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The Staudinger reaction of platinum(II)- and palladium(II)-coordinated 2-(azidomethyl)phenyl isocyanide. X-ray structure of *trans*-[PtCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}$}$(PPh_3)_2$][$BF_4$] · $CDCl_3$ · H_2O

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Abstract

2-(Azidomethyl)phenyl isocyanide, 2-$(CH_2N_3)C_6H_4N{\equiv}C$ (AziNC), coordinates to some cationic Pt(II) and Pd(II) species to afford isocyanide complexes of the type *trans*-[MCl(AziNC)$(PPh_3)_2$][BF_4] (M = Pt, **l**; Pd, **2**). AziNC is coordinated also in some neutral Pt(II) and Pd(II) species such as [MCl_2(AziNC)$_2$] (M = Pt, **3**; Pd, **4**) derived from the reactions of 2 equiv. of AziNC with [$PtCl_2$(COD)] and [$PdCl_2$($MeCN)_2$], respectively. Complexes **1** and **2** react with 1 equiv. of PPh_3 affording the heterocyclic carbene complexes *trans*-[MCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}$}$(PPh_3)_2$][$BF_4$] (M = Pt, **5**; Pd, **6**). Complexes **3** and **4** react with 1 equiv. of PPh_3 displacing the isocyanide with the formation of the complexes *cis*-[MCl_2(AziNC)(PPh_3)] (M = Pt, **7**; Pd, **8**). These latter ones react with 2 equiv. of PPh_3 affording as the final products the cationic carbene species *trans*-[MCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}$}$(PPh_3)_2$][Cl] (M = Pt, **9**; Pd, **10**). Complex **5** was also characterized by single crystal X-ray diffraction. The carbene complex is square-planar and the angle formed between the platinum square plane and the heterocyclic carbene ligand is 87.9(2)°. The C(1)–N(1) and C(1)–N(2) bond distances in the latter of 1.32(2) and 1.30(2) Å, respectively, are short for a single bond and indicate extensive π-bonding between the nitrogen atoms and the carbene carbon.

Keywords: Functionalized isocyanides; Transition metal complexes; N-heterocyclic carbene complexes

1. Introduction

The chemistry of transition metal-coordinated functional isocyanides, which are ligands that bear in the hydrocarbon chain a nucleophile or a suitable precursor of a nucleophilic center, has received a great interest in the last years both from synthetic and reactivity points of view [1–3]. Specific examples are, for instance: (i) the hydroxyalkyl isocyanides HO–$(CH_2)_n$–N≡C [4], the trichloromethyl isocyanide, CCl_3–N≡C [1,5] in the presence of amines or thiols, the hydrogen isocyanide, H–N≡C [3] in the presence of oxiranes or aziridines, and the α-metalated isocyanides $Y-\overset{(-)}{C}H-N{\equiv}C$ (Y = CO_2Et, SO_2R (R = *p*-tolyl), $\overset{+}{P}Ph_3$) [6] reported by Fehlhammer and coworkers; (ii) the β-functional phenyl isocyanides such as 2-hydroxyphenyl isocyanide, 2-$(HO)C_6H_4$–N≡C, and 2,6-dihydroxyphenyl isocyanide, 2,6-$(HO)_2C_6H_4$–N≡C, and their derivatives, described by Harm and coworkers [2] and (iii) γ-functional isocyanides of the type 2-$(CH_2Y)C_6H_4$–N≡C (Y = Cl, I [1,7]; $CpM(CO)_3$ (M = Cr, W) [8]; $\overset{+}{P}R_3$ [1,9], $OSiMe_3$, OH

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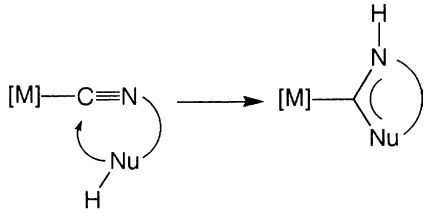
[10]; N_3 [11]) reported by some of us. The organometallic chemistry of these ligands has been addressed in many cases [1,2] to the formation of N-heterocyclic carbenes (NHC) through an intramolecular 1,2-addition of the functional moiety, usually a protic nucleophile such as an hydroxy, an amino or an ylide group, across the C≡N triple bond (Eq. (1)).



(1)

NuH = OH, NHR, $\bar{C}H-\overset{+}{P}R_3$

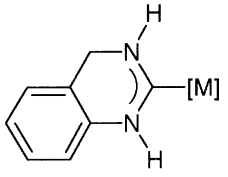
It must be noted that metal-NHC complexes [12] have been receiving increased attention in the literature since the aminocarbene ligands were found to be promising alternative ligands to the commonly used phosphines and phosphites and also for their favorable application in homogeneous catalysis [12a,12f]. 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.

We wish to report herein the synthesis and characterization of a novel type of NHC ligand, i.e. the quinazolin-2-ylidene shown in Chart 1 coordinated to a metal center, which is the result of the reactivity of the functional isocyanide 2-(azidomethyl)phenyl isocyanide (hereafter AziNC) [11] toward PPh_3 – the so called *Staudinger reaction* [13] – as it will be described in detail in the following.

2. Experimental

2.1. General procedures and materials

All work was carried out with the exclusion of atmospheric oxygen under a dinitrogen atmosphere using standard Schlenck techniques. Solvents were distilled under dinitrogen prior to use; CH_2Cl_2 was distilled from CaH_2 or used as received (Baker analyzed reagent) for the Staudinger reaction, diethyl ether and THF were distilled from sodium benzophenone. IR spectra were taken on an FT-IR AVATAR 320 (4000–400 cm^{-1}) or an FT-IR Nexus (range 600–50 cm^{-1}) of the Nicolet



M = Pt(II), Pd(II)

Chart 1.

Instrument Corporation (CH_2Cl_2 solution, KBr or polyethylene (PE)) spectrophotometers; the wavenumbers ($\tilde{\nu}$) are given in cm^{-1}. ^1H, ^{31}P $\{^1H\}$ and ^{13}C $\{^1H\}$ NMR spectra were run at 298 K, unless otherwise stated, on a Bruker 200 AC spectrometer operating at 200.13, 81.015 and 50.32 MHz, respectively; δ values in ppm are relative to $SiMe_4$ (^1H and ^{13}C) and H_3PO_4 85% (^{31}P). The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The compounds 2-(azidomethyl)phenyl isocyanide (AziNC), 2-$(CH_2N_3)C_6H_4NC$, *cis*-$[PtCl_2(AziNC)_2]$ (**3**) and *cis*-$[PdCl_2(AziNC)(PPh_3)]$ were synthesized as previously reported [11a]. The complexes $[PdCl_2(MeCN)_2]$ [9b], $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ [9b], $[MCl_2(PPh_3)]_2$ (M = Pt [14], Pd [15]) and $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) [16] were prepared according to literature procedures.

2.2. Synthesis of the complexes

2.2.1. Synthesis of trans-[PtCl(AziNC)(PPh$_3$)$_2$][BF$_4$] (*1*)

To a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.65 g, 0.82 mmol) in CH_2Cl_2 (50 ml) at room temperature was added a 1.0 M acetone solution of $AgBF_4$ (0.85 ml, 0.85 mmol). The reaction mixture was stirred for 30 min and then the solid AgCl formed was filtered off. The solution was treated with AziNC (0.14 g, 0.88 mmol). The green solution was stirred for 2.5 h. An IR spectrum showed the C≡N absorption of the coordinated isocyanide at 2201 cm^{-1}. The solution was taken to dryness to give a green solid. This latter was taken up with CH_2Cl_2 (30 ml), filtered through celite and to the resulting solution Et_2O was added to give a pale yellow solid which was filtered off and dried under vacuum. Yield 0.41 g, 52.6%. Anal. Calc. for $C_{44}H_{36}BC1F_4N_4P_2Pt \cdot 1/2\ CH_2Cl_2$: C, 51.80; H, 3.61; N, 5.43. Found: C, 52.06; H, 3.69; N, 5.29%. IR ($\tilde{\nu}$, CH_2Cl_2): 2201 (s, N≡C); *k*(N≡C) 1846 N/m (from CH_2Cl_2 data); 2104 (s, N_3); 345 (m, PtCl, PE film). ^1H NMR (δ, $CDCl_3$): 7.74–7.45 (C_6H_4, m); 3.39 (CH_2, s). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 18.80 (PPh_3, $^1J_{Pt-P} = 2183$ Hz, s).

2.2.2. Synthesis of trans-[PdCl(AziNC)(PPh$_3$)$_2$][BF$_4$] (*2*)

To a suspension of $[PdCl_2(PPh_3)_2]$ (0.42 g, 0.60 mmol) in CH_2Cl_2 (50 ml) at room temperature was added a 1.0 M acetone solution of $AgBF_4$ (0.65 ml, 0.65 mmol). The reaction mixture was stirred for 30 min and then the solid AgCl formed was filtered off. The solution was thermostated at −10 °C using a $CHCl_3$/liquid N_2 bath and then was treated with AziNC (0.10 g, 0.634 mmol). The green solution was stirred for 35 min. An IR spectrum showed the disappearance of the C≡N absorption of the free isocynaide and the simultaneous formation of a band at 2204 cm^{-1}. The solution was

treated with Et_2O (2×20 ml).The white solid was filtered off and dried under vaccum. Yield 0.46 g, 94.3%. Anal. Calc. for $C_{44}H_{36}BClF_4N_4P_2Pd \cdot CH_2Cl_2$: C, 54.25; H, 3.84; N, 5.62. Found: C, 54.57; H, 3.63; N, 5.52%. IR ($\tilde{\nu}$, CH_2Cl_2): 2204 (s, N≡C); k(N≡C) 1851 N/m (from CH_2Cl_2 data); 2105 (s, N_3); 350 (m, PdCl, PE film). ^{1}H NMR (δ, $CDCl_3$): 7.79–7.47 (C_6H_4, m); 3.38 (CH_2, s). ^{31}P {^{1}H} NMR (6, $CDCl_3$): 24.07 (PPh_3, s).

2.2.3. Synthesis of cis-[$PdCl_2$(AziNC)$_2$] (4)

Complex *cis*-[$PtCl_2$(AziNC)$_2$] (**3**) was prepared as previously reported [11a]. Complex **4** was prepared according to the following procedure. To a suspension of [$PdCl_2(MeCN)_2$] (0.88 g, 3.40 mmol) in Et_2O (70 ml) was added AziNC (1.13 g, 7.15 mmol) and the reaction mixture was stirred for 2h. Then the solid was filtered off and washed with Et_2O (3×5 ml) and dried under vacuum. Yield 1.41 g, 80.0%. Anal. Calc. for $C_{16}H_{12}Cl_2N_8Pd$: C, 38.90; H, 2.43; N, 22.70. Found: C, 38.49; H, 2.23; N, 22.18%. IR ($\tilde{\nu}$, CH_2Cl_2): 2230, 2213 (s, N≡C); k(N≡C) 1895, 1866 N/m (from CH_2Cl_2 data); 2105 (s, N_3); 350, 339 (m, PdCl, PE film). ^{1}H NMR (δ, $CDC1_3$): 7.67–7.44 (C_6H_4, m); 4.67 (CH_2, s). ^{13}C {^{1}H} NMR (δ, $CDCl_3$): 132.8–126.5 (C_6H_4, m); 51.4 (CH_2, s).

2.3. Reactivity of the AziNC complexes with PPh_3

2.3.1. Reaction of 1 with PPh_3. Synthesis of trans-[PtCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N}$(H)}($PPh_3$)$_2$][$BF_4$] (5)

To a solution of **1** (0.30 g, 0.30 mmol) in CH_2Cl_2 (30 ml) was added PPh_3 (0.09 g, 0.34 mmol). The pale green solution turns immediately to yellow. An IR spectrum showed the disappearance of the C≡N and the N_3 absorptions at 2201 and 2104 cm^{-1}, respectively, of the coordinated isocyanide. The solution was stirred at room temperature for 48 h and then was treated with Et_2O (20 ml). The pale green solid was filtered off, washed with Et_2O (3×30 ml) and dried under vacuum. Yield 0.20 g, 66.7%. Anal. Calc. for $C_{44}H_{38}BClF_4\ N_2P_2Pt \cdot 1/2Et_2O$: C, 55.23; H, 3.83; N, 2.80. Found: C, 55.25; H, 3.83; N, 2.48%. IR ($\tilde{\nu}$, CH_2C1_2): 3429, 3314 (s, NH). ^{1}H NMR (δ, $CDC1_3$): 8.45 (NH, s); 7.86–6.38 (C_6H_4, m); 3.37 (CH_2, s). ^{31}P {^{1}H} NMR (δ, $CDC1_3$): 19.18 (PPh_3, $^1J_{Pt-P} = 2615$ Hz, s). ESI-MS: m/z 887.2 ([M-BF_4]$^+$; 851.1 ([887.2-Cl]$^+$; 589.2 ([851.1-PPh_3]$^+$.

2.3.2. Reaction of 2 with PPh_3. Synthesis of trans-[PdCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N}$(H)}($PPh_3$)$_2$][$BF_4$] (6)

To a solution of **2** (0.30 g, 0.33 mmol) in CH_2Cl_2 (30 ml) was added solid PPh_3 (0.10 g, 0.38 mmol). The yellow solution turned immediately to orange. An IR spectrum showed the disappearance of the C≡N and the N_3 absorptions at 2204 cm^{-1} and at 2104 cm^{-1}, respectively, of the isocyanide. The solution was stirred at room temperature for 12 h and then was treated with Et_2O (40 ml). The yellow solid was filtered off, washed with Et_2O (2×10 ml) and dried under vacuum. Yield 0.26 g, 87.9%. Anal. Calc. for $C_{44}H_{38}BClF_4N_2P_2Pd$: C, 59.70; H, 4.33; N, 3.16. Found: C, 59.45; H, 4.32; N, 3.08%. IR ($\tilde{\nu}$, CH_2Cl_2): 3417, 3311 (s, NH). ^{1}H NMR (δ, $CDC1_3$): 8.73 (NH, s); 7.82–6.38 (C_6H_4, m); 3.38 (CH_2, s). ^{31}P {^{1}H} NMR (δ, $CDCl_3$): 21.21 (PPh_3, s).

2.3.3. Reaction of 3 with PPh_3. Synthesis of cis-[$PtCl_2$(AziNC)(PPh_3)] (7)

To a solution of **3** (0.40 g, 0.69 mmol) in CH_2Cl_2 (25 ml) was added PPh_3 (0.19 g, 0.72 mmol). The solution was stirred at room temperature for 1 h and then treated with Et_2O (20 ml) and *n*-hexane (20 ml). The yellow solid that formed was filtered off, washed with Et_2O (2×20 ml) and dried under vacuum. Yield 0.46 g, 97.0%. Anal. Calc. for $C_{26}H_{21}Cl_2N_4PPt$: C, 45.50; H, 3.08; N, 8.16. Found: C, 45.88; H, 3.35; N, 8.51%. IR ($\tilde{\nu}$, CH_2Cl_2): 2199 (s, N≡C); k(N≡C) 1842 N/m (from CH_2C1_2 data); 2104 (s, N_3); 300, 350 (m, PtCl, PE film). ^{1}H NMR (δ, $CDC1_3$): 7.81–6.58 (C_6H_4, m); 4.37 (CH_2, s). ^{31}P {^{1}H} NMR (δ, $CDC1_3$): 9.16 (PPh_3, $^1J_{Pt-P}$ 3351, s).

2.3.4. Reaction of 4 with PPh_3. Synthesis of cis-[$PdCl_2$(AziNC)(PPh_3)] (8)

To a solution of **4** (0.40 g, 0.81 mmol) in CH_2Cl_2 (25 ml) was added PPh_3 (0.22 g, 0.84 mmol). The solution was stirred at room temperature for 12 h and then treated with Et_2O (20 ml) and *n*-hexane (20 ml). The yellow solid that formed was filtered off, washed with Et_2O (3×10 ml) and dried under vacuum. Yield 0.46 g, 95.0%. Anal. Calc. for $C_{26}H_{21}Cl_2N_4PPd$: C, 52.24; H, 3.54; N, 9.73. Found: C, 51.80; H, 3.00; N, 9.57%. IR ($\tilde{\nu}$, CH_2Cl_2): 2206 (s, N≡C); k(N≡C) 1854 N/m (from CH_2Cl_2 data); 2104 (s, N_3); 339, 297 (m, PdCl, PE film). ^{1}H NMR (δ, $CDCl_3$): 7.83–6.64 (C_6H_4, m); 4.40 (CH_2, s). ^{31}P {^{1}H} NMR (δ, $CDCl_3$): 28.4 (PPh_3, s). The spectroscopic data of complex **8** are identical to that previously synthesized by a different route [11].

2.3.5. Reaction of 7 with PPh_3. Synthesis of trans-[PtCl{$\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N}$(H)}($PPh_3$)$_2$][Cl] (9)

To a yellow solution of **7** (0.29 g, 0.42 mmol) in CH_2Cl_2 (25 ml) was added PPh_3 (0.12 g, 0.47 mmol). An IR spectrum showed the reduction of the C≡N absorption at 2199 cm^{-1} and of the N_3 absorption at 2104 cm^{-1} of the isocyanide, which were still present after stirring at room temperature for 24 h. The addition of a further equiv. of PPh_3 (0.12 g, 0.47 mmol) and stirring for an additional 24 h afforded the complete disappearance of the C≡N and N_3 bands of the isocyanide.

The solution was then treated with Et_2O (30 ml) to give a cream solid, which was filtered off, washed with Et_2O (3×10 ml) and dried under vacuum. Yield 0.20 g, 52.4%. Anal. Calc. for $C_{44}H_{38}Cl_2N_2P_2Pt \cdot 1/2CH_2Cl_2$: C, 55.38; H, 4.07; N, 2.90. Found: C, 55.60; H, 3.71; N, 3.36%. IR ($\tilde{\nu}$, cm^{-1}): 3420 (w, NH, KBr), 309 (w, PtCl, PE film). ^1H NMR (δ, $CDCl_3$): 9.71, 9.13 (NH, s); 7.96–6.37 (C_6H_4, m); 3.31 (CH_2, s). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 19.17 (PPh_3, $^1J_{Pt-P}$ 2692, s).

2.3.6. Reaction of **8** with PPh_3. Synthesis of trans-[PdCl{$\overset{\frown}{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}$}$(PPh_3)_2$][Cl] (**10**)

To a yellow solution of **8** (0.20 g, 0.33 mmol) in CH_2Cl_2 (15 ml) was added PPh_3 (0.19 g, 0.74 mmol). After 30 min, an IR spectrum showed the reduction of the C≡N absorption at 2205 cm^{-1} and of the N_3 absorption at 2104 cm^{-1} of the isocyanide. The reaction mixture was stirred at room temperature for 24 h. After this time an IR spectrum showed the complete disappearance of the C≡N and N_3 bands of the coordinated isocyanide. The solution was then treated with Et_2O (30 ml) to give a cream solid, which was filtered off, washed with Et_2O (3×10 ml) and dried under vacuum. Yield 0.19 g, 71.0%. Anal. Calc. for $C_{44}H_{38}Cl_2N_2P_2]Pd \cdot 1/2CH_2Cl_2$: C, 60.98; H, 4.48; N, 3.20. Found: C, 62.20; H, 4.14; N, 2.84%. IR ($\tilde{\nu}$, cm^{-1}): 3457 (w, NH, KBr), 1525 (s, C=N, KBr), 318 (w, PdCl, PE film). ^1H NMR (δ, $CDCl_3$): not safely assigned (NH, s); 7.92–6.43 (C_6H_4, m); 3.40 (CH_2, s). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 21.2 (PPh_3,s).

2.4. X-ray measurements and structure determination of **5**

Single crystals suitable for X-ray analysis were obtained by slow precipitation from a $CDCl_3$, solution in a NMR tube. The intensities data of $5 \cdot CDCl_3 \cdot H_2O$ were collected at room temperature using a Philips PW1100 single-crystal diffractometer (FEBO system) using a graphite-monochromated (Mo–Kα) radiation, following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz polarization and absorption [17]. The structure was solved by heavy atom method [18]. Refinement was carried out by full-matrix least-squares procedures (based on F_0^2) using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2\boldsymbol{U}_{equiv}$ of the parent carbon atom). The calculations were performed with the SHELXL-97 program [19], implemented in the WinGX package [20], drawings were produced using ORTEP3 [21]. Crystallographic and experimental details of the structure are summarized in Table 1, while Table 2 reports selected bond lengths and angles.

Table 1
Crystallographic data of compound **5**

Compound	$5 \cdot CDCl_3 \cdot H_2O$
Chemical formula	$C_{45}H_{41}BCl_4F_4N_2OP_2Pt$
Formula weight	1111.48
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.596(3)
b/Å	10.931(3)
c/Å	33.395(5)
β/°	93.39(3)
V/Å^3	4590(2)
Z	4
D_{calc}/g cm^{-3}	1.608
$F(000)$	2200
μ(Mo–Kα)/mm^{-1}	3.41
Reflections collected	8626
Reflections observed [$I \geqslant 2\sigma(I)$]	7958
Final $R1, wR2$	0.059, 0.134

$R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR2 = [\sum [w(F_0^2 - F_c^2)^2] / \sum w(F_0^2)^2]^{1/2}$.

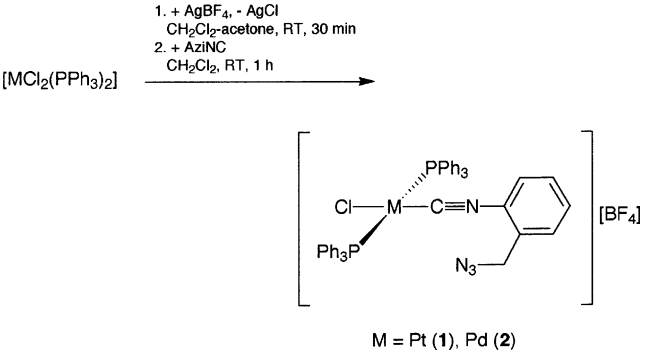
Table 2
Selected bond distances (Å) and angles (°) for compound **5**

Pt–Cl(1)	2.359(3)	Pt–P(1)	2.320(3)
Pt–P(2)	2.307(3)	Pt–C(1)	1.982(9)
P1–C(15)	1.820(9)	P1–C(9)	1.803(8)
P1–C(21)	1.816(9)	P2–C(27)	1.812(9)
P2–C(33)	1.819(9)	P2–C(39)	1.830(9)
N1–C(1)	1.32(2)	N2–C(1)	1.30(2)
N1–C(2)	1.57(2)	N2–C(4)	1.56(2)
Cl(1)–Pt–P(1)	89.5(1)	Cl(1)–Pt–P(2)	86.7(1)
Cl(1)–Pt–C(1)	177.9(4)	P(1)–Pt–P(2)	176.2(1)
P(1)–Pt–C(37)	91.7(3)	P(2)–Pt–C(1)	92.1(3)
Pt–C(1)–N(1)	120.7(8)	Pt–C(1)–N(2)	122.1(9)
N(1)–C(1)–N(2)	117.1(9)		

3. Results and discussion

3.1. Synthesis of Pt(II)- and Pd(II)-AziNC complexes

The reactions sequence leading to the synthesis of some cationic Pt(II)- and Pd(II)-AziNC complexes of the type *trans*-[MCl(AziNC)$(PPh_3)_2$][BF_4] (M = Pt, **1**; Pd, **2**) is reported in Eq. (2).

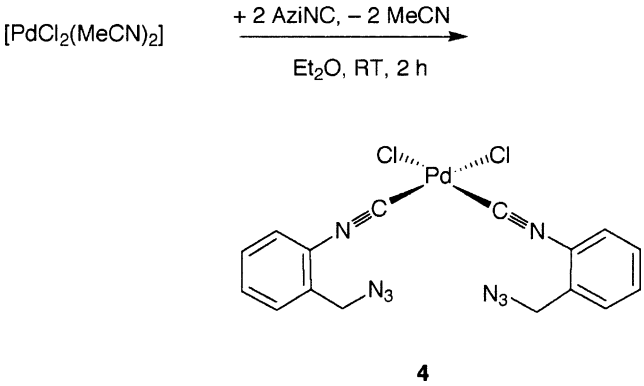


(2)

Complexes **1** and **2** are obtained in high yield from the dichloro metal derivatives $[MCl_2(PPh_3)_2]$ by initial treatment with 1 equiv. of $AgBF_4$ in CH_2Cl_2–acetone and then, after filtration of AgCl, with 1 equiv. of AziNC. They are white air-stable solids which have been characterized by elemental analysis, IR, ^1H and $^{31}P\{^1H\}$ NMR (Section 2). The IR spectra (CH_2Cl_2 solution) show two strong absorptions around 2205 and 2105 cm^{-1} corresponding to $\tilde{\nu}(N{\equiv}C)$ and $\tilde{\nu}(N_3)$, respectively. The high and positive values of $\Delta\tilde{\nu} = \tilde{\nu}(N{\equiv}C)_{coord} - \tilde{\nu}(N{\equiv}C)_{free}$ of $\approx$80 cm^{-1} observed for **1** and **2** reflect the electrophilicity of the isocyanide carbon, which is therefore a potentially reactive center toward nucleophilic attack [22]. The IR spectra (polyethylene film) of **1** and **2** show also the M–Cl stretching at $\approx$350 cm^{-1} as a medium intensity band.

The ^1H NMR spectra of **1** and **2** show the $-CH_2-$ resonance at $\approx$3.40 ppm as a singlet. In the $^{31}P\{^1H\}$ NMR spectrum of **1** the PPh_3 ligands give rise to a singlet at 18.8 ppm flanked by ^{195}Pt satellites ($^1J_{PPt}$ 2183 Hz), while the resonance of the phosphine ligands of **2** is observed at 24.0 ppm. The presence of a singlet in the $^{31}P\{^1H\}$ NMR spectra supports the *trans* geometry of both complexes.

Coordination of AziNC to neutral Pt(II) and Pd(II) species has been also examined. While the synthesis of *cis*-$[PtCl_2(AziNC)_2]$ (**3**) was recently reported, the analogous Pd-complex *cis*-$[PdCl_2(AziNC)_2]$ (**4**) was prepared as illustrated in Eq. (3) starting from $[PdCl_2(MeCN)_2]$ and 2 equiv. of AziNC.

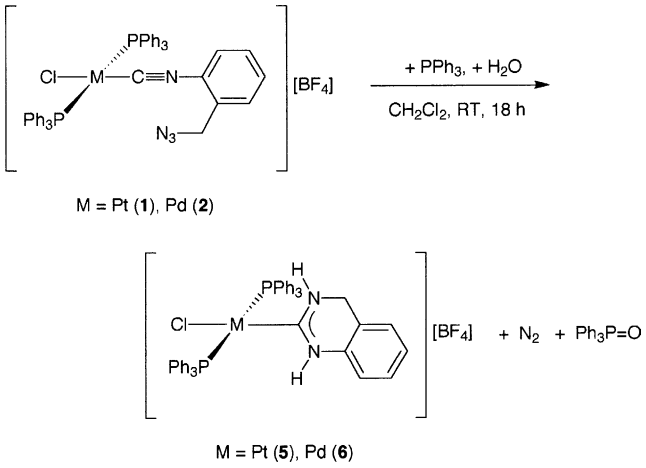


4 (3)

Complex **4** has been characterized by elemental analysis, IR, ^1H and $^{13}C\{^1H\}$ NMR (Section 2). In particular, the IR spectra (CH_2Cl_2 solution) show two strong absorptions at 2230 and 2213 cm^{-1} due to the isocyanide stretching and another strong band at 2105 cm^{-1} corresponding $\tilde{\nu}(N_3)$. For this complex the observed $\Delta\tilde{\nu}$ is $\approx$90–110 cm^{-1}, thus confirming the high electrophilicity of the isocyanide carbon atom.

3.2. Reactivity of cationic AziNC complexes of the type *trans*-[MCl(AziNC)(PPh$_3$)$_2$][BF$_4$]

The reactions of the cationic complexes *trans*-$[MCl(AziNC)(PPh_3)_2][BF_4]$ (M = Pt, **1**; Pd, **2**) with 1 equiv. of PPh_3 in a slight molar excess ($\approx$10%) were carried out in CH_2Cl_2 at room temperature (Eq. (4)).



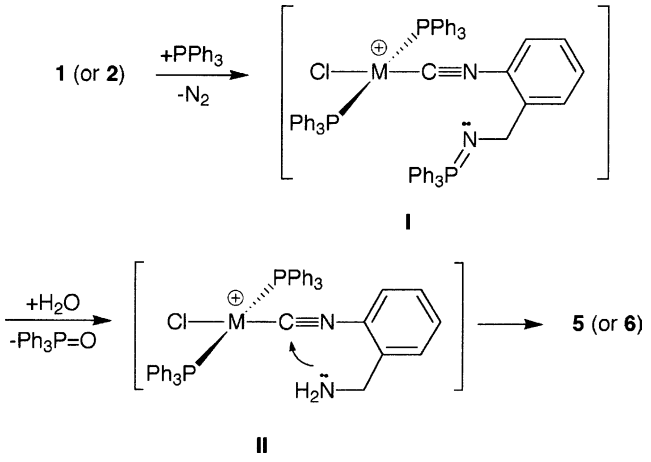
(4)

They have been followed by IR spectroscopy by monitoring the disappearance of the bands at $\approx$2200 and 2100 cm^{-1} due to the coordinated isocyanide and the azido groups. After 48 h (M = Pt) and 18 h (M = Pd) such absorptions were no more detected and the compounds **5** and **6** could be isolated as crystalline solids in high yield. They were characterized by elemental analysis, ESI-MS, IR, ^1H and $^{31}P\{^1H\}$ NMR (Section 2). Complex **5** was also characterized by an X-ray diffraction analysis (see further). The ^1H NMR spectra for **5** and **6** show the $-CH_2-$ resonance at 3.35 and 3.38 ppm and a signal at 8.36 and 8.73 ppm due to one N–H group of the heterocyclic carbene, respectively. In the $^{31}P\{^1H\}$ NMR spectra of **5** and **6** the resonance of the phosphine ligands is a singlet (flanked by ^{195}Pt satellites in the case of **5**) confirming the *trans* geometry of the complexes.

A possible mechanism for the formation of the heterocyclic carbene ligands in **5** and **6** is described in Scheme 1.

The initial step entails the formation of the isocyanide-phosphinimine intermediate **I** by attack of PPh_3 to the N_3 group and liberation of N_2 (*Staudinger reaction*), followed by hydrolysis of the phosphinimine leading to the formation of the isocyanide-amine species **II**. This latter then undergoes intramolecular cycloaddition yielding the final heterocyclic carbene product.

An alternative mechanism (Scheme 2) involves initial intramolecular attack of the phosphinimine nitrogen of intermediate **I** (which is now shown in the ylidic presentation in order to highlight the nucleophilicity of the nitrogen atom) to the isocyanide carbon to give **III**, which is then hydrolyzed to the final products.



Scheme 1.

In order to shed light on the reaction mechanisms reported in Schemes 1 and 2, we followed the reaction of complex **1** with 1 equiv. of PPh_3 by monitoring the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture in $CDC1_3$ (previously treated with dry K_2CO_3) at room and at low (253 K) temperature. In both experiments, the spectra show the presence of signals due to the starting complex **1** (18.8 ppm, $^1J_{PPt}$ 2183 Hz), the final product **5** (19.1 ppm, $^1J_{PPt}$ 2615 Hz), free PPh_3 (−5.0) and phosphine oxide, $Ph_3P{=}O$ (29.5 ppm). Other signals of low intensity were observed at 14.1 and 10.4 ppm. The former can be attributed to the phosphinimine intermediate **I** (Scheme 1) by comparison with the values reported for other isolated transition metal phosphinimine derivatives of the type $[M(CO)_5\{C{\equiv}NC_6H_4\text{-}2\text{-}(CH_2N{=}PPh_3)\}]$ (M = W, Cr), which appear in the range 14.6–14.9 ppm [11b]; however, the latter resonance could not be safely assigned, although it indicates the presence of another P-containing intermediate (perhaps the cyclic phosphinimino complex **III** of Scheme 2). Intramolecular attack of phosphinimines on coordinated carbonyl [23] and isocyanide ligands [2] have been already documented. There is no evidence of the presence of the intermediate **II**, which however is expected to be very reactive toward intramolecular cyclization [1,10] and, as a consequence, not easily detectable.

3.3. Description of the structure of *trans*-$[PtCl\{\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}\}(PPh_3)_2]^+$ $[BF_4]^-$ (5)

The asymmetric unit is composed of *trans*-$[PtCl\{\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}\}(PPh_3)_2]^+$ cations (Fig. 1), $[BF_4]^-$ anions and solvent molecules ($CDCl_3$, H_2O) of crystallization.

The carbene complex shows the usual square-planar geometry around platinum(II) with maximum deviation from the C(1), Cl(1), P(1) and P(2) plane of −0.015 Å. However, the P(1)–Pt–P(2) (176.2(1)°) and the Cl(1)–Pt–C(1) (177.9(3)°) angles deviate from linearity thus indicating the presence of a slight distortion of the Pt atom stereogeometry likely arising from the steric

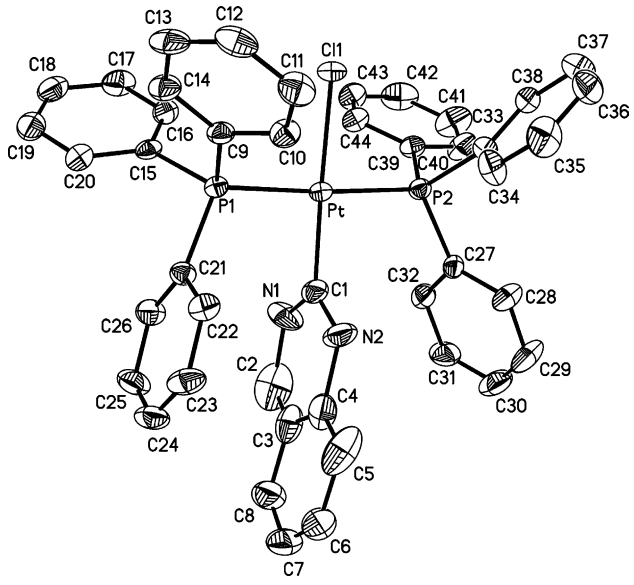
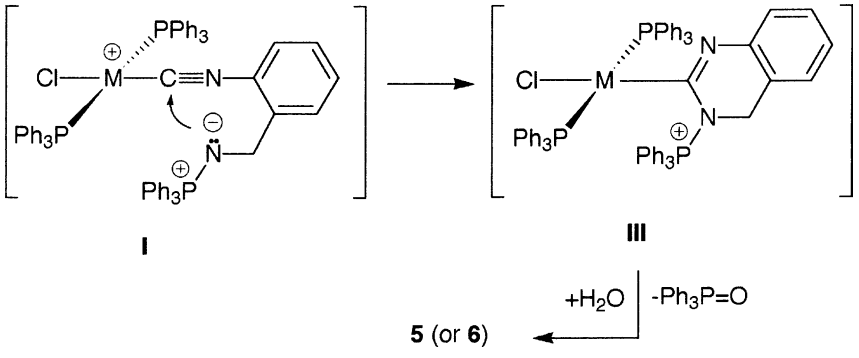


Fig. 1. ORTEP drawing of *trans*-$[PtCl\{\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N(H)}\}(PPh_3)_2]^+$ cation (**5**).



Scheme 2.

interaction between the carbene ligand and the two bulky ancillary PPh_3 ligands. The Pt–C(l) bond length of 1.982(9) Å is in good agreement with those reported for other square-planar carbene Pt(II) complexes [9b,15,24, 25], which generally occur in the range 1.82–2.01 Å when an halide is *trans* to the carbene ligand. 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,15]. 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*-$[PtBr_2\{\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2N}(H)\}(PPh_3)]$ (1.34(1), 1.36(1) Å) [24] and to the values quoted for other Pt(II)-aminocarbene derivatives ($C_{carbene}$–N bond distances range 1.30–1.37 Å) [25] and suggest extensive π-bonding between the nitrogen atoms and the carbene carbon.

3.3.1. Reactivity of neutral AziNC complexes of the type *cis*-$[MCl_2(AziNC)_2]$

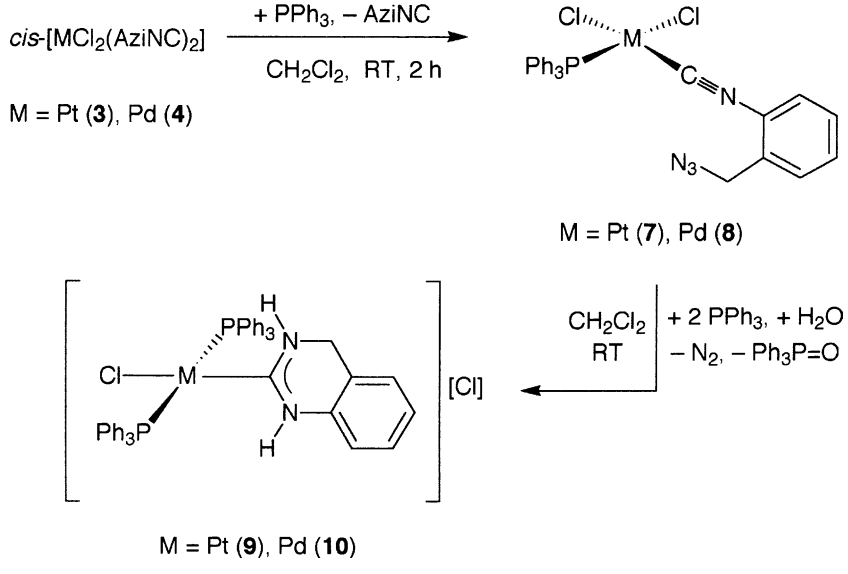
The reactions of the complexes *cis*-$[MCl_2(AziNC)_2]$ (M = Pt, **3**; Pd, **4**) with PPh_3 are reported in Scheme 3.

When the di-isocyanide derivatives **3** and **4** are treated in CH_2Cl_2 at room temperature with 1 equiv. of PPh_3, the reactions lead to the selective displacement of one coordinated isocyanide ligand with the quantitative formation of the corresponding substitution complexes *cis*-$[MCl_2(AziNC)(PPh_3)]$ (M = Pt, **7**; Pd, **8**). Complexes **7** and **8** were characterized by elemental analysis and their IR, ^1H and ^{31}P NMR spectra (see Section 2). On the other hand, addition at room temperature of 2 equiv. of PPh_3 to **7** and **8** in CH_2Cl_2 leads to the slow formation of the cationic carbene species $[MCl\{\overline{CN(H)C_6H_4\text{-}2\text{-}CH_2N}(H)\}(PPh_3)_2]^+[Cl]^-$ (M = Pt, **9**; Pd, **10**) in fair to good yield. Their structure was established by comparison of the IR, ^1H and $^{31}P\{^1H\}$ NMR data with those of the parent complexes **5** and **6** having BF_4^- as the counter ion.

4. Concluding remarks

In this study we have described the Staudinger reaction of some Pt(II)- and Pd(II)-coordinated 2-(azidomethyl)phenyl isocyanide (AziNC) complexes leading to a new type of N-heterocyclic carbene i.e. the quinazolin-2-ylidene ligand. The formation of this species has been suggested to occur as a consequence of an initial nucleophilic attack of PPh_3 to the azido group of the isocyanide to give a phosphinimine intermediate, followed by its rearrangement to the NHC ligand as proposed in Schemes 1 and 2. This type of reactivity appears to be influenced by the steric hindrance around the azido group of the coordinated AziNC. In fact, it is observed that when AziNC is bound to metal fragments of the type *trans*-$\{MCl(PPh_3)_2\}$ having two sterically hindered ancillary ligands, PPh_3 attacks selectively the N_3 moiety. On the other hand, with less encumbered metal species such as those represented by the complexes *cis*-$[MCl_2(AziNC)_2]$ or *cis*-$[MCl_2(AziNC)(PPh_3)]$ (M = Pt, Pd), the phosphane ligand preferentially adds to the electrophilic metal center.

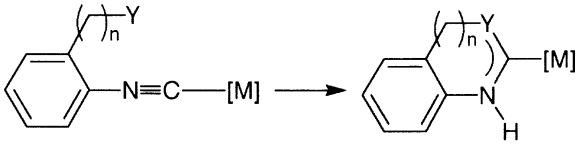
In conclusion, taking also into account previous results [11b], the Staudinger reaction of transition metal-coordinated AziNC is observed to proceed *only* when one of the following requirements is fulfilled i.e. the functional isocyanide is linked to *coordinatively satu-*



Scheme 3.

rated metal complexes such as those represented by the $\{M(CO)_5\}$ (M = Cr, W) fragments or is bound to *sterically hindered metal groups* such as those given by the *trans*-$\{MCl(PPh_3)_2\}$ (M = Pt, Pd) species. In all the other cases tested, the phosphane ligand attacks the metal center rather than the azido group.

All this experimental evidence leads to a final consideration that γ-functional isocyanides of the type **IV** ($n = 1$) appear to be less reactive, either as free ligands or metal-coordinated, toward ring closure than the corresponding β-functional ligands ($n = 0$) reported by Hahn and co-workers [2] (Eq. (5)).



(5)

IV **V**

Y = N_3, N=PPh_3, NH_2, OH; n = 0, 1

The greater tendency of intramolecular cyclization of the latter ligands could be ascribed, as previously suggested [2], to the aromaticity of the resulting heterocyclic carbene products of the type **V** ($n = 0$).

5. Supplementary data

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 214527. Copies of the available material can be obtained, free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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