

Review

# N-heterocyclic carbenes from transition metal coordinated functional isocyanides of the type $o\text{-(CH}_2\text{Y)C}_6\text{H}_4\text{N}\equiv\text{C}$ ( $\text{Y} = \text{OSiMe}_3, \text{OH}; \text{N}_3; \text{AsR}_3^+$ )

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## Abstract

The synthesis, transition metal coordination and reactivity of the functional isocyanides  $o\text{-(CH}_2\text{Y)C}_6\text{H}_4\text{-N}\equiv\text{C}$  ( $\text{Y} = \text{OSiMe}_3, \text{OH}; \text{N}_3; \text{AsR}_3^+$ ) to afford N-heterocyclic carbenes is shortly reviewed.

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**Keywords:** Carbenes; NHC ligands; Functional isocyanides; Transition metal complexes

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## 1. Introduction

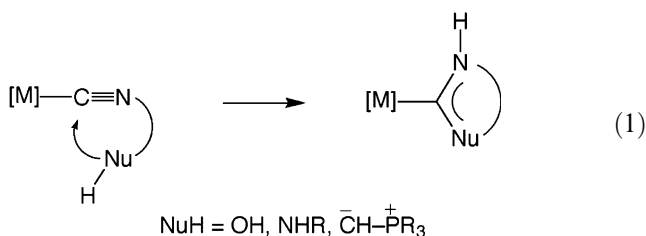
The synthesis and reactivity of functional isocyanides and their transition-metal coordination compounds have received a great interest in the last decades [1–3]. Examples of this class of ligands are: (i) the hydroxyalkyl isocyanides  $\text{HO-(CH}_2\text{)}_n\text{-N}\equiv\text{C}$  [4], the trichloromethyl isocyanide,  $\text{CCl}_3\text{-N}\equiv\text{C}$ , [1,5], the hydrogen

isocyanide,  $\text{HN}\equiv\text{C}$ , [3], and the  $\alpha$ -metalated isocyanides  $\text{Y-C H-N}\equiv\text{C}$  ( $\text{Y} = \text{CO}_2\text{Et}, \text{SO}_2\text{R}$  ( $\text{R} = p\text{-tolyl}$ ),  $\text{PPh}_3^+$ ) [6] reported by Fehlhammer and coworkers; (ii) the  $\beta$ -functional phenyl isocyanides such as  $o$ -hydroxyphenyl isocyanide,  $o\text{-(HO)C}_6\text{H}_4\text{N}\equiv\text{C}$ , and 2,6-dihydroxyphenyl isocyanide, 2,6  $\text{(HO)}_2\text{C}_6\text{H}_4\text{N}\equiv\text{C}$ , and their derivatives, described by Hahn and coworkers [2] and (iii) the  $\gamma$ -functional isocyanides of the type  $o\text{-(CH}_2\text{Y)C}_6\text{H}_4\text{-N}\equiv\text{C}$  ( $\text{Y} = \text{Cl}, \text{I}$  [1,7];  $\text{CpCr(CO)}_3$ ,  $\text{CpW(CO)}_3$  [8];  $\text{PR}_3$  [1,9]) reported by some of us. Their organometallic chemistry has been addressed in many cases [1,2] to the formation of N-heterocyclic carbenes

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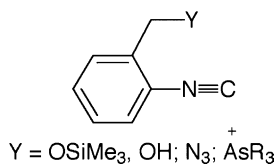
E-mail address: [rino.michelin@unipd.it](mailto:rino.michelin@unipd.it) (R.A. Michelin).

(NHC) through an intramolecular addition of the nucleophilic group across the C≡N triple bond (Eq. 1).



In the last years, the metal–NHC complexes [10] have been receiving great attention in the literature since the aminocarbene ligands were found to be promising alternative ligands to the commonly used phosphines and phosphites and also for their favorable application in homogeneous catalysis [10a,10b,10c,10d,10e,10j].

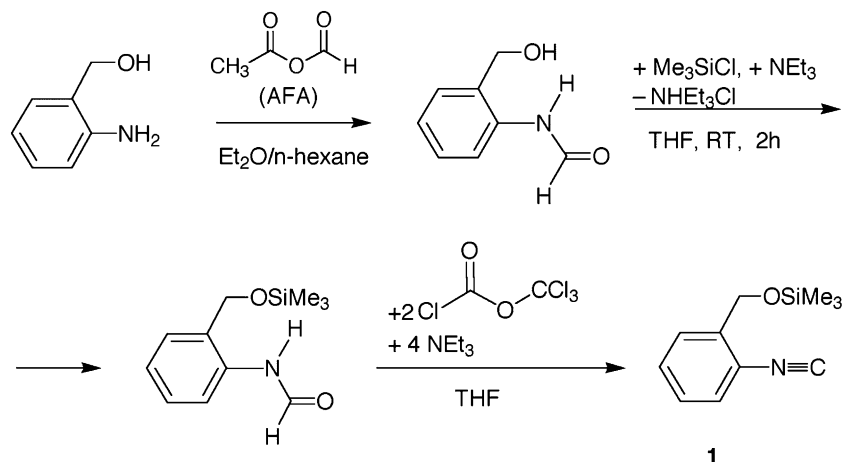
We wish to report herein, a short account of the recent results on the synthesis and the organometallic chemistry of the functional isocyanides *o*-(CH<sub>2</sub>Y)C<sub>6</sub>H<sub>4</sub>N≡C illustrated below specifically addressed to the formation of NHC transition metal complexes.



## 2. Synthesis of the functional isocyanide ligands

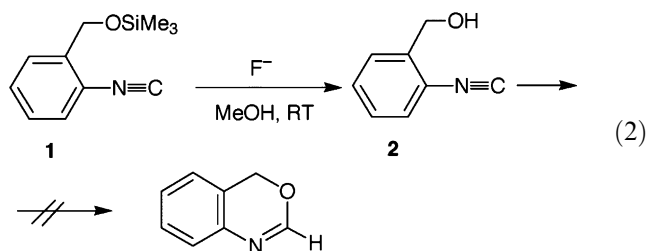
The reactions sequence leading to the synthesis of 2-(trimethylsiloxymethyl)phenyl isocyanide (**1**) is reported in Scheme 1 [11].

The first stage involves the conversion of the amino group of the commercially available 2-aminobenzyl alcohol to the corresponding formamide using acetic formic anhydride (AFA) as previously reported [12].



Scheme 1.

Subsequent reaction with a stoichiometric amount of Me<sub>3</sub>SiCl in the presence of a slight excess of NEt<sub>3</sub> in THF affords the *o*-silylated formamide in good yield. This latter is then dehydrated with trichloromethyl chloroformate in the presence of NEt<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C [11] to give the isocyanide **1** as a pale yellow oil. Characteristic spectral features are reported in Table 1. The isocyanide **1** is stable in CDCl<sub>3</sub> solution. However, it can be readily converted to the corresponding 2-(hydroxymethyl)phenyl isocyanide (**2**) in the presence of a catalytic amount of F<sup>-</sup> ions in MeOH at room temperature. The isocyanide **2**, which is isolated as a pale green oil, is also stable as free ligand and shows no tendency to undergo intramolecular cyclization to 4H-benzo[1,3]oxazine (Eq. 2) as can be inferred by monitoring the <sup>1</sup>H NMR spectrum of a CDCl<sub>3</sub> solution for two days at room temperature [11].



Selected spectral data of **2** are reported in Table 1.

The synthesis of 2-(azidomethyl)phenyl isocyanide (**3**) is reported in Scheme 2. The reaction of 2-(chloromethyl)phenyl formamide, which has been prepared as previously reported [9b], with a slight molar excess of NaN<sub>3</sub> in DMSO [13] at room temperature affords in good yield 2-(azidomethyl)phenyl formamide (**3**) as a pale cream solid. The formamide is then dehydrated with SOCl<sub>2</sub>/DMF [9b,14] to give the isocyanide **3** in good yield as a green oil, which was found to be stable in air and in solution, but was stored under N<sub>2</sub> in the cold. Typical spectral data of **3** are given in Table 1.

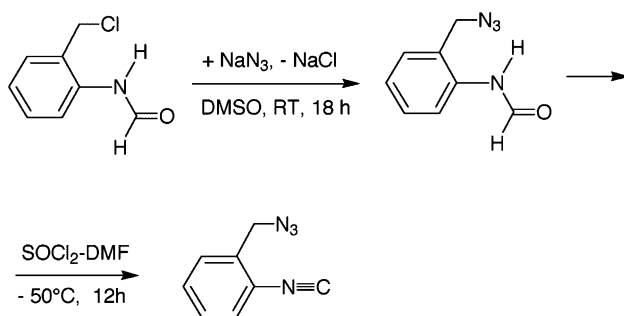
Table 1  
Selected spectroscopic data of the functional isocyanides 1–4

Compound	$\bar{\nu}(\text{N}\equiv\text{C})^a$ ( $\text{cm}^{-1}$ )	$k(\text{N}\equiv\text{C})^b$ (N/m)	$\delta(\text{N}\equiv\text{C})^c$ (ppm)	Reference
1	2122 (vs)	1728	167.5 (s)	[12]
2	2122 (vs)	1728	166.8 (s)	[12]
3	2124 (vs)	1731	168.8 (s)	[15a]
4a	2120 (vs)	1725	Not detected	[16]
4b	2120 (vs)	1725	Not detected	[16]
4c	2119 (vs)	1723	168.2 (s)	[16]

<sup>a</sup> IR in  $\text{CH}_2\text{Cl}_2$ : vs, very strong.

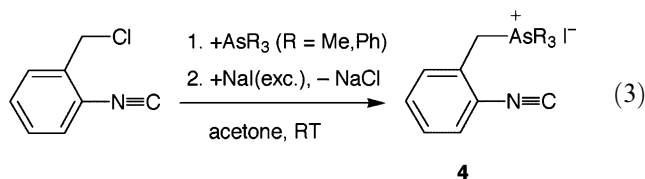
<sup>b</sup> Calculated by  $k = (2\pi c \bar{\nu})^2 \times \mu$  with  $\bar{\nu}$  the wavenumber in  $\text{cm}^{-1}$  and  $\mu$  the reduced mass of vibrating atoms.

<sup>c</sup>  $^{13}\text{C}$  { $^1\text{H}$ } NMR in  $\text{CDCl}_3$ : s, singlet.



Scheme 2.

The synthesis of the arsonium-substituted isocyanide ligands, **4**, are reported in Eq. (2). They are obtained in moderate to high yield by reaction of the known *o*-(chloromethyl)phenyl isocyanide [9b], *o*-( $\text{CH}_2\text{Cl}$ ) $\text{C}_6\text{H}_4\text{N}\equiv\text{C}$ , with a ca. 20% molar excess of the arsine  $\text{AsR}_3$  ( $\text{AsR}_3 = \text{AsPh}_3, \text{AsMePh}_2, \text{AsMe}_2\text{Ph}$ ) in the presence of a 3-fold excess of NaI in acetone at room temperature for 6 h (Eq. 3).

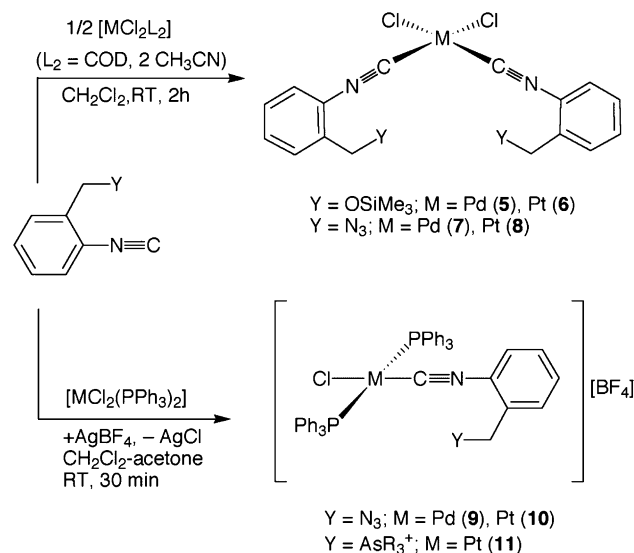


Diagnostic spectral features of the isocyanide ligands, **1–4**, are shown in Table 1.

### 3. Transition metal coordination and cyclization reactions to heterocyclic aminocarbene complexes

The coordinating ability of the isocyanide ligands **1**, **3** and **4** has been tested in a series of reactions with some transition metal complexes which have been appropriately chosen in order to investigate more deeply their chemical behaviour. The coordination to some Pd(II) and Pt(II) complexes is illustrated in Scheme 3.

Complexes **5–8** were readily obtained in good yield from the precursors  $[\text{MCl}_2\text{L}_2]$  ( $\text{M} = \text{Pt}$ ,  $\text{L}_2 = 1,5$ -cyclo-



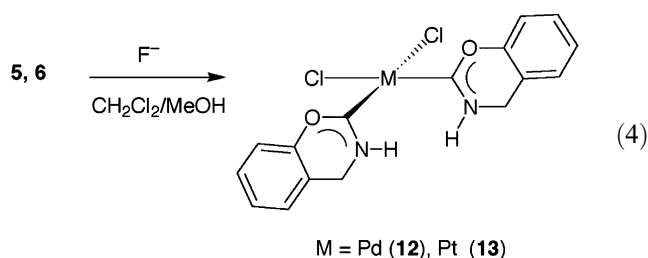
Scheme 3.

octadiene;  $\text{M} = \text{Pd}$ ,  $\text{L}_2 = 2\text{CH}_3\text{CN}$ ) by reaction with 2 equiv. of **2** in  $\text{CH}_2\text{Cl}_2$  at room temperature. These complexes display the  $\bar{\nu}(\text{N}\equiv\text{C})$  absorption in the range 2200–2230  $\text{cm}^{-1}$  ( $k(\text{N}\equiv\text{C})$  ca. 1830–1890 N/m), with a  $\Delta\bar{\nu} = \bar{\nu}(\text{N}\equiv\text{C})_{\text{coord}} - \bar{\nu}(\text{N}\equiv\text{C})_{\text{free}}$  [17] of ca. 80–110  $\text{cm}^{-1}$ , as expected for isocyanides coordinated to  $\text{Pt}^{2+}$  and  $\text{Pd}^{2+}$  metal ions [17]. As also previously observed, a high positive shift indicates the susceptibility of the isocyanide carbon to nucleophilic attack.

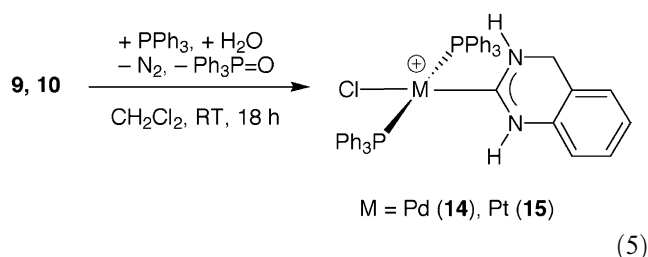
Complexes **9–11** are obtained in high yield from the dichloro metal derivatives  $[\text{MCl}_2(\text{PPh}_3)_2]$  by initial treatment with 1 equiv. of  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$ -acetone and then, after filtration of  $\text{AgCl}$ , with 1 equiv. of the isocyanide. The IR spectra ( $\text{CH}_2\text{Cl}_2$  solution) of **9** and **10** show two strong absorptions around 2205 and 2105  $\text{cm}^{-1}$  corresponding to  $\bar{\nu}(\text{N}\equiv\text{C})$  and  $\bar{\nu}(\text{N}_3)$ , respectively. The high and positive values of  $\Delta\bar{\nu} = \bar{\nu}(\text{N}\equiv\text{C})_{\text{coord}} - \bar{\nu}(\text{N}\equiv\text{C})_{\text{free}}$  of ca. 80  $\text{cm}^{-1}$  observed for **1** and **2** reflect the electrophilicity of the isocyanide carbon, which is therefore a potentially reactive centre nucleophilic attack [17]. The IR spectra (nujol mull) of complexes of the type **11** show a strong absorption around 2180  $\text{cm}^{-1}$  corresponding to  $\bar{\nu}(\text{N}\equiv\text{C})$ , which is shif-

ted to lower wavenumbers of ca.  $10\text{ cm}^{-1}$  with respect to the parent phosphonium-substituted isocyanide complexes *trans*-[PtCl( $\{o\text{-BF}_4^-\text{R}_3\text{P}^+\text{-CH}_2\}$ )C<sub>6</sub>H<sub>4</sub>N≡C)-(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (PR<sub>3</sub> = PPh<sub>3</sub>, PMePh<sub>2</sub>, PMe<sub>2</sub>Ph, PMe<sub>3</sub>) [9b].

Complexes **5** and **6** are converted in MeOH in the presence of a catalytic amount of F<sup>-</sup> ions to the corresponding benzo[1,3]oxazin-2-ylidene derivatives, **12** and **13**, respectively, which are likely formed by intramolecular attack of the in situ generated OH function (due to the presence of F<sup>-</sup> ions) on the electrophilic isocyanide carbon (Eq. 4). The <sup>13</sup>C {<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>) spectra of **12** and **13** display the carbene carbon at 200.9 and 181.3 ppm, respectively, which are typical chemical shift values that of other aminoxy- or diaminocarbene complexes of Pd(II) and Pt(II) [9c,11,18,19].



The cationic complexes **9** and **10** undergo the Staudinger reaction upon treatment with a slight molar excess (ca. 10%) of PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (Eq. 5) to afford the heterocyclic carbene complexes **14** and **15**, respectively [15c].



When the di-isocyanide derivatives **7** and **8** are treated in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with 1 equiv. of PPh<sub>3</sub>, the reactions lead to the selective displacement of one coordinated isocyanide ligand (AziNC) with the quantitative formation of the corresponding substitution complexes *cis*-[MCl<sub>2</sub>(AziNC)(PPh<sub>3</sub>)] (Scheme 4). Further addition in CH<sub>2</sub>Cl<sub>2</sub> at room temperature of 2 equiv. of PPh<sub>3</sub> to these latter compounds leads to the slow formation of the cationic carbene species **14** and **15** [15c].

The X-ray structure of compound **15** is reported in Fig. 1. The carbene complex shows the usual square-planar geometry around platinum (II). The Pt–C(1) bond length of 1.982(9) Å is in good agreement with those reported for other square-planar carbene Pt(II) complexes [9b,18,20], which generally occur in the range 1.82–2.01 Å when an halide is *trans* to the carbene ligand.

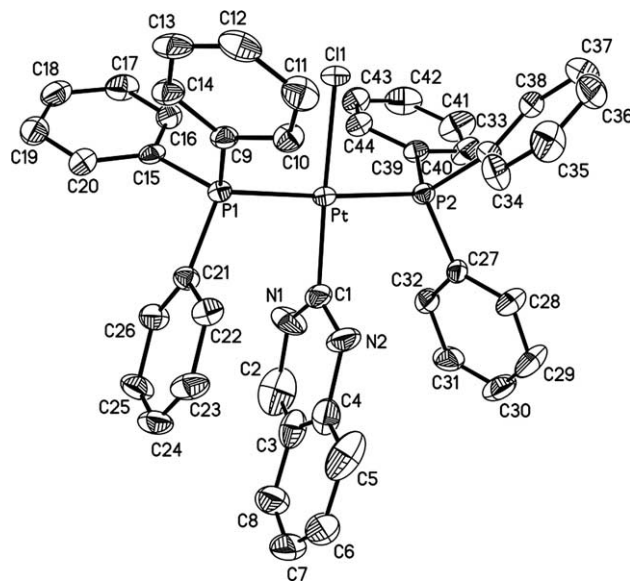
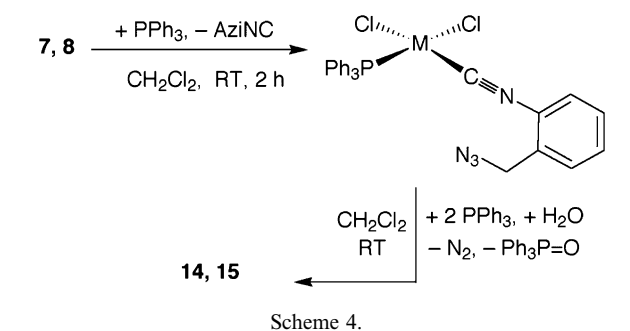
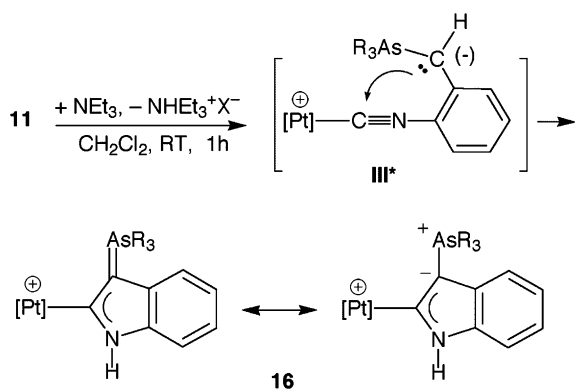


Fig. 1. ORTEP drawing of *trans*-[PtCl( $\overline{\text{CN}(\text{H})\text{C}_6\text{H}_4\text{-2-CH}_2\text{N}(\text{H})}$ )(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation (**15**).

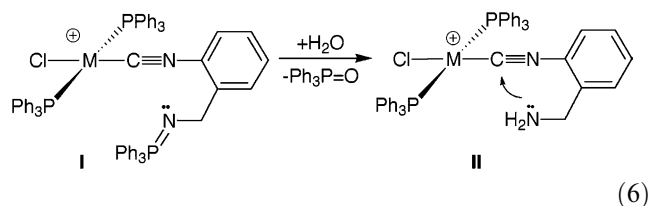
Similarly, the Pt–P bond distances of 2.320(3) and 2.307(3) Å and the Pt–Cl bond length of 2.359(3) Å are within the expected values for these interactions in complexes of similar structure [9b,20a]. The heterocyclic carbene ligand is nearly perpendicular to the co-ordination plane as evidenced by the value of the dihedral angle of 87.9(2)°. The values of C(1)–N(1) and C(1)–N(2) bond lengths of 1.32(2) and 1.30(2) Å, respectively, are short and comparable to those found for the imidazolidin-2-ylidene ligand in the platinum(II) complex *cis*-[PtBr<sub>2</sub>{ $\overline{\text{CN}(\text{C}_6\text{H}_4\text{-}p\text{-Me})\text{CH}_2\text{CH}_2\text{N}(\text{H})}$ }(PPh<sub>3</sub>)] (1.34(1), 1.36(1) Å) [20b] and to the values quoted for other Pt(II)-aminocarbene derivatives (C<sub>carbene</sub>–N bond distances range 1.30–1.37 Å) [18] and suggest extensive  $\pi$ -bonding between the nitrogen atoms and the carbene carbon.

A possible mechanism for the formation of the heterocyclic carbene ligands, **14** and **15**, is described in Eq. (6). The initial step entails the formation of the isocyanide–phosphinimine intermediate **I** by attack of PPh<sub>3</sub> to the N<sub>3</sub> group and liberation of N<sub>2</sub> (Staudinger reaction), followed by hydrolysis of the phosphinimine

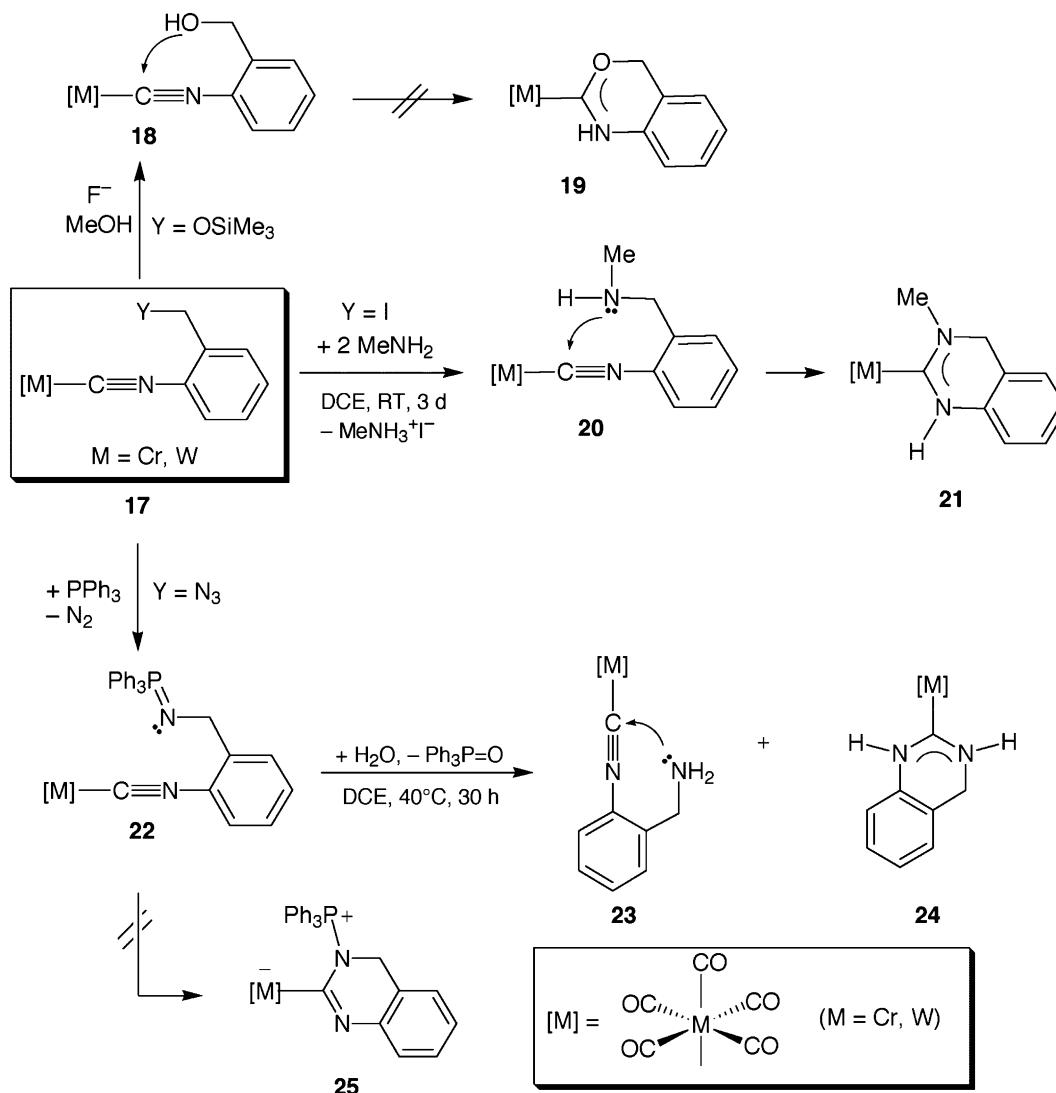


Scheme 5.

leading to the formation of the isocyanide–amine species **II**. This latter then undergoes intramolecular cycloaddition yielding the final heterocyclic carbene product.



Isocyanide **3** coordinates [15b] also to some Au(I) species such as  $[\text{AuCl}(\mathbf{3})]$ , derived from the reaction of  $[\text{AuCl}(\text{Me}_2\text{S})]$  with **3**, and  $[\text{Au}(\mathbf{3})_2][\text{BF}_4]$ , obtained from the reaction of  $[\text{AuCl}(\mathbf{3})]$  with  $\text{AgBF}_4$ , followed by treatment with **3**. Complexes  $[\text{AuCl}(\mathbf{3})]$  and  $[\text{Au}(\mathbf{3})_2][\text{BF}_4]$  do not undergo, however, the Staudinger reaction as previously described for the Pd(II) and Pt(II) complexes, but react with 1 or 2 equiv. of  $\text{PPh}_3$  displacing the isocyanide with the formation of the species  $[\text{AuCl}(\text{PPh}_3)]$  and  $[\text{Au}(\text{PPh}_3)_2][\text{BF}_4]$ , respectively. The reactivity of **3** toward  $\text{PR}_3$  ligands is observed to occur *only* when the



Scheme 6.



isocyanide is ligated to *coordinatively saturated metal complexes* such as those represented by the  $\{M(CO)_5\}$  ( $M = Cr, W$ ) fragments (see Scheme 6) or is bound to *sterically encumbered metal species* such as those given, for instance, by  $\{trans-[MCl(PPh_3)_2]^+\}$  ( $M = Pd, Pt$ ) moieties.

Complexes of the type **11** are found to react [16] with a 5-fold excess of  $NEt_3$  in  $CH_2Cl_2$  at room temperature to afford in good yield the C-2 metal bonded indole derivatives **16** (Scheme 5). As previously reported for the corresponding phosphonium-substituted complexes [9b], the proposed mechanism for their formation entails the initial deprotonation of the methylene group of the  $-CH_2AsR_3^+$  arsonium moiety by  $NEt_3$  to produce the reactive ylide-isocyanide-metal intermediate **III\***, which then intramolecularly adds to the adjacent coordinated isocyanide giving the final 3-(arsonio)indolin-2-ylidene derivatives **16**.

In order to explore the chemical behavior of the isocyanides, **1** and **3**, also in comparison with that shown by other functional isocyanides (see Section 1), we have prepared the carbonyl complexes shown in Scheme 6 [11,15a,15b]. The  $N\equiv C$  IR absorption of  $\{M(CO)_5\}$  ( $M = Cr, W$ ) isocyanide complexes ( $Y = OSiMe_3, OH, N_3$ ) is observed around  $\bar{\nu} = 2134\text{--}2138\text{ cm}^{-1}$  ( $k(N\equiv C) = 1735\text{--}1741\text{ N/m}$ ) with a  $\Delta\bar{\nu}$  of ca.  $10\text{--}15\text{ cm}^{-1}$ , thus reflecting a much lower electrophilicity of the carbene carbon compared to the Pt(II) and Pd(II) complexes previously described. Upon treatment with  $F^-$  ions in MeOH compounds **17** ( $Y = OSiMe_3$ ) are converted to the corresponding derivatives **18**, having the coordinated 2-(hydroxymethyl)phenyl isocyanide ligand, which show no tendency to the formation of the ylidene compounds **19**. On the other hand, the corresponding reaction of **17** ( $M = W; Y = I$ ) with 5 equiv. of  $MeNH_2$  in 1,2-dichloroethane for three days at room temperature gave, after work-up of the reaction mixture, a pale yellow product whose spectroscopic data are in agreement with the carbene structure of complex **21** derived by an intramolecular attack of the intermediate methylamino group **20**, formed by the reaction of the iodomethyl moiety of **17** with  $MeNH_2$ , on the metal-coordinated isocyanide.

Complexes **17** ( $Y = N_3$ ) undergo the Staudinger reaction with  $PPh_3$  affording the phosphinimine-isocyanide derivatives **22**, which react with  $H_2O$  affording a mixture of the aminoisocyanide **23** and the carbene complexes **24**. There is, however, no spectroscopic evidence that complexes **22** undergo intramolecular nucleophilic attack by the phosphinimine nitrogen to the isocyanide carbon as reported for other phosphinimine-isocyanide metal species [2].

The whole of these data indicate that this type of functional isocyanides exhibit good coordinating properties towards low oxidation state metal species of the type  $\{M(CO)_5\}$  ( $M = Cr, W$ ) as well as towards medium

oxidation state metal complexes of Pd(II) and Pt(II). It is generally observed that these latter are much more reactive in promoting the intramolecular nucleophilic attack of the functional group to the coordinated isocyanide carbon affording stable heterocyclic carbene derivatives. We are currently investigating such reactions with different metal centres in order to assess how the electron density of the metal may influence the coordination and the intramolecular rearrangements of this type of functional isocyanides.

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