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Synthesis, characterization and X-ray crystal structure determination of cyclopalladated [Csp^2,N,N′]$^-$, zwitterionic and chelated compounds in the reaction of 3,5-diphenyl-*N*-alkylaminopyrazole derived ligands with Pd(II)

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ABSTRACT

The synthesis of two *N*-alkylaminopyrazole ligands, 1-[2-(diethylamino)ethyl]-3,5-diphenylpyrazole (**L1**) and 1-[2-(dioctylamino)ethyl]-3,5-diphenylpyrazole (**L2**), is reported. These ligands present, a priori, one pyrazole nitrogen and one amine nitrogen as potential donor atoms. However, in the reaction of the ligands (**L1** and **L2**) with $[PdCl_2(CH_3CN)_2]$ one of the C_{phenyl} atoms can also behave as a donor atom. As a result, we have obtained the formation of three different compounds for each one of the ligands: chelated ($[PdCl_2(L)]$ L = L1 (**1a**), L2 (**2a**)), zwitterionic ($[PdCl_3(LH)]$ LH = LH1 (**1b**), LH2 (**2b**)), and cyclopalladated compounds ([PdCl(LC)] (LC = LC1 (**1c**), LC2 (**2c**)). The solid-state structures for **1a**, **1b** and **1c** were determined by single crystal X-ray diffraction methods. The potentially [C,N,N′]$^-$ ligand is coordinated through the N_{pz} and the N_{amino} to the metal atom for **1a**, through the N_{pz} for **1b**, and through the N_{pz}, the N_{amino} and a C_{phenyl} for **1c**.

1. Introduction

Cyclometallated compounds have been widely studied over the last three decades [1], and have acquired great interest because of the applications of metallacycles in many areas including organic synthesis [2], catalysis [3] and material science [4], and as biologically active compounds [5].

Palladium compounds containing at least one metal–carbon bond intramolecularly stabilized by at least one donor atom, termed cyclopalladated compounds or palladacycles, are one of the most popular classes of cyclometallated compounds [6].

A wide variety of palladacycles containing a σ(Pd–Csp^2) or a σ(Pd–Csp^3) bond from a bidentate [C,X]$^-$ {X = N,P,O,S} or a tridentate [C,X,Y]$^-$ or [X,C,Y]$^-$ {X,Y = N,P,O,S} ligand, including palladacycles containing heterocyclic system, have been described so far [7]. In particular, studies of tridentate intramolecular coordination systems [N,C,N]$^-$ have become one of the central themes in the development of organometallic chemistry [8]. Besides that, cyclopalladated non-symmetrical compounds containing a [Csp^2,N,N]$^-$ chelating ligand with mixed five- and six-membered rings are not common [9].

Our group has previously reported the synthesis of 3,5-dimethyl-*N*-alkylaminopyrazole ligands, and studied their reactivity with Pd(II), Pt(II) [10] and Rh(I) [11]. Other ligands have been synthesized with phenyl and pyridyl groups in positions 3 and 5 of the pyrazole ring: 2-(1-ethyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine and 2-(1-octyl-5-phenyl-*1H*-pyrazol-3-yl)pyridine. Their reactivity with Pd(II) and Pt(II) has also been studied, yielding *cis*-$[MCl_2(L)]$ complexes [12]. The allylpalladium complexes of these ligands have also been obtained [13]. Some of these pyridylpyrazole palladium complexes have been tested as catalysts in the Heck reaction giving rise to highly efficient catalytic results [14].

Moreover, we have described the synthesis of ligands containing a phenyl and a methyl group in positions 3 and 5 of the pyrazole ring (1-ethyl-5-methyl-3-phenyl-*1H*-pyrazole and 5-methyl-1-octyl-3-phenyl-*1H*-pyrazole) and we have studied their reactivity with $[PdCl_2(CH_3CN)_2]$ and K_2PtCl_4, resulting in *trans*-$[MCl_2(L)_2]$ complexes [15].

In this paper, we present the synthesis and characterization of two 3,5-diphenyl-*N*-alkylaminopyrazole ligands containing a dialkylaminoethyl group at the N1 position, 1-[2-(diethylamino)-ethyl]-3,5-diphenylpyrazole (**L1**) and 1-[2-(dioctylamino)ethyl]-3,5-diphenylpyrazole (**L2**), and the study of their reactivity with Pd(II). The ligands make use of one pyrazole nitrogen, one amine nitrogen, and/or one C_{phenyl} as donor atoms (Scheme 1).

2. Results and discussion

2.1. Synthesis of the ligands

Although 1-[2-(diethylamino)ethyl]-3,5-diphenylpyrazole (**L1**) has already been described in the literature [16], a modified

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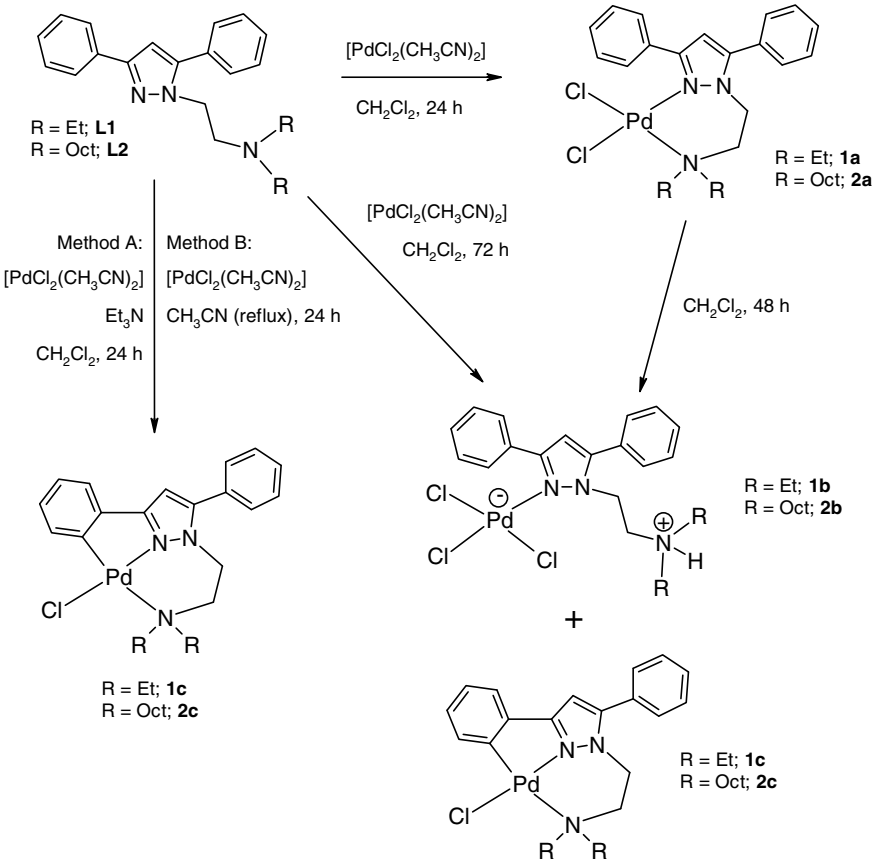

Scheme 1.

pathway for its synthesis is presented here. This new method is also useful to develop a new ligand that had not been previously described: 1-[2-(dioctylamino)ethyl]-3,5-diphenylpyrazole (**L2**).

The synthesis of the two ligands consists of the treatment of 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole [17] with the appropriate secondary amine (L1: diethylamine; L2: dioctylamine) in the presence of sodium hydroxide in a mixture of tetrahydrofuran and water (L1, 4:1; L2, 7:3). Each product is obtained as yellow oil. **L2** ligand is further purified by chromatography (silica gel 60 Å) with ethyl acetate as the eluent.

Ligands were characterized by elemental analyses, mass spectrometry and IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies. The NMR signals were assigned by reference to the literature [18] and from DEPT, COSY and HMQC NMR experiments.

2.2. Synthesis and characterisation of the complexes

Complexes $[PdCl_2(L)]$ (L = L1 (**1a**), L2 (**2a**)) were obtained by treatment of the corresponding ligand with $[PdCl_2(CH_3CN)_2]$ [19] in a 1:1 or 1:2 M/L ratio in dry dichloromethane for 24 h. If this reaction is continued for 72 h at room temperature, compounds **1a** and **2a** practically disappear, leading to the formation of compounds $[PdCl_3(L1H)]$ **1b**, [PdCl(L1C)] **1c** (**1b**/**1c,** 1:1) and $[PdCl_3(L2H)]$ **2b**, [PdCl(L2C)] **2c** (**2b**/**2c,** 1:1), respectively (Scheme 1). ^{1}H NMR controls were performed to follow the reaction evolution. L1H and L2H correspond to L1 and L2 ligands, respectively, with the amine group protonated; L1C and L2C correspond to L1 and L2 ligands, respectively, with a carbon atom deprotonated in an *ortho* position of one phenyl group.

Complexes **1a** and **2a** have a chelated *N*,*N*′ ligand, whereas complexes **1b** and **2b** are zwitterionic species with a N_{pz}-coordinated cationic ligand. The most interesting products of these reactions are complexes **1c** and **2c** which are cyclopalladated species. These metallated compounds can be easily separated from zwitterionic derivatives (**1b** and **2b**, respectively) due to their high solubility in dichloromethane. Therefore, zwitterionic compounds are isolated by precipitation from the reaction medium (**1b**) or forcing the precipitation with dry and cool diethyl ether (**2b**). The filtered solutions contain compounds with Pd–C bond (**1c** and **2c**, respectively) (Scheme 1).

In the literature, cyclopalladation reactions are known to proceed through a wide variety of mechanisms such as C–H activation, oxidative addition, transmetallation or nucleophilic addition onto an unsaturated bond [1a,6]. In general, cyclopalladation of aromatic derivates complexes is considered to occur by a simple electrophilic aromatic substitution pathway [20].

Most of palladium assisted palladation of C–H bonds include chloropalladium compounds with a base or acetate derivatives that act as proton acceptors. In our case, the reaction works because the amino group of a chelated complex acts as a phenyl proton acceptor leading to zwitterionic compounds **1b** and **2b** and to cyclometallated **1c** and **2c**, respectively, so no extra base is needed.

In order to improve the yield of the cyclometallated compounds described in this paper, different experiments were performed. On one hand, reactions at higher temperature (reflux in dry acetonitrile for 24 h) were carried out. In this study, the cyclometallated compound is the only species obtained with a yield of 42% for **1c** and 46% for **2c**. On the other hand, reactions with additional triethylamine base with ligands **L1** and **L2** were also performed in dry dichloromethane. In both cases, chloro salts precipitated and metallated **1c** and **2c** compounds were formed in a shorter time. No zwitterionic complexes were detected during the reaction. These

results suggest that the presence of a proton acceptor is indeed needed in the formation of these metallated complexes and complexes **1a** and **2a** or bases such as triethylamine can play this role.

Several techniques were used for the characterization of all complexes: elemental analyses, mass spectrometry, conductivity measurements, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies and X-ray diffraction, when possible.

The elemental analyses for complexes **1a** and **2a** are consistent with the formula $[PdCl_2(L)]$ (L = L1, L2), for **1b** and **2b** with $[PdCl_3(LH)]$ (LH = L1H, L2H) and for **1c** and **2c** with [PdCl(LC)] (LC = L1C, L2C). The positive ionization spectra MS−(ESI+) of compounds **1a**, **1b**, and **1c** give a peak with a *m/z* value of 424.1 (100%) attributable to $(Pd(L1C)^+)$, and for **2a**, **2b**, and **2c** a peak at 592.3 (100%), attributable to $(Pd(L2C)^+)$ is observed.

Conductivity values in acetonitrile for all complexes are in agreement with the presence of non-electrolyte compounds (6.7–84.0 Ω^{-1} cm^2 mol^{-1}) [21].

In the IR spectra of **1b** and **2b**, some distinguished signals appear corresponding to the protonated amino group, $\nu(N–H^+)$ and $\delta(N–H^+)$ (2695, 1613 cm^{-1} for **1b** and 2693, 1624 cm^{-1} for **2b**) [18]. The IR spectra for all complexes in the region 600–100 cm^{-1} were also studied. Complexes **1a** and **2a** show one well-defined band corresponding to ν(Pd–N) at 449 and 441 cm^{-1}, respectively, and two bands for ν(Pd–Cl) between 335–330 and 326–319 cm^{-1}, which are typical of compounds with a *cis* disposition of the chloro ligands around the Pd(II) [22]. For complexes **1b** and **2b**, only two bands were assigned, one for ν(Pd–N) at 411 and 444 cm^{-1}, respectively, and another one for ν(Pd–Cl) at 335 and 340 cm^{-1}, respectively [22]. For complexes **1c** and **2c**, one band was observed for ν(Pd–N) at 418 and 417 cm^{-1}, respectively, and one band for ν(Pd–Cl) at 279 cm^{-1} for both complexes [23].

The ^1H, $^{13}C\{^1H\}$NMR, DEPT, COSY, HMQC, and NOESY spectra were recorded in $CDCl_3$ for **1a**, **1c**, **2a**, and **2c,** and in CD_3CN for **1b** and **2b** due to the poor solubility of these complexes in $CDCl_3$ and other solvents.

The ^1H NMR spectra of complexes **1a** and **2a** at room temperature show the ethylene protons of the $N_{pz}–CH_2–CH_2–N_{amino}$ chain as two poorly defined broad signals. This behaviour implies that a dynamic process is taking place in solution at this temperature. For this reason, we recorded variable temperature spectra (233–298 K) (Fig. 1).

Lowering of the temperature provokes a progressive splitting of the two signals corresponding to each CH_2. At 233 K, four well-defined bands are observed at δ = 5.25, 4.48, 3.76 and 3.17 ppm for **1a**

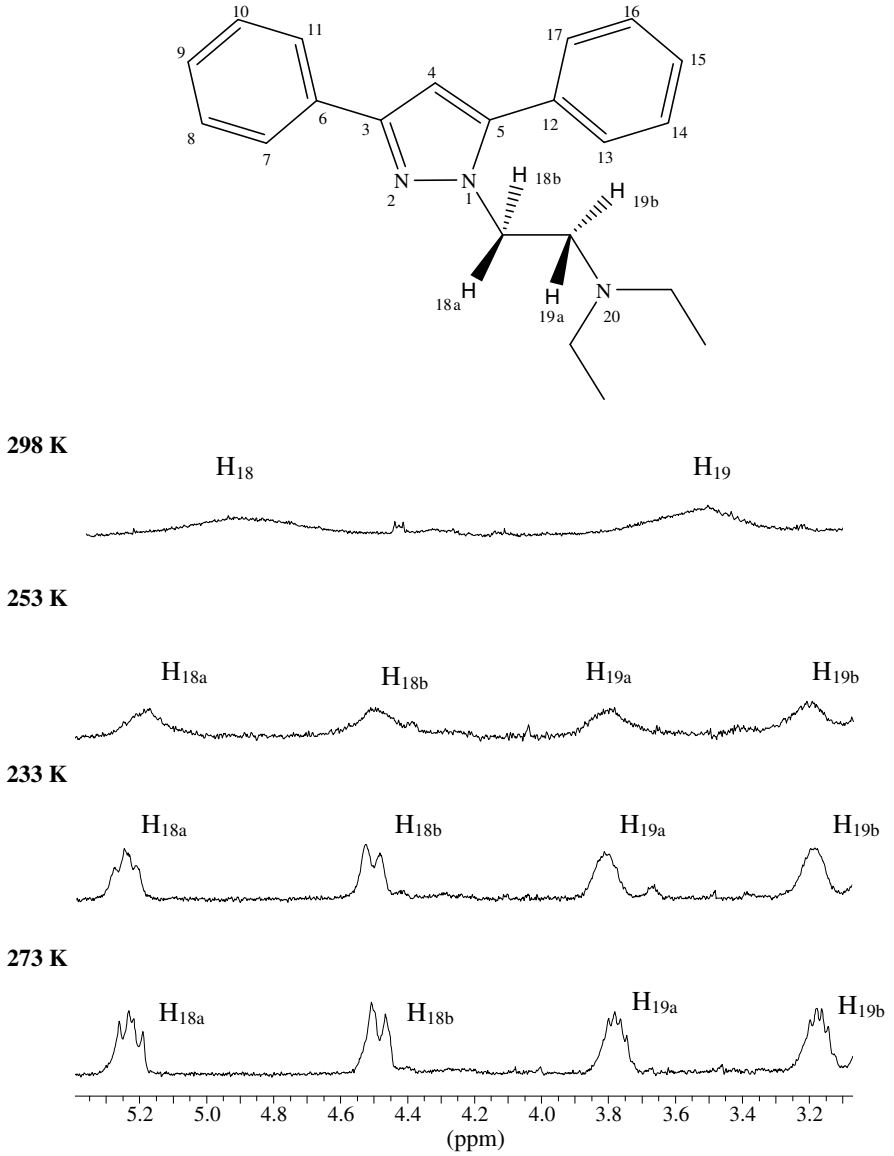

Fig. 1. 1H NMR spectra (250 MHz) of complex **1a** in $CDCl_3$ at various temperatures (233–298 K) and numbering scheme for all the compounds.

and at δ = 5.23, 4.51, 3.79 and 3.14 ppm for **1b**. The fluxional process takes place with $\Delta G^{\ddagger}$ values of ca. 57 kJ mol^{-1} for **1a** and ca. 58 kJ mol^{-1} for **2a**, as deduced from the coalescence behaviour of the ethylene resonances [24]. These values are consistent with other data described in the literature attributable to the ring-flipping of six-membered rings [11b,25].

In the ^{1}H NMR spectra of **1b** and **2b**, protons H_{18} of the N_{pz}–CH_2–CH_2–N_{amino} chain can be assigned as a triplet at δ = 4.49 ppm for **1b** and at δ = 4.54 ppm for **2b**. On the other hand, protons corresponding to H_{19} appear as a quadruplet at δ = 3.58 ppm for **1b** and at δ = 3.61 ppm for **2b** (H_{19} protons are coupled with H_{18} protons and the hydrogen of the amino moiety with similar coupling constants) (numbering from Fig. 1). Moreover, a broad band can be observed at δ = 8.65 ppm for **1b** and δ = 9.05 ppm for **2b**, attributable to the protonated amine nitrogen (N–H$^+$) (H_{20}).

No significant differences between ^{13}C{^{1}H} NMR spectra for free and coordinated ligands were observed for complexes **1a**, **1b**, **2a** and **2b**.

Finally, the ^{1}H NMR spectra for complexes **1c** and **2c** have also been studied. The CH_2 protons of the N_{pz}–CH_2–CH_2–N_{amino} chain appear as two sharp signals at δ = 4.30 ppm (H_{18}) and δ = 3.13 ppm (H_{19}) for **1c** and at δ = 4.28 ppm (H_{18}) and δ = 3.15 ppm (H_{19}) for **2c** (numbering from Fig. 1). The signals that appear at δ = 7.93 ppm for **1c** and at δ = 7.92 ppm for **2c**, which integrate only one proton, are attributable to H_{11} (numbering from Fig. 1). This observation is consistent with the *ortho*-palladation of the 3-phenyl ring. In the ^{13}C{^{1}H} NMR spectra for compounds **1c** and **2c**, the signals corresponding to the terminal chain and the phenyl carbons, except *C*–Pd, do not show significant differences compared to the same signals in the free ligands. The signal for *C*–Pd of these complexes appears at lower fields (δ = 136.8 ppm for **1c** and δ = 145.2 ppm for **2c**) compared to the same signals for the free ligands (δ = 129.5–126.0 ppm). The signal for pyrazolic carbon *C*–H is observed at δ = 101.2 ppm for **1c** and **2c** and for the free ligands it appears at δ = 103.7 ppm. These values are also consistent with the *ortho*-palladation of the 3-phenyl ring [9,26].

2.3. Crystal and molecular structure of [$PdCl_2$(L1)] (**1a**)

Compound **1a** consists of monomeric *cis*-[$PdCl_2$(L1)] molecules (Fig. 2). The palladium centre has a typical square-planar geometry with a tetrahedral distortion. This distortion can be observed in the mean separation (0.018(3) Å) of the atoms coordinated to the Pd atom. The environment consists of two chlorine atoms in *cis* disposition and one ligand coordinated via one N_{pz} and one N_{amino} to the Pd(II). Selected bond lengths and angles data are gathered in Table 1. Ligand **L1** acts as a bidentated chelate, forming a six-membered metallacycle ring, with twist boat conformation.

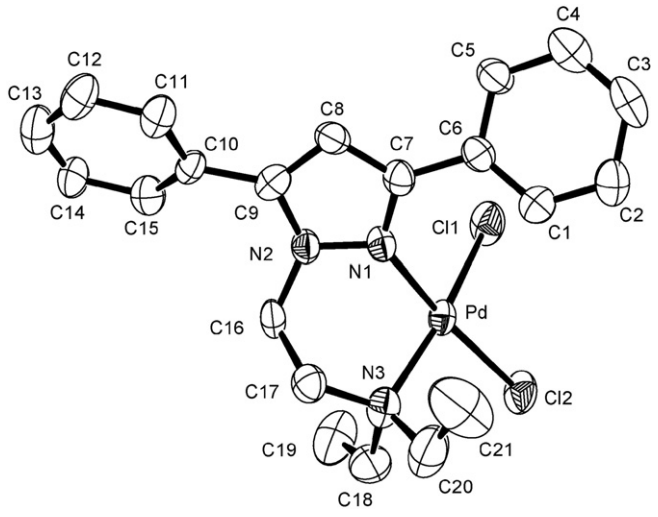

Fig. 2. ORTEP drawing of complex **1a**, showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1a**, **1b** · 1/4CH_2Cl_2 · 1/4CH_3CN and **1c**

1a			
Pd–N(1)	2.037(5)	Pd–Cl(2)	2.2935(18)
Pd–N(3)	2.114(6)	Pd–Cl(1)	2.301(2)
N(1)–Pd–N(3)	90.3(2)	N(1)–Pd–Cl(1)	88.96(15)
N(1)–Pd–Cl(2)	171.95(15)	N(3)–Pd–Cl(1)	170.26(15)
N(3)–Pd–Cl(2)	91.92(17)	Cl(2)–Pd–Cl(1)	90.19(7)
1b			
Molecule A		Molecule B	
Pd(1)–N(11)	2.033(4)	Pd(2)–N(21)	2.037(4)
Pd(1)–Cl(12)	2.2967(16)	Pd(2)–Cl(22)	2.3208(16)
Pd(1)–Cl(11)	2.3035(15)	Pd(2)–Cl(21)	2.3007(16)
Pd(1)–Cl(13)	2.3083(15)	Pd(2)–Cl(23)	2.2771(14)
N(11)–Pd(1)–Cl(12)	89.74(12)	N(21)–Pd(2)–Cl(22)	89.59(13)
N(11)–Pd(1)–Cl(11)	87.99(12)	N(21)–Pd(2)–Cl(21)	89.74(13)
Cl(12)–Pd(1)–Cl(11)	177.25(5)	Cl(21)–Pd(2)–Cl(22)	178.24(5)
N(11)–Pd(1)–Cl(13)	179.51(12)	N(21)–Pd(2)–Cl(23)	178.72(11)
Cl(12)–Pd(1)–Cl(13)	90.73(6)	Cl(23)–Pd(2)–Cl(22)	89.61(6)
Cl(11)–Pd(1)–Cl(13)	91.55(6)	Cl(23)–Pd(2)–Cl(21)	91.03(6)
1c			
Pd–N(1)	1.977(3)	Pd–C(1)	2.014(5)
Pd–N(3)	2.207(4)	Pd–Cl	2.3108(16)
N(1)–Pd–C(1)	80.06(17)	N(1)–Pd–Cl	174.58(11)
N(1)–Pd–N(3)	90.77(14)	C(1)–Pd–Cl	95.80(14)
C(1)–Pd–N(3)	168.84(16)	N(3)–Pd–Cl	93.72(10)

The $PdCl_2(N_{pz})(N)$ *core* (containing terminal chlorine atoms) is found in the literature as part of 43 crystal structures [27], but only two of them contain an aliphatic amine [10a,b]. The Pd–N_{amino} bond length (2.114(6) Å) is clearly longer than Pd–N_{pz} bond length (2.037(5) Å), and also longer than those reported for other structures described in the literature with the same environment, [$PdCl_2$(*NN′*)] (*NN′* = 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole and 1-[2-(*tert*-butylamino)ethyl]-3,5-dimethylpyrazole, whose Pd–N_{amino} distances are 2.061(5) and 2.097(4) Å, respectively [10a,b]. Both distances, (Pd–N_{amino} and Pd–N_{pz}), are consistent with previously described values for Pd–N_{amino} (2.017–2.280 Å) [10a,b,28], and for Pd–N_{pz} (1.979–2.141 Å) bonds [15,25b,29]. The Pd–Cl bond lengths (2.301(2), 2.2935(18) Å) can also be regarded as normal compared with distances found in the literature (2.280–2.341 Å) [10a,b,15,25b,29a–g]. The value of N–Pd–N bite angle is 90.3(2)°. Moreover, the Cl–Pd–Cl angle is 90.19(7)°, showing the small deviation from the square-planar geometry. The bite angle is slightly bigger than those found in the literature for complexes [$PdCl_2$(*NN′*)] (*NN′* = 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole and 1-[2-(*tert*-butylamino)ethyl]-3,5-dimethylpyrazole), 89.3(2)° and 88.16(18)°, respectively [10a,b].

2.4. Crystal and molecular structure of [$PdCl_3$(L1H)] · 1/4CH_2Cl_2 · 1/4CH_3CN (**1b** · 1/4CH_2Cl_2 · 1/4CH_3CN)

Compound **1b** · 1/4CH_2Cl_2 · 1/4CH_3CN consists of two molecules (**A** and **B**) of [Pd^{2+}(L1H)$^+$(Cl^-)$_3$] (Fig. 3), and solvent molecules. In each molecule, the palladium ion is surrounded by one pyrazole nitrogen and three chlorine atoms in a distorted square-planar geometry (with a tetrahedral distortion, where the metallic atom lies 0.014 Å (molecule **A**) and 0.026 Å (molecule **B**) out of the coordination plane). Selected bond lengths and angles data are gathered in Table 1.

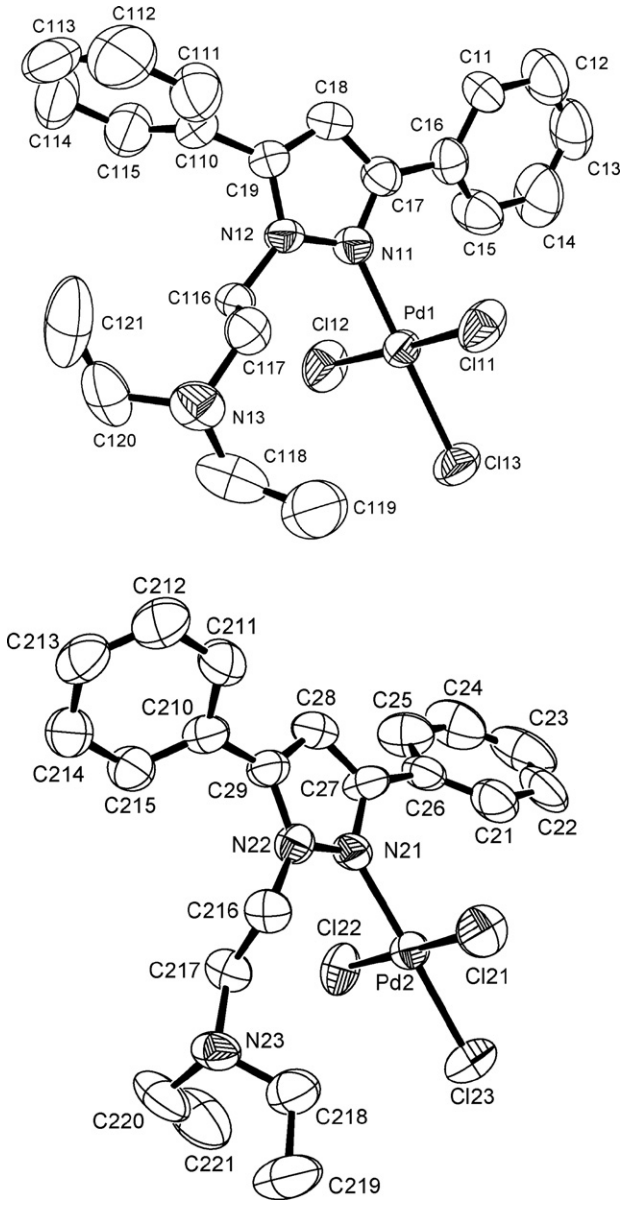

Fig. 3. ORTEP drawing of the two different molecules of complex **1b**, showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

The Pd–N and Pd–Cl bond lengths are normal compared to the values described in the literature. These values lay between 1.979–2.141 Å for Pd–Npz [15,25b,29] and 2.280–2.341 Å for Pd–Cl [10a,b,15,25b,29a–g]. The N–Pd–Cl and Cl–Pd–Cl bond angles slightly deviate from the square-planar angles. The N_{amino} atom (N(13), molecule **A**; N(23), molecule **B**) is protonated. Only one structure with $PdCl_3(N_{pz})$ *core* (containing terminal chlorine atoms) had been previously described in the literature. This compound is [$PdCl_3L'$] (L′ = 1-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(4-fluorobenzyl)-3*H*-imidazol-1-ium) [30]. Two other zwitterionic structures with pyrazolic derived ligands have been found in the literature, ([$MCl_3(L'')$]: M = Cu(II), L″ = 2-(3,5-dimethyl-1-pyrazol-yl)ethylamine [31]; M = Ni(II) , L″ = 1-1′-(dithiodiethylene)-bis-(3,5-dimethylpyrazole) [29e]).

In molecules **A** and **B,** the N_{amino}–H proton (N(13) (**A**), N(23) (**B**)) is intermolecularly hydrogen bridged to a chlorine atom (Cl(13) (**A**), Cl(22) (**B**)), from another molecule, linking the molecules into a chain. In molecule **A**, the N(13)–H bond length has been geometrically fixed in the refinement (0.91 Å) and the contact parameters

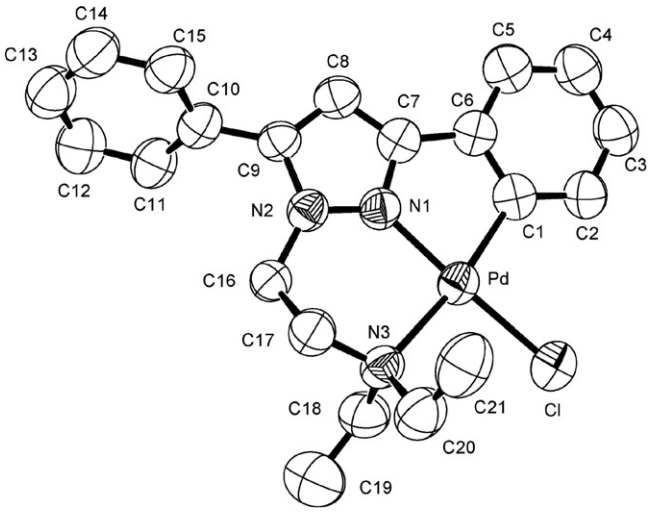

Fig. 4. ORTEP drawing of complex **1c**, showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

between N(13)–H(13)N and Cl(13) are 2.34 Å for H···Cl(13), 3.231(5) Å for N(13)···Cl(13) and 164° for N(13)–H···Cl(13). The symmetry code for molecule **A** is $1/2 - x$, $1/2 + y$, $1 - z$. In molecule **B** the N(23)–H bond length has been geometrically fixed in the refinement (0.91 Å) and the contact parameters between N(23)–H(23)N and Cl(22) are 2.32 Å for H···Cl(22), 3.184(4) Å for N(13)···Cl(22) and 158° for N(23)–H···Cl(22). The symmetry code for molecule **B** is $1/2 - x$, $1/2 + y$, $-z$.

2.5. Crystal and molecular structure of [PdCl(L1C)] (*1c*)

The crystal structure of **1c** consists of monomeric [PdCl(L1C)] molecules (Fig. 4). The palladium centre is coordinated to **L1** ligand by three atoms (one nitrogen atom of the pyrazolyl group, one nitrogen atom of the amine moiety and one deprotonated carbon of the phenyl group), along with one chlorine atom in a slightly distorted square-planar geometry. The tetrahedral distortion can be observed from the bond angles and from the mean separation (0.025 Å) of the atoms coordinated to the Pd atom in relation to the mean plane that contains these four atoms and the Pd atom. The dihedral angle between the planes N(3)–Pd–Cl and N(1)–Pd–Cl is 12.13(17)°. In this structure, **L1** ligand acts as a tridentated chelate and forms a six-membered ring and a five-membered ring, with an envelope conformation for Pd–N(1)–N(2)–C(16)–C(17)–N(3) and a plane conformation for Pd–C(1)–C(6)–C(7)–N(1), which share an edge (Pd–N_{pz}). Some selected bond lengths and bond angles for this complex are listed in Table 1.

The $PdClC(N_{pz})(N)$ *core* is present in five complexes previously described in the literature [8a–c,32]. Three of them present a Pd–C bond forming a cyclopalladated compound. Two of these compounds are [N,Csp^2, N] [8a,b] and the other one is [N,Csp^3,N] [8c]. The Pd–N_{pz} (1.977(3) Å), the Pd–N_{amino} (2.207(4) Å), the Pd–Cl (2.3108(16) Å), and the Pd–C bond length (2.014(5) Å) can be regarded as normal compared to the distances found in the literature. The Pd–C and Pd–N bond distances are consistent with those reported for a wide variety of palladacycles holding $[C,N]^-$, $[C,N,N]^-$ or $[C,N,N']^-$ ligands [27]. For Pd–Cl, the literature described values between 2.280 and 2.341 Å [8b,10a,b,15,29a–g].

3. Conclusions

The reaction of 3,5-diphenyl-*N*-alkylaminopyrazole ligands, **L1** and **L2**, with [$PdCl_2(CH_3CN)_2$] yields three different compounds for

each ligand, in one pot but two steps reaction. The reaction begins with the formation of a *N*,*N*′ chelated compound (**1a** and **2a**) as it happens with other *N*-alkylamine ligands reported in our group. Pd–N_{amino} bond lengths of compounds **1a** and **2a** are longer than the ones that have already been reported [10a,b]. The rearrangement of the chelated compounds produces two different new species in a 1:1 ratio, zwitterionic compounds (**1b** and **2b**) and cyclopalladated compounds (**1c** and **2c**). In zwitterionic complexes, the ligand is coordinated through the N_{pz} and displays the amino group in the protonated form, and Pd(II) is bonded to three chloro ligands that confer a formal negative charge to the metal centre. On the other hand, in cyclometallated compounds **1c** and **2c**, the metal centre is coordinated through the N_{pz}, the N_{amino} and a C_{phenyl}. It consists of a non-symmetrical $[Csp^2,N,N']^-$ pincer-type palladacycle. The simultaneous formation of zwitterionic and metallated products is explained by the need of acid acceptor molecules (complexes **1a** and **2a**) in the reaction medium. They act as bases that capture the aromatic proton and that are the driving force towards the cyclopalladation reaction. The method we report here is a simple pathway to obtain cyclopalladated compounds in mild conditions.

4. Experimental

4.1. General details

All reagents were commercial grade materials and were used without further purification. The reactions were carried out under nitrogen using vacuum-line and Schlenk techniques. Solvents were dried and distilled according to standard procedures and stored under nitrogen. Elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of Universitat Autònoma de Barcelona on an EuroVector 3011 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile solutions employing a CyberScan CON 500 (Euthech Instruments) conductimeter. Infrared spectra were run on a Perkin–Elmer FT spectrophotometer, series 2000 cm^{-1} as NaCl disks, KBr pellets or polyethylene films in the range 4000–100 cm^{-1}. ^1H, $^{13}C\{^1H\}$, DEPT, COSY, HMQC, and NOESY NMR spectra were recorded with a NMR-FT Bruker 250 MHz spectrometer in $CDCl_3$ or CD_3CN solutions at room temperature. All chemical shift values (δ) are given in ppm. Mass spectra (ESI+) were obtained with an Esquire 3000 ion-trap mass spectrometer from Bruker Daltonics in methanol. The complex $[PdCl_2(CH_3CN)_2]$ was synthesized according to published methods [19]. The precursor 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole was prepared as described in the literature [17].

4.2. Synthesis of the ligands 1-[2-(diethylamino)ethyl]-3,5-diphenylpyrazole (*L1*) and 1-[2-(dioctylamino)ethyl]-3,5-diphenylpyrazole (*L2*)

The synthesis consists of the reaction between 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole (1.50 g, 3.58 mmol), 23.6 mmol of the appropriate secondary amine (**L1**: diethylamine 99% , 2.5 mL; **L2**: dioctylamine 97%, 7.3 mL), and sodium hydroxide (98%, 0.85 g, 20.8 mmol). The reaction was carried out in a 20 mL solution of tetrahydrofuran:water (**L1**: 4:1; **L2**: 7:3) with continuous stirring at reflux for 48 h. The mixture was then cooled down to room temperature and extracted three times with 10 mL of chloroform. The organic phase was collected and dried overnight with anhydrous Na_2SO_4. The solution was filtered off and the solvent was removed under vacuum. **L1** ligand was obtained as pure pale-yellow oil. **L2** ligand was obtained as yellow oil that consists of a mixture of **L2** and initial secondary amine. In order to purify **L2**, a silica gel column with ethyl acetate as eluent was used. The fractions containing **L2** pure were gathered and the solvent was removed under vacuum. After evaporation pale-yellow oil was obtained. (Yield: **L1**, 47% (0.54 g); **L2**, 43% (0.75 g)).

L1: Anal. Calc. for $C_{21}H_{25}N_3$ (319.2): C, 78.96; H, 7.89; N, 13.15. Found: C, 78.73; H, 7.61; N, 12.95%. ν_{max} (NaCl)/cm^{-1} 3040 ν(C–H)$_{ar}$, 2971–2806 ν(C–H)$_{al}$, 1602 ν(C=C)$_{ph}$, 1547 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1460, 1432 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1070 δ(C–H)$_{ip}$, 761, 693 δ(C–H)$_{oop\ ar}$. ^1H NMR (250 MHz, $CDCl_3$; 298 K): 7.78 (d, 2H, ^3J = 8.1 Hz, H_7, H_{11}), 7.39 (m, 8H, H_{8-10} , H_{13-17}), 6.49 (s, 1H, H_4), 4.14 (t, 2H, ^3J = 7.2 Hz, H_{18}), 3.37 (q, 4H, ^3J = 7.1 Hz, $N_{amino}(CH_2CH_3)_2$), 2.82 (t, 2H, ^3J = 7.2 Hz, H_{19}), 0.82 (t, 6H, ^3J = 7.1 Hz, $N_{amino}(CH_2CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 151.0, 145.7, 134.1, 131.4 (C_3, C_5, C_6, C_{12}), 129.5–126.0 (C_{7-11}, C_{13-17}), 103.7 (C_4), 53.4 (C_{19}), 48.7 (C_{18}), 48.0 ($N_{amino}(CH_2CH_3)_2$), 12.3 ($N_{amino}(CH_2CH_3)_2$) ppm. *m/z* (ESI+) 342.1 (MNa^+) (33%), 326.1 (MLi^+) (100%), 320.1 (MH^+) (88%).

L2: Anal. Calc. for $C_{33}H_{49}N_3$ (487.4): C, 81.26; H, 10.13; N, 8.61. Found: C, 80.99; H, 9.84; N, 8.59%. ν_{max} (NaCl)/cm^{-1} 3061 ν(C–H)$_{ar}$, 2925–2854 ν(C–H)$_{al}$, 1607 ν(C=C)$_{ph}$, 1549 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1485, 1462 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 760, 693 δ(C–H)$_{oop\ ar}$. ^1H NMR (250 MHz, $CDCl_3$; 298 K): 7.89 (d, 2H, ^3J = 7.2 Hz, H_7, H_{11}), 7.44 (m, 8H, H_{8-10}, H_{13-17}), 6.61 (s, 1H, H_4), 4.25 (t, 2H, ^3J = 7.1 Hz, H_{18}), 2.91 (t, 2H, ^3J = 7.1 Hz, H_{19}), 2.35 (t, 4H, ^3J = 7.0 Hz, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 1.26 (br, 24H, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 0.93 (t, 6H, ^3J = 7.0 Hz, $N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 151.0, 145.6, 134.1, 131.4 (C_3, C_5, C_6, C_{12}), 129.5–126.0 (C_{7-11}, C_{13-17}), 103.7 (C_4), 55.2 (C_{18}), 54.4 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 48.7 ($C_{19}$), 32.3–23.1 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 14.5 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. *m/z* (ESI+) 488.4 (MH^+) (100%).

4.3. Synthesis of the complexes $[PdCl_2(L)]$ (L = L1 (*1a*), L = L2 (*2a*)), $[PdCl_3LH]$ (LH = L1H (*1b*), L = L2H (*2b*)), [PdCl(LC)] (LC = L1C (*1c*), L = L2C (*2c*))

4.3.1. Synthesis of complexes *1a* and *2a*

A solution of 0.27 mmols of the corresponding ligand (**L1** (0.086 g); **L2** (0.130 g)) dissolved in 10 mL of dry dichloromethane was added to a solution of 0.27 mmols (0.070 g) of $[PdCl_2(CH_3CN)_2]$ in 10 mL of the same solvent. The solution was stirred for 24 h at room temperature. The resultant solution was concentrated to 5 mL under vacuum and 3 mL of cool and dry diethyl ether was added to induce precipitation. The resulting precipitate (**1a** and **2a**, respectively) was filtered and washed twice with 3 mL of cool and dry diethyl ether, and dried under vacuum. The ratio 1 M:2 L has also been tested, and showed the same results. (Yield: **1a**, 48% (0.064 g); **2a**, 55% (0.098%)).

4.3.2. Synthesis of complexes *1b*, *2b* and *1c*, *2c*

A solution of 0.27 mmols of the corresponding ligand (**L1** (0.086 g); **L2** (0.130 g)) dissolved in 10 mL of dry dichloromethane was added to a solution of 0.27 mmol (0.070 g) of $[PdCl_2(CH_3CN)_2]$ in 10 mL of the same solvent. The solution was stirred at room temperature for 72 h and ^1H NMR controls were made every 24 h. Controls show the evolution of three species on the reaction. As the reaction progresses, the molar ratios **1b**:**1a**, **1c**:**1a** and **2b**:**2a** and **2c**:**2a** increase. For the reaction with the ligand **L1** a precipitate appeared in the solutions (**1b**), and for the reaction with the ligand **L2** the precipitation of **2b** was induced by adding 5 mL of cool and dry diethyl ether to the solution. Solids were filtered off and washed three times with 5 mL of dry dichloromethane and dried under vacuum. The resultant solutions were reduced to 5 mL, and 3 mL of cool and dry diethyl ether was added to induce the precipitation of a brown solid. The resulting precipitate (**1c**/**2c**) was filtered and washed twice with 3 mL of cool and dry diethyl

ether and dried under vacuum. (Yield: **1b**, 39% (0.059 g), **1c**, 30% (0.037 g); **2b**, 45% (0.085 g), **2c** 23% (0.039 g)).

*4.3.3. Alternative synthesis of complexes **1c** and **2c***

(a) A solution of 0.27 mmols of the corresponding ligand (**L1** (0.086 g); **L2** (0.130 g)) dissolved in 10 mL of dry acetonitrile was added to a solution of 0.27 mmol (0.070 g) of $[PdCl_2(CH_3CN)_2]$ in 10 mL of the same solvent. The solution is left under reflux for 24 h giving rise to the carbopalladated species. The solution was reduced to 5 mL, and 3 mL of cool and dry diethyl ether was added to induce the precipitation of **1c** and **2c**, respectively. Solids were washed twice with 3 mL of cool and dry diethyl ether and dried under vacuum. (Yield: **1c**, 42% (0.052 g), **2c**, 46% (0.078 g)).

(b) A solution of 0.27 mmols of the corresponding ligand (**L1** (0.086 g); **L2** (0.130 g)) dissolved in 10 mL of dry dichloromethane was added to a solution of 0.27 mmol (0.070 g) of $[PdCl_2(CH_3CN)_2]$ in 10 mL of the same solvent. 0.27 mmol of triethylamine (99%, 0.028 g) was added to the solution and almost immediately a white solid corresponding to Et_3HNCl appeared. The solution was filtered and stirred at room temperature for 24 h. ^{1}H NMR controls show the evolution of two species on the reaction. As the reaction progresses the molar ratio **1c**/**2c**:**1a**/**2a** (carbopalladated compounds:chelated compounds) increases. The solution was reduced to 5 mL, and 3 mL of cool and dry diethyl ether was added to induce the precipitation of some impurities. The resulting filtered solutions containing **1c** and **2c**, respectively, were reduced to 5 mL and 5 mL of dry diethyl ether were added to induce precipitation of **1c**/**2c**. Solids were washed twice with 3 mL of cool and dry diethyl ether and dried under vacuum. (Yield: **1c**, 50% (0.062 g), 2**c**, 49% (0.083 g)).

1a: Anal. Calc. for $C_{21}H_{25}Cl_2N_3Pd$ (495.0): C, 50.77; H, 5.07; N, 8.46. Found: C, 50.83; H, 5.32; N, 8.17%. Ω^{-1} cm^2 mol^{-1} (1.1×10^{-3} M in acetonitrile) 7.5. ν_{max} (KBr)/cm^{-1} 3058 ν(C–H)$_{ar}$, 2959–2853 ν(C–H)$_{al}$, 1620 ν(C=C)$_{ph}$, 1547 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1476, 1469, 1447 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1004 δ(C–H)$_{ip}$, 760, 695 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 449 ν(Pd–N), 335, 326 ν(Pd–Cl). ^{1}H NMR (250 MHz, $CDCl_3$; 298 K): 8.31 (d, 2H, ^3J = 7.1 Hz, H_7, H_{11}), 7.53 (m, 8H, H_{8-10}, H_{13-17}), 6.81 (s, 1H, H_4), 4.87 (br, 2H, H_{18}), 3.42 (br, 2H, H_{19}), 2.87 (m, 2H, $N_{amino}(CH_2CH_3)_2$), 2.65 (br, 2H, $N_{amino}(CH_2CH_3)_2$), 1.57 (br, 6H, $N_{amino}(CH_2CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 156.6, 148.6, 132.7, 130.5 (C_3, C_5, C_6, C_{12}), 129.5–125.7 (C_{7-11}, C_{13-17}), 107.5 (C_4), 56.5 (C_{18}), 50.6 (C_{19}), 47.6 ($N_{amino}(CH_2CH_3)_2$), 12.2 ($N_{amino}(CH_2CH_3)_2$) ppm. *m/z* (ESI+) 424.1 (Pd(L1C)$^+$) (100%).

1b: Anal. Calc. for $C_{21}H_{26}Cl_3N_3Pd \cdot 1/4CH_2Cl_2 \cdot 1/4\ CH_3CN$ (564.7): C, 46.29; H, 4.86; N, 8.06. Found: C, 46.58; H, 4.84; N, 8.05%. Ω^{-1} cm^2 mol^{-1} (1.0×10^{-3} M in acetonitrile) 84.0. ν_{max} (KBr)/cm^{-1} 3114 ν(C–H)$_{ar}$, 2983–2849 ν(C–H)$_{al}$, 2695 ν(N–H$^+$), 1613 δ(N–H$^+$), 1587 ν(C=C)$_{ph}$, 1554 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1482, 1462, 1443 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1378 δ(CH$_3$), 1016 δ(C–H)$_{ip}$, 771, 698 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 411 ν(Pd–N), 335 ν(Pd–Cl). ^{1}H NMR (250 MHz, CD_3CN; 298 K): 8.65 (br, 1H, H_{20}), 7.87 (d, 2H, ^3J = 7.6 Hz, H_7, H_{11}), 7.55 (m, 8H, H_{8-10}, H_{13-17}), 6.86 (s, 1H, H_4), 4.49 (t, 2H, ^3J = 4.7 Hz, H_{18}), 3.58 (q, 2H, ^3J = 4.7 Hz, H_{19}), 3.34 (m, 4H, $N_{amino}(CH_2CH_3)_2$), 1.32 (t, 6H, ^3J = 7.0 Hz, $N_{amino}(CH_2CH_3)_2$) ppm. ^{13}C NMR (63 MHz, CD_3CN; 298 K): 129.8–126.0 (C_3, C_{5-11}, C_{12-17}), 104.3 (C_4), 52.5 ($N_{amino}(CH_2CH_3)_2$), 48.2 (C_{18}), 30.3 (C_{19}), 8.8 ($N_{amino}(CH_2CH_3)_2$) ppm. *m/z* (ESI+) 424.1 (Pd(L1C)$^+$) (100%).

1c: Anal. Calc. for $C_{21}H_{24}ClN_3Pd$ (459.1): C, 54.79; H, 5.26; N, 9.13. Found: C, 54.62; H, 5.55; N, 9.09%. Ω^{-1} cm^2 mol^{-1} (1.4×10^{-3} M in acetonitrile) 6.7. ν_{max} (KBr)/cm^{-1} 3114–3040 ν(C–H)$_{ar}$, 2959–2853 ν(C–H)$_{al}$, 1580, 1539 ν(C=C)$_{ph}$, 1506 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1451 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1015 δ(C–H)$_{ip}$, 761, 724, 695 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 418 ν(Pd–N), 279 ν(Pd–Cl). ^{1}H NMR (250 MHz, $CDCl_3$; 298 K): 7.93 (d, 1H, ^3J = 7.1 Hz, H_{11}), 7.46, 7.01 (m, 8H, H_{8-10}, H_{13-17}), 6.49 (s, 1H, H_4), 4.30 (m, 2H, H_{18}), 3.46 (m, 2H, $N_{amino}(CH_2CH_3)_2$), 3.13 (m, 2H, H_{19}), 3.01 (m, 2H, $N_{amino}(CH_2CH_3)_2$), 1.32 (t, 6H, ^3J = 7.1 Hz, $N_{amino}(CH_2CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 159.4, 148.6, 145.2, 137.5 (C_3, C_5, C_6, C_{12}), 136.8 (C_7), 129.9–122.2 (C_{8-11}, C_{13-17}), 101.2 (C_4), 50.9 ($N_{amino}(CH_2CH_3)_2$), 50.7 (C_{19}), 44.8 (C_{18}), 10.4 ($N_{amino}(CH_2CH_3)_2$) ppm. *m/z* (ESI+) 424.1 (Pd(L1C)$^+$) (100%).

2a: Anal. Calc. for $C_{33}H_{49}Cl_2N_3Pd$ (663.2): C, 59.59; H, 7.43; N, 6.32. Found: C, 59.71; H, 7.41; N, 6.56%. Ω^{-1} cm^2 mol^{-1} (9.8×10^{-4} M in acetonitrile) 11.4. ν_{max} (KBr)/cm^{-1} 3048 ν(C–H)$_{ar}$, 2924, 2853 ν(C–H)$_{al}$, 1605 ν(C=C)$_{ph}$, 1552 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1480, 1467, 1453 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1019 δ(C–H)$_{ip}$, 762, 693 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 441 ν(Pd–N), 330, 319 ν(Pd–Cl). ^{1}H NMR (250 MHz, $CDCl_3$; 298 K): 8.33 (d, 2H, ^3J = 7.6 Hz, H_7, H_{11}), 7.33 (m, 8H, H_{8-10} , H_{13-17}), 6.61 (s, 1H, H_4), 4.86 (br, 2H, H_{18}), 3.51 (br, 2H, H_{19}), 2.63 (br, 4H, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 1.27 (br, 24H, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 0.88 (t, 6H, ^3J = 7.0 Hz, $N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 156.9, 147.8, 131.3, 130.4 (C_3, C_5, C_6, C_{12}), 129.6–125.4 (C_{7-11}, C_{13-17}), 107.7 (C_4), 58.4 (C_{19}), 49.9 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 31.9 ($C_{18}$), 31.7–21.6 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 14.2 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. *m/z* (ESI+) 592.3 (Pd(L2C)$^+$) (100%).

2b: Anal. Calc. for $C_{33}H_{50}Cl_3N_3Pd$ (699.2): C, 56.50; H, 7.18; N, 5.99. Found: C, 56.71; H, 7.28; N, 6.06%. Ω^{-1} cm^2 mol^{-1} (1.2×10^{-3} M in acetonitrile) 68.2. ν_{max} (KBr)/cm^{-1} 3114–3040 ν(C–H)$_{ar}$, 2984–2855 ν(C–H)$_{al}$, 2693 ν(N–H$^+$), 1624 δ(N–H$^+$),1609 ν(C=C)$_{ph}$, 1553 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1451 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1076 δ(C–H)$_{ip}$, 759, 696 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 444 ν(Pd–N), 340 ν(Pd–Cl). ^{1}H NMR (250 MHz, CD_3CN; 298 K): 9.05 (br, 1H, H_{20}), 7.89 (d, 2H, ^3J = 7.2 Hz, H_7, H_{11}), 7.58 (m, 8H, H_{8-10}, H_{13-17}), 6.89 (s, 1H, H_4), 4.54 (t, 2H, ^3J = 4.4 Hz, H_{18}), 3.61 (q, 2H, ^3J = 4.4 Hz, H_{19}), 3.23 (br, 8H, $N_{amino}((CH_2)_2(CH_2)_5CH_3)_2$), 1.30 (br, 20H, $N_{amino}((CH_2)_2(CH_2)_5CH_3)_2$), 0.89 (t, 6H, ^{3}J = 7.2 Hz, $N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. ^{13}C NMR (63 MHz, CD_3CN; 298 K): 155.6, 148.3, 131.4, 130.7 (C_3, C_5, C_6, C_{12}), 130.0–128.9 (C_{7-11}, C_{13-17}), 108.9 (C_4), 54.2 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 52.8 ($C_{19}$), 45.3 ($C_{18}$), 32.1, 23.0 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 14.5 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. *m/z* (ESI+) 592.3 (Pd(L2C)$^+$) (100%).

2c: Anal. Calc. for $C_{33}H_{48}ClN_3Pd$ (627.3): C, 63.05; H, 7.70; N, 6.68. Found: C, 62.73; H, 7.61; N, 6.57%. Ω^{-1} cm^2 mol^{-1} (1.1×10^{-3} M in acetonitrile) 19.5. ν_{max} (KBr)/cm^{-1} 3108–3054 ν(C–H)$_{ar}$, 2956–2853 ν(C–H)$_{al}$, 1587, 1540 ν(C=C)$_{ph}$, 1511 ν(C=C)$_{pz}$, ν(C=N)$_{pz}$, 1465, 1454, 1421 δ(C=C)$_{ar}$, δ(C=N)$_{ar}$, 1025 δ(C–H)$_{ip}$, 759, 689 δ(C–H)$_{oop\ ar}$. ν_{max} (polyethylene)/cm^{-1} 417 ν(Pd–N), 279 ν(Pd–Cl). ^{1}H NMR (250 MHz, $CDCl_3$; 298 K): 7.92 (1H, m, H_{11}), 7.33 (8H, m, H_{8-10}, H_{13-17}), 6.49 (1H, s, H_4), 4.28 (2H, m, H_{18}), 3.33 (2H, m, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 3.15 (2H, m, H_{19}), 2.62 (2H, m, $N_{amino}(CH_2(CH_2)_6CH_3)_2$), 1.25 (24H, br, N_{amino}-$(CH_2(CH_2)_6CH_3)_2$), 0.87 (6H, t, ^3J = 7.0 Hz, $N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$; 298 K): 159.5, 148.6, 137.5, 136.9 (C_3, C_5, C_6, C_{12}), 145.2 (C_7), 130.0–122.2 (C_{8-11}, C_{13-17}), 101.2 (C_4), 57.6 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 51.9 ($C_{19}$), 45.0 ($C_{18}$), 31.9–22.8 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$), 10.4 ($N_{amino}(CH_2(CH_2)_6CH_3)_2$) ppm. *m/z* (ESI+) 592.3 (Pd(L2C)$^+$) (100%).

*4.4. X-ray crystal structure analyses of complexes **1a**, **1b** · 1/4CH_2Cl_2 · 1/4CH_3CN and **1c***

Suitable crystals for X-ray diffraction of compounds **1a**, **1b** and **1c** were obtained through crystallization from a dichloromethane/diethyl ether (2:1) mixture.

For compound **1a**, a prismatic crystal was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21°$) and refined by least-squares method. For com-

pounds **1b** · 1/4CH_2Cl_2 · 1/4CH_3CN and **1c**, a prismatic crystal was selected and mounted on a MAR 345 diffractometer with an image plate detector. Unit-cell parameters were determined from 2594 reflections for **1b** and 2167 reflections for **1c** ($3 < \theta < 31°$) and refined by least-squares method.

Intensities were collected with graphite monochromatized Mo Kα radiation, using $\omega/2\theta$ scan-technique. For **1a**, 13 118 reflections were measured in the range $2.24 \leqslant \theta \leqslant 29.99$ and 6193 of which were non-equivalent by symmetry (R_{int}(on I) = 0.037). Reflections (2250) were assumed as observed applying the condition $I \geqslant 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. For **1b**, 59 442 reflections were measured in the range $2.63 \leqslant \theta \leqslant 30.00$ and 15 023 reflections of which were non-equivalent by symmetry (R_{int}(on I) = 0.098). Reflections (10 116) were assumed as observed applying the condition $I > 2\sigma(I)$. For **1c**, 34 736 reflections were measured in the range $2.83 \leqslant \theta \leqslant 30.00$ and 5649 of which were non-equivalent by symmetry (R_{int}(on I) = 0.055). Reflections (5627) were assumed as observed applying the condition $I \geqslant 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made.

The structures were solved by direct methods, using SHELXS computer program (SHELXS-97) [33] and refined by full matrix least-squares method with SHELXL-97 [34] computer program using 13 118 reflections for **1a**, 59 442 reflections for **1b** and 34 736 reflections for **1c** (very negative intensities were not assumed). The function minimized was $\sum w||F_0^2 - |F_C|^2|^2$, where for **1a** $w = [\sigma^2(I) + 0.0432P]^2]^{-1}$, for **1b** $w = [\sigma^2(I) + (0.0907P)^2 + 0.5167P]^{-1}$ and for **1c** $w = [\sigma^2(I) + 5.4658P]^{-1}$ and $P = (|F_O|^2 + 2|F_C|^2)/3$ for all the structures. For **1a** and **1c**, all H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which is linked. For **1b**, all H atoms were computed and refined with an overall isotropic temperature.

The final $R(F)$ factor and $R_w(F^2)$ values as well as the number of parameters refined and other details concerning the refinement of the crystal structure are gathered in Table 2.

Table 2
Crystallographic data for **1a**, **1b** · 1/4 CH_2Cl_2 · 1/4 CH_3CN and **1c**

	1a	1b	1c
Formula	$C_{21}H_{25}Cl_2N_3Pd$	$C_{87}H_{109}N_{13}Cl_{14}Pd_4$	$C_{21}H_{24}N_3ClPd$
Formula weight	496.74	2258.77	460.28
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
System, space group	Orthorhombic *Pbca*	Monoclinic $P2_1/a$	Orthorhombic *Pbca*
Unit-cell dimensions			
a (Å)	14.705(7)	20.553(7)	12.578(6)
b (Å)	20.909(7)	13.765(4)	14.840(5)
c (Å)	13.832(6)	20.546(4)	21.747(8)
α (°)	90	90	90
β (°)	90	114.62(2)	90
γ (°)	90	90	90
U (Å^3)	4253(3)	5284(3)	4059(3)
Z	8	2	8
D_{calc} (g cm^{-3})	1.552	1.420	1.506
μ (mm^{-1})	1.135	1.069	1.055
F(000)	2016	2288	1872
Crystal size (mm^3)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
hkl ranges	$-19 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 29$, $0 \leqslant l \leqslant 20$	$-30 \leqslant h \leqslant 30$, $-20 \leqslant k \leqslant 20$, $-30 \leqslant l \leqslant 30$	$-17 \leqslant h \leqslant 18$, $-22 \leqslant k \leqslant 22$, $-32 \leqslant l \leqslant 32$
2θ Range (°)	2.24–29.99	2.63–30.00	2.83–30.00
Reflections collected/ unique [$R_{(int)}$]	13 118/6193 [0.0379]	59 442/15 023 [0.0983]	34 736/5649 [0.0552]
Completeness to θ (%)	99.9% (θ = 29.99°)	97.4% (θ = 30.00°)	95.4% (θ = 30.00°)
Absorption correction	None	Empirical	Empirical
Maximum and minimum transmission	0.337 and 0.282	0.89 and 0.87	0.901 and 0.87
Data/restrains/parameters	6193/0/244	15023/6/562	5649/2/237
Goodness-of-fit on F^2 (GOF)	0.930	1.120	1.549
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0578, wR_2 = 0.1101	R_1 = 0.0667, wR_2 = 0.1749	R_1 = 0.0659, wR_2 = 0.0976
R indices (all data)	R_1 = 0.2220, wR_2 = 0.1518	R_1 = 0.1116, wR_2 = 0.1963	R_1 = 0.0659, wR_2 = 0.0976
Largest difference peak and hole (e Å^{-3})	0.978 and −0.804	0.924 and −0.699	0.517 and −0.354

Supplementary material

CCDC 675557, 675558 and 675559 contains the supplementary crystallographic data for **1a**, **1b** and **1c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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