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Reactivity of cyclopalladated compounds derived from biphenyl-2-ylamine towards carbon monoxide, ^{t}butyl isocyanide and alkynes

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Abstract

The reactivity of the dimeric cyclopalladated compounds derived from biphenyl-2-ylamine (μ-X)$_2$[κ^2-***N2′***,***C1***-1-Pd-2-{(2′-$NH_2C_6H_4$)C_6H_4}]$_2$ [X = OAc (**1**), X = Cl (**2**)] towards unsaturated organic molecules is reported. Compound **1** reacted with carbon monoxide and ^{t}butyl isocyanide producing phenanthridin-6(5*H*)-one and *N*-*tert*-butylphenanthridin-6-amine in 63% and 88% yield, respectively. Compound **2** reacted separately with diphenylacetylene and 3-hexyne, affording the mononuclear organopalladium compounds [κ^2-***N2″***,***C1***-η^2-***C2***,***C3***- 1-Pd{(R–C═C–R)$_2$-2′-(2″-$NH_2C_6H_4$)C_6H_4}Cl] [R = Ph (**5**), R = Et (**6**)] in 50–60% yield, which derived from the insertion of two alkyne molecules into the C–Pd σ bonds of **2**. The crystal structure of compounds **5** and **6** has been determined. Compound **5** crystallized in the monoclinic space group $P2_1/n$ with $a = 13.3290(10)$ Å, $b = 10.6610(10)$ Å and $c = 22.3930(10)$ Å and $\beta = 100.2690(10)°$. Compound **6** crystallized in the triclinic space group $P\bar{1}$ with $a = 7.271(7)$ Å, $b = 10.038(3)$ Å and $c = 16.012(5)$ Å, and $\alpha = 106.79(3)°$, $\beta = 96.25(4)°$ and $\gamma = 99.62(4)°$. The crystal structures of **5** and **6** have short intermolecular Pd–Cl···H–N–Pd non-conventional hydrogen bonds, which associated the molecules in chains in the first case and in dimers in the second.

Keywords: Cyclometallated; Primary amine; Palladium; Insertion; Carbon monoxide; Organic isocyanide; Alkyne; Non-conventional hydrogen bond

1. Introduction

Interest in the cyclometallation reaction has been renewed in recent years due to the incorporation of this reaction in catalytic cycles that transform C–H bonds of heterosubstituted organic molecules into C–X bonds (X = B, C, Si, N, O or halogen) [1–12]. In spite of this, the reactivity of the C–M σ bond of cyclometallated compounds has not been extensively studied, although its usefulness in stoichiometric organic and organometallic synthesis is well recognized [13–17].

In light of this, we chose to study the reactivity of the dimeric cyclopalladated compounds derived from biphenyl-2-ylamine (μ-X)$_2$[κ^2-***N2′***,***C1***-1-Pd-2-{(2′-$NH_2C_6H_4$)C_6H_4}]$_2$ [X = OAc (**1**), X = Cl (**2**)] towards carbon monoxide, ^{t}butyl isocyanide, diphenylacetylene and 3-hexyne.

In earlier papers, we described (i) the synthesis of compounds **1** and **2** in high yield by cyclopalladation of biphenyl-2-ylamine using as metallating agent palladium(II) acetate and the system $PdCl_2$/NaCl/NaOAc, respectively [18], and (ii) the monoinsertion of but-2-ynedioic acid dimethyl ester into the C–Pd σ bonds of the dimeric cyclopalladated compound (μ-Br)$_2$[κ^2-***N2′***,***C1***-1-Pd-2-{(2′-$NH_2C_6H_4$)C_6H_4}]$_2$ [19]. This latter reaction afforded an unusual example of formation of an eight-membered cyclopalladated compound by monoinsertion of an alkyne into

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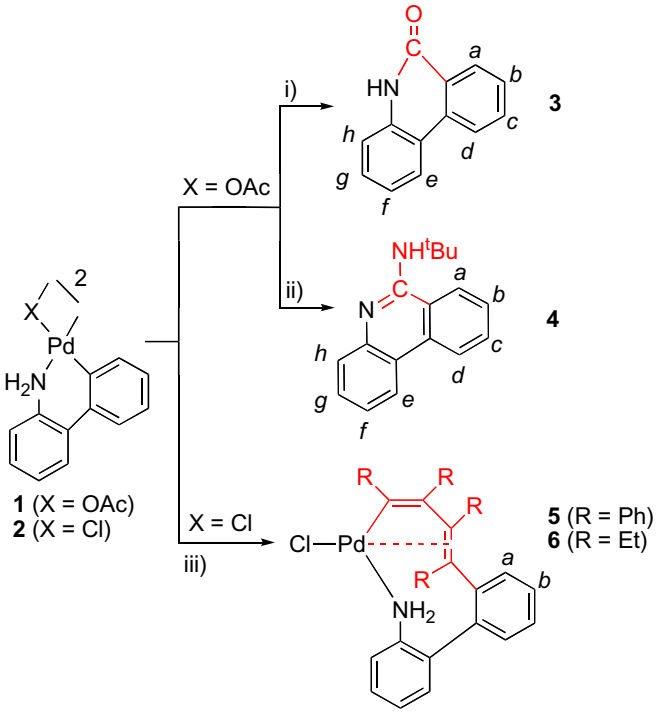
the C–Pd σ bond of its precursor six-membered palladacycle [19–25]. In addition, in the experimental section, we describe an adaptation of the previously reported method of synthesis of compound **2** [18] that produces this compound in high yield and improved purity.

2. Results and discussion

2.1. Synthesis and characterization of compounds 3–6

Scheme 1 shows the compounds prepared in this paper and the labelling assigned to the aromatic protons.

The treatment of compound **1** with carbon monoxide at 1.4 bar in toluene at room temperature for 24 h, and with ^{t}butyl isocyanide at reflux of chloroform for 4 days in a molar ratio ^{t}butyl isocyanide/**1** = 2, produced in both cases a significant amount of palladium(0). Then, after an adequate work up (see Section 3), phenanthridin-6(5*H*)-one (compound **3**) and *N*-*tert*-butylphenanthridin-6-amine (compound **4**) were isolated in 63% and 88% yield, respectively. These organic compounds were formed by a mono-insertion of the corresponding unsaturated molecule into the C–Pd σ bonds of the dimeric cyclopalladated compound **1**, followed by a reductive elimination of palladium(0) in the corresponding acyl and iminoacyl intermediate complexes. In addition, *N*-*tert*-butylphenanthridin-6-amine could be formed by a tautomerization of its precursor iminoacyl organic compound (Fig. 1). The



Scheme 1. (i) CO, 1.4 bar, toluene, room temperature, 24 h; (ii) ^{t}butyl isocyanide (molar ratio ^{t}butyl isocyanide/**1** = 2), chloroform, reflux, 4 days; (iii) alkyne (molar ratio alkyne/**2** = 4), chloroform, reflux, 4 h.

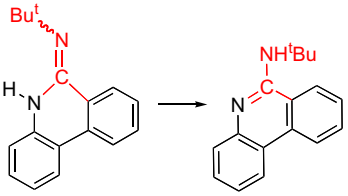


Fig. 1. Tautomerization leading to *N*-*tert*-butylphenanthridin-6-amine.

driving force of this tautomerization process would be the aromatic nature of the phenanthridinamine.

Phenanthridin-6(5*H*)-ones and phenanthridin-6-amines are well-known organic compounds with applications in bioorganic and medicinal chemistry, e.g., as poly(ADP-rybose)polymerase1 [26] and prion inhibitors [27], respectively. There are well-established methods of synthesis for these two kind of compounds based on stoichiometric organic or metal catalyzed reactions [28,29]; for example, phenanthridin-6(5*H*)-one can be produced with a 97% yield starting from 2'-iodo-biphenyl-2-ylamine in a catalytic intramolecular carbonylation reaction using as catalyst a palladium dendrimer supported on silica [30].

Phenanthridin-6(5*H*)-one and *N*-*tert*-butylphenanthridin-6-amine were characterized by IR, ^{1}H NMR and mass spectrometry. The latter compound has not been previously reported in the literature, and was therefore subjected to elemental analysis, affording satisfactory values for the % of C, H and N. The IR and ^{1}H NMR of compound **3** were identical to those previously reported [30]. In addition, a DEPCI mass spectrum of compound **3** produced intense signals corresponding to $[M+H^+]$ and $[M+H^+-CO]$, as expected for its structure. As new NMR data for compound **3**, we included a complete assignment of its protons on basis of bidimensional gCOSY, NOESY and gHMBC NMR experiments.

In the IR spectrum of compound **4**, a band at 1615 cm^{-1} was assigned to a stretching of the CNC aromatic fragment of the phenanthridinyl group, and a band at 3455 cm^{-1} to the N–H stretching of the amino group. Bidimensional gCOSY, NOESY and gHMBC NMR experiments allowed a complete assignment of the protons of compound **4**. The low-field shifted protons, which appeared at 8.50 and 8.31 ppm as doublets, were assigned to the d and e protons of the phenanthridinyl group, in agreement with the literature assignments of the aromatic protons of related phenanthridinamines [27]. The NH proton and the ^{t}Bu protons of compound **4** appeared at 5.22 ppm as a broad signal and at 1.66 ppm as a sharp singlet, respectively. ESI and EI mass spectra of compound **4** were consistent with its proposed molecular and structural formula. In the ESI mass spectrum a unique intense signal was observed at *m*/*z* 251 corresponding to $[M+H^+]$. The EI mass spectrum, together with the molecular radical cation $[M]^+$ and peaks corresponding to its expected fragmentation, produced a peak at *m*/*z* = 178 that was assigned to the molecular cation $[M-NH^tBu]^+$. This latter peak is an

indication of the existence of a single bond between the phenanthridinyl group and the amino nitrogen atom in compound **4**.

Compound **2** reacted separately with diphenylacetylene and 3-hexyne in chloroform at reflux for 4 h in a molar ratio alkyne/**2** = 4, affording orange solutions from which were isolated, after concentration of the solvent and elution of the residues through a silica gel chromatographic column, the mononuclear organopalladium complexes **5** and **6** in 50–60% yield.

Compounds **5** and **6** were studied by elemental analysis, mass spectrometry, IR, ^{1}H NMR and X-ray diffraction. Their elemental analysis and mass spectra were consistent with those of mononuclear organopalladium compounds derived from the insertion of two alkyne molecules into the C–Pd σ bonds of compound **2**. The FAB$^+$ of compound **5** and the MALDI-TOF$^+$ of compound **6** presented an intense signal at *m/z* 630 and 439, respectively, which was assigned to the molecular cation [M+H$^+$−HCl], indicating that the chlorine atom is bonded directly to the palladium atom [31]. The ^{1}H NMR of compound **6** presented four groups of signals for the protons of the ethyl groups. In addition, each of the ethyl CH_2 protons produced an AB spin system, indicating that compound **6** presents a chiral structure. Interestingly, the amino protons of compound **5** produced only one broad signal centred at 4.25 ppm, while those of compound **6** appeared as two broad signals centred at 4.00 and 3.39 ppm.

Compounds **5** and **6** produced single crystals for the determination of their structure by X-ray diffraction. Fig. 2 shows the X-ray molecular structure of compounds **5** and **6**, and Table 1 gives selected bond distances and angles. The molecules of **5** and **6** are chiral, and the new butadienyl fragments [C13, C20, C27, C34 for compound **5** and C13, C16, C19, C22 for compound **6**] present a *trans–cis* configuration and are η^2-κ^1 coordinated to the palladium(II) centres (Fig. 2). Thus, these compounds adopt the structure found in most organopalladium compounds derived from the insertion of two alkyne molecules into the C–Pd σ bonds of five- and six-membered cyclopalladated compounds, in which the resulting butadienyl fragment presents a *trans–cis* configuration and is η^2-κ^1 coordinated to the palladium(II) centre [16].

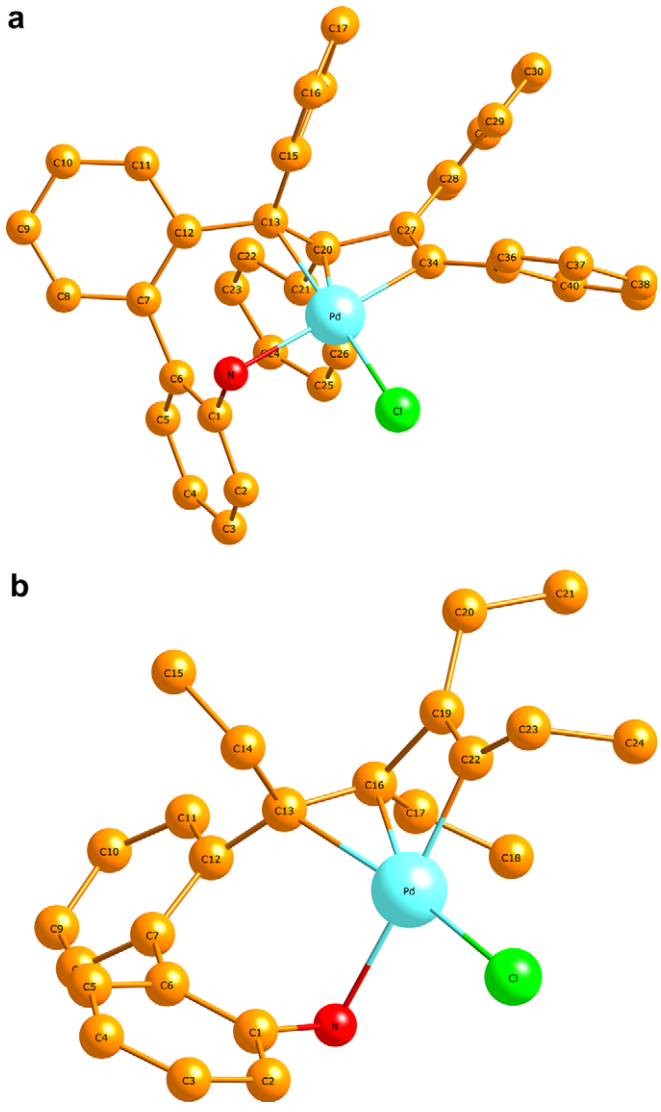


Fig. 2. Molecular crystal structure of **5** (a) and **6** (b).

Table 1
Selected bond distances (Å) and angles (°) for **5** and **6**

5		**6**	
Pd–Cl	2.3157(6)	Pd–Cl	2.328(3)
Pd–N	2.1810(19)	Pd–N	2.196(4)
Pd–C34	1.983(2)	Pd–C22	2.045(5)
Pd–C13	2.215(2)	Pd–C13	2.312(4)
Pd–C20	2.253(2)	Pd–C16	2.213(4)
N–C1	1.414(3)	N–C1	1.443(5)
C1–C6	1.388(3)	C1–C6	1.420(6)
C6–C7	1.495(3)	C6–C7	1.444(5)
C7–C12	1.412(3)	C7–C12	1.419(5)
C12–C13	1.523(3)	C12–C13	1.385(6)
C13–C20	1.409(3)	C13–C16	1.387(6)
C20–C27	1.513(3)	C16–C19	1.610(6)
C27–C34	1.325(3)	C19–C22	1.376(7)
Cl–Pd–N	84.57(5)	Cl–Pd–N	90.55(9)
Cl–Pd–C13	174.42(5)	Cl–Pd–C13	169.29(11)
Cl–Pd–C20	148.69(5)	Cl–Pd–C16	154.51(11)
Cl–Pd–C34	96.11 (6)	Cl–Pd–C22	94.23 (15)
N–Pd–C34	179.15(8)	N–Pd–C22	175.22(17)
N–Pd–C13	92.96(7)	N–Pd–C13	86.32(12)
N–Pd–C20	114.35(7)	N–Pd–C16	105.37(13)
C34–Pd–C13	86.42(8)	C22–Pd–C13	89.05(17)
C34–Pd–C20	64.82(8)	C22–Pd–C16	70.03(18)
Pd–N–C1	99.19(14)	Pd–N–C1	103.1(2)
N–C1–C6	118.5(2)	N–C1–C6	117.7(3)
C1–C6–C7	121.5(2)	C1–C6–C7	123.0(4)
C6–C7–C12	126.9(2)	C6–C7–C12	126.5(3)
C7–C12–C13	128.16(18)	C7–C12–C13	125.6(3)
C12–C13–C20	122.60(18)	C12–C13–C16	126.0(4)
C13–C20–C27	118.07(18)	C13–C16–C19	118.0(3)
C20–C27–C34	106.81(18)	C16–C19–C22	109.8(4)
C27–C34–Pd	102.72(15)	C19–C22–Pd	96.3(3)

Distances and angles around the palladium(II) centre in compounds **5** and **6** were within the normal range for this kind of organopalladium compound [20,24,32–48]. As expected (i) the carbon–carbon distances of the alkene units coordinated η^2 to the palladium(II) centres were larger than the carbon–carbon distances of the alkene units coordinated κ^1 to the palladium(II) centres –1.409(3) Å and 1.325(3) Å for compound **5** and 1.387(6) Å and 1.376 (7) Å for compound **6** – and (ii) the alkene units coordinated η^2 to the palladium(II) centre were no longer planar – the dihedral angles C14-C13–C20–C21 for compound **5** and C14-C13–C16–C17 for compound **6** were 152.1(2)° and 164.5(4)°, respectively. The Pd–Cl distances – 2.3157(6) Å for compound **5** and 2.328(3) Å for compound **6** – and the Pd–N distances – 2.1810(19) Å for compound **5** and 2.196(4) Å for compound **6** – were shorter and longer, respectively, than the analogous distances in mononuclear cyclopalladated compounds of general formula *trans-**N**,**P***-[Pd(C,N)Cl(phosphine)] [49–51]. This is due to the weaker *trans* influence of an η^2-coordinated alkene in relation to a metallated carbon atom and to the stronger *trans* influence of a metallated carbon atom in relation to a phosphine ligand [52]. Interestingly, in both compounds **5** and **6**, if we consider that the C13 atom of the alkene unit bonded η^2 occupies the fourth coordination position of the palladium(II) centre, the coordination angles are close to 90° and 180° (see Table 1), which suggests that the coordination of the butadienyl fragment in compounds **5** and **6** could be better described as η^1-κ^1 rather than η^2-κ^1.

On the basis of the X-ray molecular structure of compound **5**, the equivalence of the amino protons of compound **5** in the ^{1}H NMR at 500 MHz in $CDCl_3$ solution and at room temperature, is ascribed to the dynamic process shown in Fig. 3, in which the amino protons of compound **5** are exchanging their positions, probably by decoordination of the amino group, inversion at the nitrogen atom, rotation through the C–N single bond and coordination of the amino group. The driving force of this process would be the release of steric tension in compound **5** through the intermediate compound shown in Fig. 3, which presents the nitrogen atom uncoordinated to the palladium(II) centre.

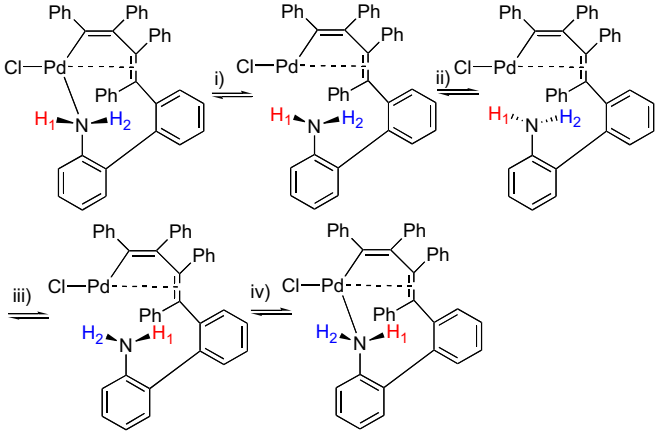


Fig. 3. Mechanism for the exchange of the amino protons of compound **5**: (i) decoordination, (ii) inversion, (iii) rotation, (iv) coordination.

Finally, it should be noted that the crystal structures of compounds **5** and **6** presented intermolecular non-conventional Pd–Cl···H–N–Pd hydrogen bonds [53,54], which associated the molecules of **5** in chains and those of **6** in dimers (Fig. 4). The Cl···H distances for these non-conventional hydrogen bonds were 2.42 Å and 2.52 Å for compounds **5** and **6**, respectively, which are short contacts according to a previously reported search in the Cambridge Structural Database [54].

2.2. Final remarks

In this paper and in a precedent one [19], we have demonstrated the versatility of the acetato- (compound **1**), chloro- (compound **2**) and bromo- (compound **A**) bridged cyclopalladated dimers of biphenyl-2-ylamine in stoichiometric organic and organometallic synthesis. These six-membered *ortho*-cyclopalladated compounds can be obtained in moderate to high yield, depending on the reaction conditions and the palladating agent [18,55]. Compound **1** reacts with carbon monoxide and ^{t}butyl isocyanide, affording organic compounds derived from the monoinsertion of the corresponding unsaturated molecule into the C–Pd σ bond of **1**, while compound **2** reacts with diphenylacetylene and 3-hexyne producing mononuclear organopalladium compounds derived from a double insertion of the corresponding alkyne into the C–Pd σ bonds of **2**. In addition, compound **A**, in adequate reaction conditions, reacts with but-2-ynedioic acid dimethyl ester, affording a dimeric eight-membered cyclopalladated compound derived from the monoinsertion of the alkyne into the C–Pd σ bonds of **A** [19].

3. Experimental

3.1. Instruments and reagents

Elemental analyses of C, H and N were performed with an Eager 1108 microanalyzer. Infrared spectra were recorded on a Nicolet Impact-400 spectrophotometer using pressed discs of dispersed samples of compounds **3**–**6** in KBr. NMR experiments were recorded using Varian Inova 500 and Varian Mercury 400 instruments. Chemical shifts are reported in δ values (ppm) relative to $SiMe_4$ and coupling constants in Hz. The mass spectra were recorded with the following instruments: EI and DEPCI with a Thermo-Finnigan TRACE DSQ instrument – this latter experiment used as reactive gas NH_3– ESI with a Mass ZQ instrument, FAB^+ with a VG-Quatro Fisions instrument using 3-nitrobenzylalcohol as matrix, and MALDI-TOF^+ with a VOYAGER-DE-RP instrument using dithranol as matrix. All chemicals and solvents were of commercial grade and used as received. Carbon monoxide was CON47 Alphagaz, which contained less than 1 ppm of hydrogen.

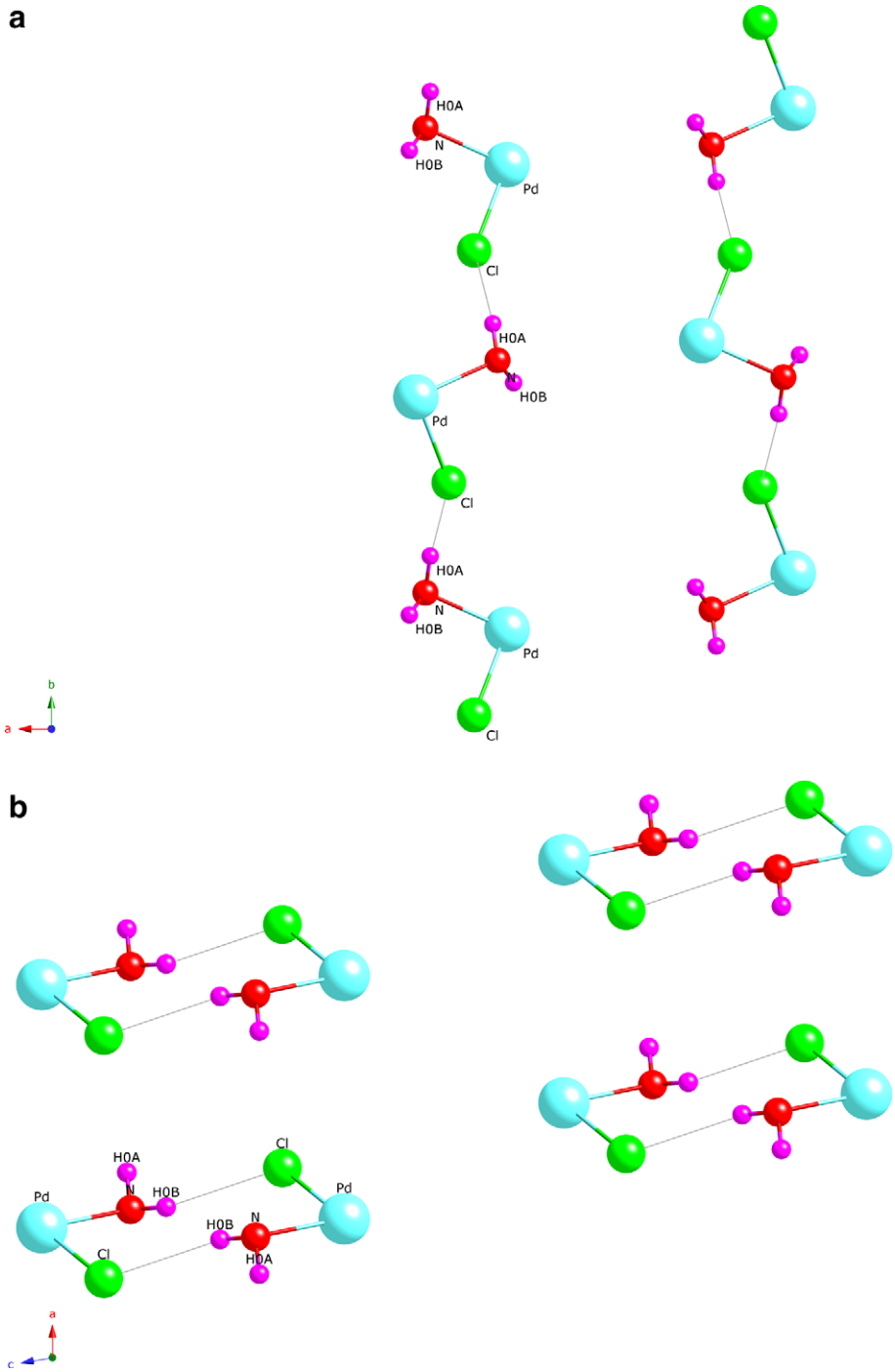


Fig. 4. (a) Crystal structure of compound **5** down of the *c* axis. (b) Crystal structure of compound **6** down of the *b* axis. For simplicity, only the molecular fragment involved in the formation of the intermolecular Pd–N–H···Cl–Pd non-conventional hydrogen bond is represented.

3.2. Preparation of *1* and *2*

Compound **1** was prepared as previously described [18]. Compound **2** was prepared using an adaptation of the previously reported method [18]: a suspension formed by 0.585 g (3.46×10^{-3} mol) of biphenyl-2-ylamine, 0.612 g (3.45×10^{-3} mol) of $PdCl_2$, 0.402 g (6.88×10^{-3} mol) of NaCl, 0.276 g (3.36×10^{-3} mol) of NaOAc and 30 mL of MeOH was stirred at room temperature for 9 days. The precipitate was filtered, washed with 5 mL of water and 5 mL of diethylether and dried under vacuum. The solid was dissolved in acetone and the solution was filtered through silica gel. The filtered solution was concentrated under vacuum. Addition of 10 mL of diethylether to the residue precipitated compound **2** as a white powder, which was filtered and dried in vacuum. The yield was 81%.

3.3. Preparation of **3**

A 250 mL cylindrical glassware reactor was charged in a ventilated fume hood with 0.100 g (1.5×10^{-4} mol) of compound **1**, 25 mL of toluene and carbon monoxide at 1.4 bar. The resulting suspension was stirred at room temperature for 24 h, after which a voluminous precipitate of palladium(0) formed and the reactor was opened to release the excess of carbon monoxide. The palladium(0) was then filtered through celite and washed with 15 mL of THF. The organic solutions were combined and concentrated under vacuum. Addition of 10 mL of diethylether to the residue produced compound **3** as a white powder, which was filtered and dried under vacuum. The yield was 63%. Characterization data: DEPCI (*m/z*): $[M+H^+] = 196$, $[M+H^+-CO] = 168$. IR (cm^{-1}): $\nu(NH) = 3170$, 3107; $\nu(C{=}O) = 1666$. ^1H NMR (400 MHz, DMSO-d_6, 298 K): 8.50 (d, $^3J_{HH} = 8.1$, H_d), 8.38 (d, $^3J_{HH} = 7.9$, He), 8.32 (d, $^3J_{HH} = 7.3$, H_a), 7.85 (td, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.1$, H_c), 7.64 (t, $^3J_{HH} = 7.5$, H_b), 7.49 (td, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.0$, H_g), 7.37 (d, $^3J_{HH} = 7.8$, H_h), 7.26 (td, $^3J_{HH} = 7.6$, $^4J_{HH} = 0.9$, H_f). The NH proton was not observed in DMSO-d_6. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 9.50 (br s, NH), 8.53 (dd, $^3J_{HH} = 8.0$, $^4J_{HH} = 1.0$, H_d), 8.30 (d, $^3J_{HH} = 8.5$, H_a), 8.23 (d, $^3J_{HH} = 7.5$, H_e), 7.81 (td, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$, H_b), 7.61 (td, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$, H_c), 7.48 (td, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$, H_g), 7.31 (td, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$, H_f), 7.23 (d, $^3J_{HH} = 8.0$, H_h).

3.4. Preparation of **4**

A suspension formed by 0.103 g of **1** (1.5×10^{-4} mol), 0.026 g of ^{t}butyl isocyanide (3.1×10^{-4} mol) and 25 mL of chloroform was refluxed for 4 days. The palladium(0) formed was filtered through celite and the solution concentrated under vacuum. The residue of the solution was passed through a short silica gel chromatographic column (ca. 10 cm) eluting with chloroform. The first eluted band was concentrated under vacuum, producing compound **4** in an 88% yield. Characterization data: Anal. Calc. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 80.4; H, 7.2; N, 11.0%. ESI (*m/z*): $[M+H^+] = 251$. EI (*m/z*): $[M]^+ = 250$, $[M-CH_3]^+ = 235$, $[M-CH_3-CH_4]^+ = 219$, $[M-{}^tBu]^+ = 194$, $[M-NH{}^tBu]^+ = 178$. IR (cm^{-1}): ν (NH) = 3455, $\nu(CNC_{st\ phenanthridinyl}) = 1615$. ^1H NMR (500 MHz, $CDCl_3$, 298 K): 8.50 (d, $^3J_{HH} = 8.2$, H_d), 8.31 (d, $^3J_{HH} = 8.0$, H_e), 7.77 (d, $^3J_{HH} = 7.9$, H_h), 7.76 (d, $^3J_{HH} = 7.5$, H_a), 7.71 (t, $^3J_{HH} = 7.6$, H_c), 7.56 (t, $^3J_{HH} = 7.2$, H_b), 7.53 (td, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.0$, H_g), 7.30 (t, $^3J_{HH} = 7.2$, H_f), 5.22 (s, NH), 1.66 (s, ^{t}Bu).

Table 2
Crystallographic data for **5** and **6**

Compound	**5**	**6**
Empirical formula	$C_{40}H_{30}ClNPd$	$C_{24}H_{30}ClNPd$
Formula weight	666.50	474.34
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.3290(10)	7.271(7)
b (Å)	10.6610(10)	10.038(3)
c (Å)	22.3930(10)	16.012(5)
α (°)		106.79(3)
β (°)	100.2690(10)	96.25(4)
γ (°)		99.62(4)
Volume ($Å^3$)	3131.1(4)	1087.7(11)
Z	4	2
D_{Calc} (Mg/m^3)	1.414	1.448
Absorption coefficient (mm^{-1})	0.707	0.984
F(000)	1360	488
Crystal size (mm)	$0.1 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$
Theta range for data collection (°)	2.93–31.64	2.16–29.96
Index ranges	$-19 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 32$	$-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 22$
Reflections collected/unique [R_{int}]	35012/9865 [0.0733]	6279/6279 [0.0000]
Completeness	To theta 31.64°	To theta 29.96°
	93.5%	99.4%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9865/0/388	6279/0/248
Goodness-of-fit on F^2	1.176	1.232
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0536$, $wR_2 = 0.0830$	$R_1 = 0.0424$, $wR_2 = 0.0948$
R indices (all data)	$R_1 = 0.0761$, $wR_2 = 0.0890$	$R_1 = 0.0689$, $wR_2 = 0.1283$
Largest difference in peak and hole (e $Å^{-3}$)	0.484 and −0.797	0.369 and −0.542

3.5. Preparation of 5 and 6

A suspension formed by 0.100 g of compound **2** (1.6×10^{-4} mol), 6.4×10^{-4} mol of the corresponding alkyne and 20 mL of chloroform was refluxed for 4 h. The resulting solution was concentrated under vacuum and the residue was purified by a silica gel column chromatography using chloroform/methanol (100/2) as eluent. The first yellow band was collected and concentrated under vacuum. Addition of 5 mL of diethylether to the residue precipitated the corresponding compound **5** or **6** as a yellow powder, which was filtered and dried under vacuum. Characterization data: Compound **5**: Yield = 55%. Anal. Calc. for $C_{40}H_{30}NClPd$: C, 72.08; H, 4.54; N, 2.10. Found: C, 70.7; H, 4.6; N, 2.3%. FAB$^+$ (*m/z*): [M+H$^+$−HCl] = 630. IR (cm^{-1}): $\nu_a(NH_2) = 3339$, $\nu_s(NH_2) = 3212$. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) (selected data): 6.57 (td, $^3J_{HH} = 7.5$, $^4J_{HH} = 3.5$, H_b), 5.81 (d, ^{3}JHH = 8.0, H_a), 4.25 (br s, NH_2). Compound **6**: Yield = 61%. Anal. Calc. for $C_{24}H_{30}NClPd$: C, 60.77; H, 6.37; N, 2.95. Found: C, 62.3; H, 6.3; N, 3.0%. MALDI-TOF$^+$ (*m/z*): [M+H$^+$−HCl] = 439. IR (cm^{-1}): $\nu_a(NH_2) = 3329$, $\nu_s(NH_2) = 3226$. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 7.44 (td, 1 H_{ar}, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.7$), 7.38–7.15 (m, 5H_{ar}), 7.15 (d, 2H_{ar}, $^3J_{HH} = 5.0$ Hz, $^4J_{HH} = 0.9$), 4.00 (br s, 1H, NH_2), 3.39 (br s, 1H, NH_2), 2.44–1.94 (8H, CH_2), 1.50 (t, CH_3, $^3J_{HH} = 7.4$), 1.04 (t, CH_3, $^3J_{HH} = 7.2$), 0.95 (t, CH_3, $^3J_{HH} = 7.6$), 0.41 (t, CH_3, $^3J_{HH} = 7.4$).

3.6. Crystal structures

Single crystals for the X-ray molecular structure determination of **5** and **6** were obtained by slow evaporation of the solvents of a solution of **5** in chloroform/methanol (1/1), and a solution of **6** in dichloromethane/diethylether (2/1). A prismatic crystal was mounted on a MAR 345 diffractometer with an image plate detector for **5** and on a Enraf-Nonius CAD4 four circle diffractometer for **6**. In both cases, intensities were collected with graphite-monochromatized Mo Kα radiation. The structure of **5** was solved by direct methods, and that of **6** by a Patterson synthesis, using the SHELXS computer program in both cases [56]. Both structures were refined by the full-matrix least squares method with the SHELXL97 computer program [57]. For the structure of **5**, 21 hydrogens were located and 9 were calculated, whereas for the structure of **6** all hydrogens were computed. A summary of crystallographic data and some details of the refinement are given in Table 2.

4. Supplementary material

CCDC 649364 and 649365 contain the supplementary crystallographic data for **5** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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