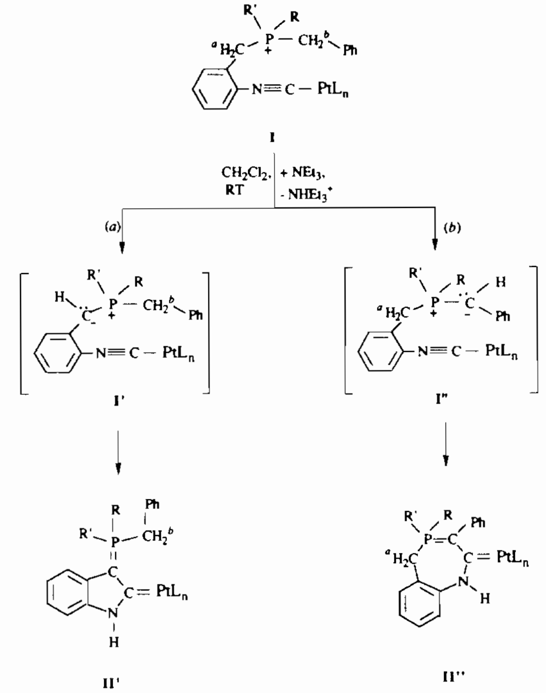
In an attempt to isolate the free ylide–isocyanide ligands o-(R_3P^+–CH^-)C_6H_4NC, we reacted o-($BF_4^-Ph_3P^+$–CH_2)C_6H_4NC with a base [46]. While no reaction occurs with excess NEt_3, a fast reaction takes place in THF at room temperature in the presence of excess of a stronger base such as $NaNH_2$ (Scheme 8).



PtL_n = *cis*-$[(PPh_3)_2PtCl]^+$; *trans*-$[(PPh_3)PtCl_2]$

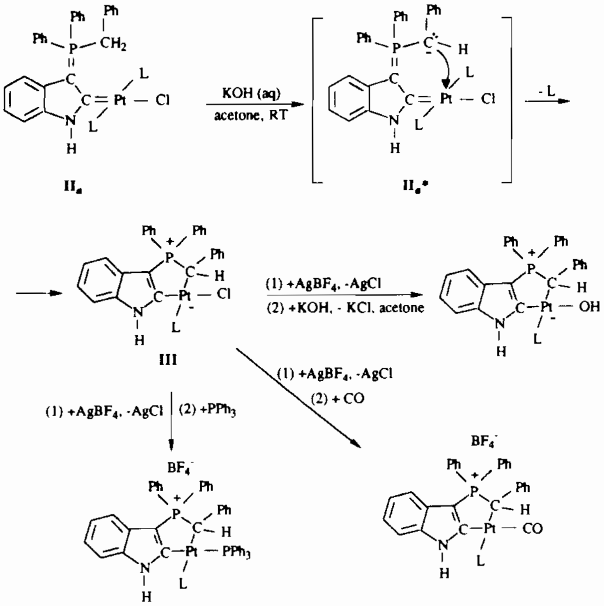
Scheme 8.

The structure of this heterocyclic derivative is based on elemental analysis, mass spectra and ^{31}P NMR data, and its IR spectrum which does not show ν(NH), ν(N≡C) and $\nu(BF_4)$ stretchings. Its structure is further confirmed by its coordination chemistry resulting in the formation of Pt(II)–indole derivatives, in which the Pt atom is bound to the nitrogen atom of the indole ring.



R, R' = CH_2Ph or Ph. L_nPt = *trans*-$[PtCl(PPh_3)_2]^+$

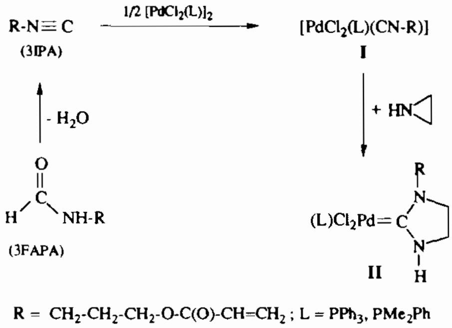
Scheme 9.



Scheme 10.

In order to explore the generality of the synthetic strategy developed in Scheme 7, we tested reactions with Pt(II)-coordinated benzylphosphonium-substituted isocyanide ligands of the type **I** shown in Scheme 9 [48]. Interest in these ligands stems from the presence of several (up to four) potentially reactive $-CH_2PR_3^+$ moieties, one of which belongs to the isocyanide ligand ($-CH_2{}^a$-type, structure **I**) and all the others to the benzylphosphine ligand ($-CH_2{}^b$-type). Since $-CH_2{}^a$ and $-CH_2{}^b$ methylene protons are electronically similar, the two groups can each generate the corresponding ylide functionality **I′** (route (*a*)) and **I″** (route (*b*)) by attack of base. Molecular models indicate that the generated ylide carbanion in both of these intermediates is in a favourable position to interact with the isocyanide carbon to give ring closure to **II′** and **II″**, respectively. However, it is observed that treatment of complexes of type **I** with an excess of NEt_3 leads only to the isolation of complexes of type **II′**, as evidenced by analytical, spectroscopic and structural data [48]. The $-CH_2{}^b$ protons, which are unreactive towards NEt_3, do, however, undergo nucleophilic attack by a stronger base such as KOH, as shown for the benzyldiphenylphosphonium derivative $\mathbf{II}_a$ in Scheme 10. This reaction leads to the formation of the stable platinaheterocycle **III**, presumably via a ylide–carbene intermediate $\mathbf{II}_a$*, formed by deprotonation of the methylene group of $\mathbf{II}_a$ by OH^- ions and subsequent nucleophilic attack on the metal center with a loss of a PPh_3 ligand. Chloride abstraction with Ag^+ from complex **III** and further treatment with OH^-, CO or PPh_3, yields the corresponding hydroxo, carbonyl and phosphine derivatives.

As a further example of the potential role of certain functionalized isocyanide and carbene ligands in the development of polymer-supported coordination chemistry we have reported the synthesis and coordination ability toward Pd(II) metal centers of 3-isocyanopropylacrylate (3IPA) [49] and the derived cyclic diaminocarbene complex [50] (Scheme 11). 3IPA, which can be obtained by dehydration of 3-formamidopropylacrylate (3FAPA), reacts with stoichiometric amounts of $[PdCl_2(L)]_2$ (L = PPh_3, PMe_2Ph) to give the corresponding coordinated isocyano complexes **I**, one of which has been structurally characterized. These react further with aziridine to yield the cyclic diaminocarbene derivatives **II** and the X-ray analysis of the PPh_3 derivatives has been reported [50]. Complexes of type **I** and **II** could be 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 type shown below, which are potentially useful for diverse catalytic applications.



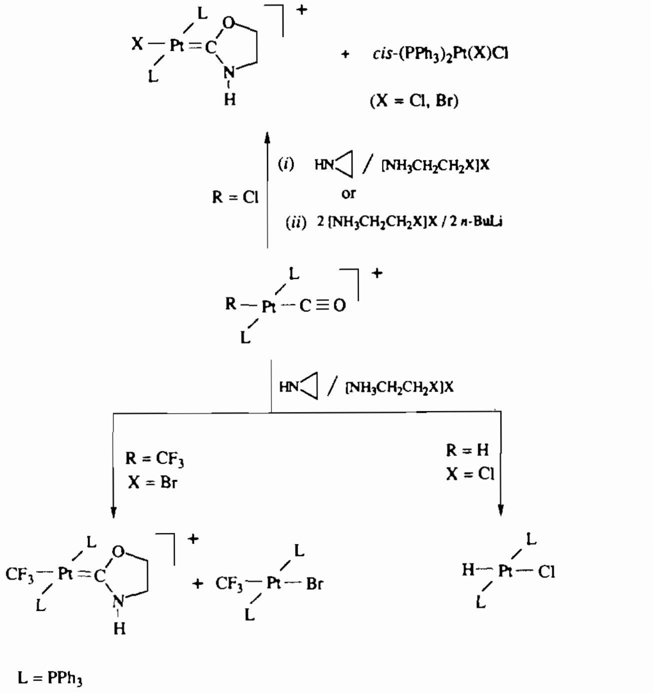
Scheme 11.

Ⓟ-NC-ML$_n$ Ⓟ-N—C-ML$_n$

To this regard a Pd(II) complex with 3IPA has been reported to be successfully copolymerized with dimethylacrylamide by γ-ray initiation [51].

Reactions of carbonyl ligands

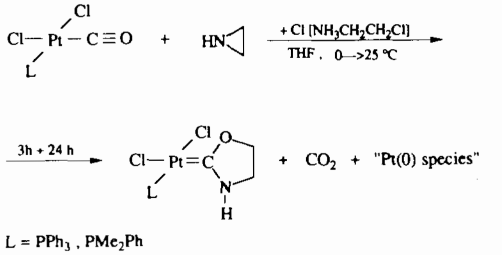
Although platinum group carbonyls (with k_{CO} force constants equal to or greater than 17.0 mdyn/Å) are susceptible to nucleophilic attack and their reactions with amines, alcohols and water yield carbamoyl, alkoxy carbonyl and hydroxy carbonyl complexes, respectively [52], yet none has been reported to afford a carbene ligand. On the other hand, recent work by some of us and Angelici with the reactions of 2-haloethanols, 2-haloethylamines and the three-membered heterocycles $\overline{YCH_2CH_2}$ (Y = NH, O, S) with electrophilic isocyanides (see above) and carbonyls [19, 22], led us to explore the generality of these reactions also with some square planar Pt(II) carbonyls [36].



Scheme 12.

Scheme 12 reports the reactions of some cationic carbonyl complexes to yield the five-membered aminooxycarbene derivatives. The CO ligand conversion to carbene depends markedly on the σ-donor ability of the *trans* ligand R. When R = Cl, the carbene complex is recovered in high yield after a few hours of reaction either with aziridine in the presence of the 2-haloethylammonium salt (method *i*) or with 2-haloethylamine generated by reaction of $[NH_3CH_2CH_2X]X$ with n-BuLi (method *ii*). These reactions are always accompanied by the formation of small amounts of the dihalo derivative *cis*-$(PPh_3)_2Pt(X)Cl$, presumably from CO displacement by X^- ions. When R = CF_3 or H, the reactions with aziridine/halide ion systems indicate that the Pt^{II}–CO → Pt^{II}–carbene conversion decreases with increasing σ-donor ability of the R ligand, and when R = H, the CO substitution process is the only occurring reaction.

The reactions of the neutral carbonyl complexes with aziridine/Cl^- [36] lead also to the formation of cyclic aminooxycarbenes as reported in eqn. (20). The carbene products are obtained in low yield (*c*. 40%) due to a concomitant nucleophilic attack by adventitious



(20)

H_2O to give an unstable Pt–COOH intermediate that subsequently decomposes to produce CO_2 and unidentified Pt(0) species [53].

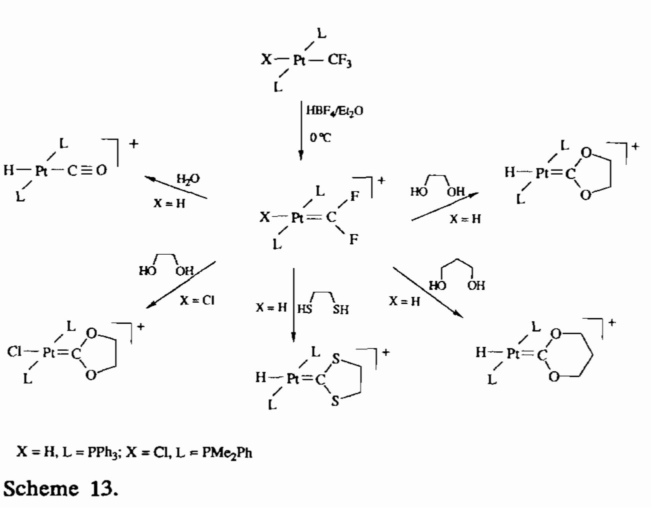
The formation of the aminooxycarbene complexes (Scheme 12 and eqn. (20)) may be explained through the intermediacy of a carbamoyl derivative of the type Pt–C(=O)N(H)CH_2CH_2X, formed by attack of aziridine/X^- or (haloethyl)amine to the coordinated CO, which rapidly cyclizes by X^- displacement [19, 22].

The cationic and neutral aminooxycarbenes derived from Pt(II) carbonyls can be deprotonated by strong bases in the presence of haloalkyls R′–X to give N–R′ functionalized aminocarbenes or dinuclear derivatives with bridging carbenes as reported for the reactions of diaminocarbenes (see eqns. (10) and (12)).

No carbene formation is observed by reaction of cationic or neutral Pt(II) complexes with 2-haloethylalcohols either alone or in the presence of a base.

Reactions of trifluoromethyl ligands

Although σ-perfluoroalkyl complexes of the transition metals show higher thermal stability as compared to their σ-alkyl counterparts and the perfluoroalkyl group is quite resistant to chemical attack [43], C–F bonds α to the transition metal are, however, susceptible to electrophilic attack under mild conditions by proton and Lewis acids to give carbene and carbonyl complexes [54]. Such reactivity has been explained by a weakening of the C–F bonds α to the metal, which accounts for the reduced C–F stretching frequencies and increased bond lengths in comparison with aliphatic compounds [55]. Trifluoromethyl complexes of platinum(II) are no exception. A low temperature X-ray structure determination [56] carried out for *trans*-$L_2Pt(H)(CF_3)$ ($L = PPh_3$) shows that the C–F distance is *c.* 1.404(9) Å (av.), which is significantly longer than that observed in organic fluorocarbon compounds (*c.* 1.34 Å) and this bond weakening is reflected in the reactivity of C–F bonds α to platinum as shown in Scheme 13.



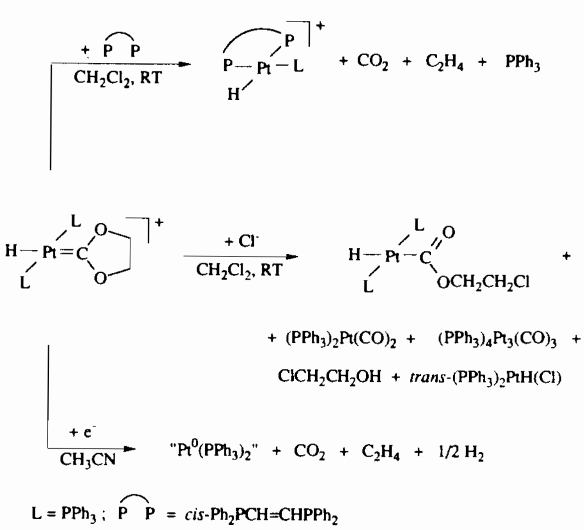
X = H, L = PPh_3; X = Cl, L = PMe_2Ph

Scheme 13.

Electrophilic attack on *trans*-$L_2Pt(H)(CF_3)$ ($L = PPh_3$) by electrophiles such as HBF_4, $NOBF_4$ or *p*-toluensulfonic acid gives C–F bond cleavage producing the highly reactive difluorocarbene intermediate, which could not be isolated but was spectroscopically characterized by low temperature ^1H, ^{31}P and ^{19}F NMR spectra [56]. The $Pt{=}CF_2{}^+$ species reacts with protic nucleophiles such diols and thiols to give five- and six-membered cyclic carbenes, whereas the reaction with H_2O leads to the formation of the carbonyl derivative. In order to gain more information on the role of electronic and/or steric factors which may affect the reactivity of the CF_3 group in Pt(II) complexes, we examined the reactions of complexes of the type *trans*-$L_2Pt(Cl)(CF_3)$ ($L = PPh_3, PMePh_2, PMe_2Ph$). The results indicate that these halo–trifluoromethyl Pt(II) complexes are less reactive than the parent hydrido derivatives and only the complex containing the more basic phosphine PMe_2Ph reacts to give the corresponding carbene species as shown in Scheme 13.

There appear to be only a few hydrido–transition metal carbene complexes [56]. The X-ray structure of *trans*-$[(PPh_3)_2PtH(\overline{COCH_2CH_2O})]BF_4$ shows that the coordination geometry around Pt(II) is distorted square planar with the carbene ligand rotated with respect to the coordination plane by 61.3(2)°. The five-membered cyclic dioxycarbene is almost planar with C(sp^2) bond distances of 1.30(1) Å, indicating significant π-bonding between the oxygen and the carbene carbon. Furthermore, the Pt–C(carbene) distance is 2.01(2) Å, which is longer than that found for related carbene complexes having a halide as *trans* ligand and may be reasonably explained with the higher *trans* influence of hydride compared to halide [18]. This latter feature might also be responsible for the higher reactivity of hydrido–carbene complexes compared to the corresponding halo derivatives as shown in Scheme 14.

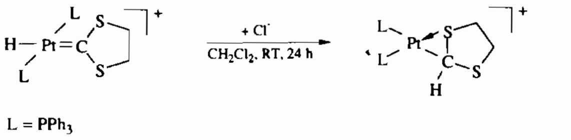
The reaction with a chelating diphosphine leads to the complete fragmentation of the carbene ring with formation of carbon dioxide and ethylene, while the analogous reactions with the dihalo–diaminocarbene complexes *cis*-$Cl_2M[\overline{CN(R)CH_2CH_2N}(H)]_2$ (M = Pd, Pt; R = *p*-$MeOC_6H_4$) with the same diphosphine lead in all cases to chloride displacement from the metal and formation of the cationic derivatives *cis*-$\{(Ph_2PCH{=}CHPPh_2)M[\overline{CN(R)CH_2CH_2N}(H)]\}Cl_2$ [30]. The reaction with Cl^- ions yields a complex mixture of products, among them the alkoxycarbonyl derivative, presumably formed by attack of Cl^- to the carbene ring [30]. Other species detected were Pt(0) carbonyl compounds, 2-chloroethanol, this latter likely to be formed by hydrolysis of the alkoxycarbonyl species, and the hydrido–chloro complex. Furthermore, also the electrochemical behaviour of the hydrido–carbene Pt(II) complex parallels the aforementioned chemical reac-



Scheme 14.

tivity, since complete fragmentation of the dioxycarbene ligand occurs upon exhaustive cathodic CPE to give quantitatively CO_2 and C_2H_4 [27, 30]. Moreover, since extensive H_2 evolution results from the cathodic CPE, it is likely that Pt(0) derivatives of the type $[Pt(PPh_3)_2]$ are formed in these reactions. These species are known to cathodically be electrogenerated from *cis*-$Cl_2Pt(PPh_3)_2$ [57]. It is observed that the chemical and electrochemical behaviour of the dioxycarbene ligand in the hydrido–Pt(II) complex is similar to that described for $CpFe(CO)_2[\overline{COCH_2CH_2O}]^+$ [58].

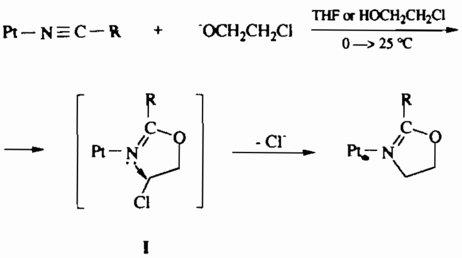
It is worthwhile noting that, markedly in contrast with the behaviour of the dioxycarbene ligand, the parent hydrido–dithiocarbene complex does not decompose upon reaction with Cl^- ions, but rather it undergoes hydride to carbene carbon migration with formation of a $C(sp^3)$ bond and S-coordination to the Pt center (eqn. (21)) [59]. This reaction is unprecedented for Pt(II)–carbene chemistry and, as far as we know, only two examples with Fe and Mo complexes have been reported [60].



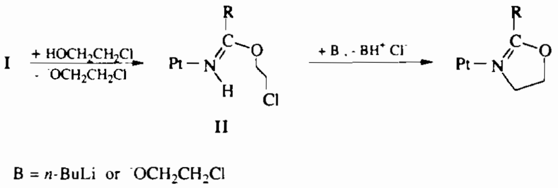
(21)

Reactions of nitrile ligands

The reactions of the nitrile complexes *cis*- and *trans*-$Cl_2Pt(NCR)_2$ (R = Me, Ph) with the organic nucleophiles 2-chloroethanol/base and oxirane/Cl^- yield 2-(R)oxazoline derivatives [61], as illustrated in the general Scheme 15. One synthetic feature of these reactions is that both nitriles are converted to oxazolines, which are formed under basic conditions, while they are generally obtained from nitriles and aminoalcohols under strongly acidic conditions [62]. A reasonable mechanism for this transformation involves nucleophilic attack of $^-OCH_2CH_2Cl$, generated either by deprotonation of $HOCH_2CH_2Cl$ with n-BuLi in THF or by ring opening of $\overline{OCH_2CH_2}$ by Cl^- ion in 2-chloroethanol, on the nitrile carbon affording the intermediate **I**, which converts to the oxazoline product by intramolecular cyclization. The influence of the haloalkoxide concentration on the nitrile–oxazoline conversion has been tested with the oxirane/Cl^- reactions. With a nitrile complex/Cl^- molar ratio in the range 1/2.1–1/0.4 and sufficiently long reaction times (*c*. 2 days at room temperature), the oxazoline product is isolated in high yield. At lower nitrile/Cl^- molar ratios a mixture of the oxazoline derivative and the acyclic imido ester **II** (eqn. (22)) is formed. The imido ester **II**, which has been isolated for R = Ph, can be converted to the oxazoline product by reaction with a base such as n-BuLi.

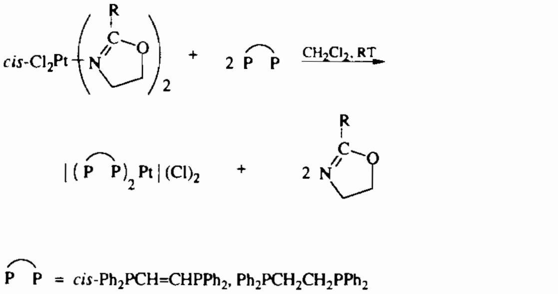


Scheme 15.



(22)

The Pt(II)-coordinated oxazolines are stabilized in comparison with the free compounds toward ring opening by reaction with mineral acids or Cl^- ions. However, reactions with chelating diphosphines give free oxazolines as outlined in eqn. (23).



(23)

Concluding remarks

Pd(II) and Pt(II) metal centers promote the conversion of RNC, CO, CF_3 and RCN ligands to five- or six-membered heterocycles, which are carbenes when starting from C–metal bound ligands or N-coordinated oxazolines, when starting from nitriles. Heterocyclic systems such as oxazoles, imidazoles and thiazoles have been obtained by addition to coordinated isocyanides of suitable nucleophiles such as β-haloalcohols, β-haloamines, which have an easily displaced X^- at the β carbon atom, or the three-membered heterocycles YCH_2CH_2 (Y = NH, S, O), which are susceptible to undergo ring opening reactions. Indoles are obtained by intramolecular cyclization reactions via a ylide intermediate of phosphonium-substituted phenylisocyanides coordinated to Pt(II) species. Further cyclization of the coordinated indole ligand can be achieved under more basic conditions to produce platinaheterocycles. Nucleophilic attack on Pt(II) carbonyls by aziridine/Cl^- affords C-2 ligated oxazolines. Electrophilic attack by Lewis or proton acids in the presence of diols and thiols on Pt–CF_3 complexes yield C-2 metal bonded 1,3-dioxolane and 1,3-dithiolane derivatives. Nitrile ligands are converted to N-bound oxazolines by reaction 2-chloroethanol/base or oxirane in the presence of Cl^- ions. As a general feature, it is observed that the reactivity of the coordinated ligands and derived heterocyclic systems in Pd(II) and Pt(II) complexes is strongly influenced by the σ-donor ability of the *trans* ligand. For instance, heterocyclic carbenes having hydride as the *trans* ligand may undergo carbene–carbon cleavage, carbene fragmentation or hydride to carbene migration, which are not observed with the parent halo derivatives.

Further investigation on the cyclization of other Pd(II)- or Pt(II)-coordinated ligands such as alkynes as well as the development of catalytic processes involving some of these reactions are in progress.

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