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Synthesis and Characterization of New *N*-Alkylamino-3,5-diphenylpyrazole Ligands and Reactivity Toward Pd^{II} and Pt^{II}. Study of the *cis–trans* Isomerization

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In this paper, the synthesis and characterization of two new *N*-alkylaminopyrazole ligands, 1-[2-(ethylamino)ethyl]-3,5-diphenylpyrazole (dpea) and 1-[2-(octylamino)ethyl]-3,5-diphenylpyrazole (dpoa) are reported. The reaction of these ligands with $[MCl_2(CH_3CN)_2]$ (M = Pd^{II}, Pt^{II}) affords the following square planar complexes: *cis*-$[MCl_2(NN')]$ (M = Pd^{II}: NN' = dpea, **1**; dpoa, **2**; M = Pt^{II}: NN' = dpea, **3**; dpoa, **4**). Reaction of $[PdCl_2(CH_3CN)_2]$ and dpea or dpoa in 1:2 M:NN′ molar ratio, in the presence of $NaBF_4$, yields complexes $[Pd(NN')_2](BF_4)_2$ (NN' = dpea, [**5**](BF4)$_2$); dpoa, [**6**](BF4)$_2$). The solid-state structures of complexes **1**, **3**, and [**5**](BF$_4$)$_2$ have been determined by single-crystal X-ray diffraction methods. In complexes **1** and **3**, the dpea ligand is coordinated through the N_{pz} and N_{amino} atoms to the metallic centre, which completes its coordination with two chlorine atoms in a *cis* disposition. For complex [**5**](BF$_4$)$_2$, the crystal structure consists of cations involving a $[Pd(N_{pz})_2(N_{amino})_2]^{2+}$ core with a *cis* disposition of the two dpea ligands in a square-planar geometry and BF_4^- anions. Theoretical calculations were carried out to optimize the geometries of the *cis* and *trans* isomers of the $[Pd(dpea)_2]^{2+}$ cation and of the $[Pd(dpea)_2](BF_4)_2$ complex. The results show that the *trans* isomer is the most stable for $[Pd(dpea)_2]^{2+}$, in contrast with the *cis* stereochemistry observed in the crystal structure of $[Pd(dpea)_2](BF_4)_2$. The calculations also predict that in acetonitrile solution, the dissociation of this complex into the corresponding ions is thermodynamically favourable. The *cis–trans* isomerization process of $[Pd(dpea)_2]^{2+}$ in acetonitrile solution has been studied by NMR spectroscopy at different temperatures. These experimental results confirm that the *trans* isomer is the thermodynamically most stable form of the complexes [**5**](BF$_4$)$_2$ and [**6**](BF$_4$)$_2$.

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Introduction

The coordination study of amino ligands, and basically of chelating nitrogen donor atoms, is of great importance owing to the information that it provides to understand these systems in nature and to indicate new roles for metal ions in therapeutic strategies.[1] Moreover, the coordination of these kinds of ligands with some specific metals like palladium, platinum, or zinc allows the isolation of new compounds with applications in different fields such as catalysis[2] and luminescence,[3] and also as therapeutic agents.[4]

It is necessary to emphasize the importance of the relationship between the structure (*cis/trans* isomer) and the activity of the coordination compounds, mostly for medical applications.[5] For this reason, it is important to continue the characterization and structural studies of such complexes.

Heterocyclic compounds containing nitrogen donor atoms and alkylamino chains, such as *N*-alkylaminopyrazole ligands and their coordination with Ni^{II}, Cu^{II}, and Co^{II}, have been widely studied by Driessen et al.[6] This information has been complemented by other compounds presented by Mukherjee.[7]

In this context, our group has reported, in recent years, the synthesis and bonding properties of several new *N*-alkylamino-3,5-dimethylpyrazole ligands (NN': 1-(2-(isopropylamino) ethyl)-3,5-dimethylpyrazole and 1-(2-(*tert*-butylamino)ethyl)-3,5-dimethylpyrazole; $NN'N$: bis((3,5-dimethyl-1-pyrazolyl) methyl)isopropylamine, bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl) isopropylamine, and bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)*tert*-butylamine) toward Pd^{II},[8] Pt^{II},[9] Rh^{I},[10] and Zn^{II}.[11]

Moreover, we recently synthesized four *N*-alkylamino-pyrazole ligands containing phenyl groups in the 3 and 5 positions of the pyrazole ring (NN': 1-(2-(diethylamino)ethyl)-3,5-diphenylpyrazole and 1-(2-(dioctylamino)ethyl)-3,5-diphenyl-pyrazole; $NN'N$: bis(2-(3,5-diphenyl-1-pyrazolyl)ethyl)amine

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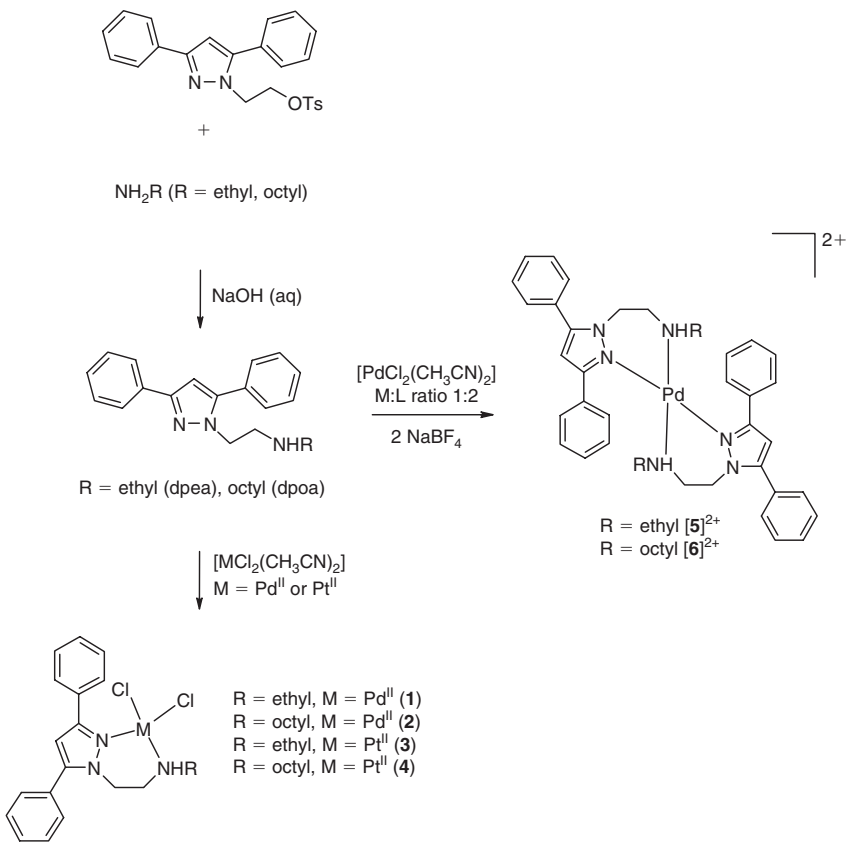

Scheme 1.

and bis(2-(3,5-diphenyl-1-pyrazolyl)ethyl)ethylamine) and studied their reactivity toward Pd^{II}.[12]

The presence of one alkyl-chain group instead of two at the amine moiety is expected to affect the ability of the ligand to coordinate the metal centre. With the aim of extending our last work, and in order to evaluate this effect on the ligand coordination mode, in the current paper, we present the synthesis and characterization of two new *N*-alkylamino-3,5-diphenylpyrazole ligands: 1-(2-(ethylamino)ethyl)-3,5-diphenylpyrazole (dpea) and 1-(2-(octylamino)ethyl)-3,5-diphenylpyrazole (dpoa), along with the study of their reactivity toward $[MCl_2(CH_3CN)_2]$ ($M = Pd^{II}$, Pt^{II}), obtaining the complexes $[MCl_2(NN')]$ ($M = Pd^{II}$, Pt^{II}; $NN' =$ dpea, dpoa). We also report the preparation and spectroscopic properties of complexes $[Pd(NN')_2](BF_4)_2$ ($NN' =$ dpea, dpoa) (Scheme 1). Structural studies of these complexes are also presented. The *cis* and *trans* isomers of $[Pd(dpea)_2]^{2+}$ and $[Pd(dpea)_2](BF_4)_2$ have been studied through theoretical calculations and the results have been used to rationalize the experimental observations.

Results and Discussion

Synthesis and Characterization of the Ligands

The dpea and dpoa ligands were obtained from the reaction of 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole[13] with the appropriate primary amine (dpea: ethylamine; dpoa: octylamine) in the presence of sodium hydroxide in a tetrahydrofuran (THF):water solution (dpea, 4:1; dpoa, 7:3). Both products were obtained as yellow oils. The dpoa ligand was further purified by chromatography (silica gel 60 Å) with ethyl acetate as eluent.

The ligands were characterized by elemental analyses, mass spectrometry and IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR signals were assigned by reference to the literature[14] and from Distortionless Enhancement by Polarization Transfer (DEPT), COrrelation SpectroscopY (COSY), and Heteronuclear Multiple Quantum Coherence (HMQC) NMR experiments.

Synthesis and Characterization of the Complexes $[MCl_2(NN')]$ ($M = Pd^{II}$ or Pt^{II})

The reaction of $[MCl_2(CH_3CN)_2]$ ($M = Pd^{II}$ or Pt^{II}) with the corresponding ligand (NN′), dpea or dpoa, in a 1:1 or 1:2 M:NN′ molar ratio in dichloromethane for Pd^{II} or acetonitrile for Pt^{II} complexes, yields compounds $[MCl_2(NN')]$ ($M = Pd^{II}$: $NN' =$ dpea, **1**; dpoa, **2**; $M = Pt^{II}$: $NN' =$ dpea, **3**; dpoa, **4**). Stoichiometries of these complexes do not depend on the M:NN′ molar ratio.

Several techniques were used for the characterization of the complexes: elemental analyses, mass spectrometry, conductivity measurements, IR, ^1H, $^{13}C\{^1H\}$, $^1H\{^{195}Pt\}$, and $^{195}Pt\{^1H\}$ NMR spectroscopy and X-ray diffraction methods. The NMR signals were assigned from DEPT, COSY, HMQC, and nuclear Overhauser effect correlation spectroscopy (NOESY) NMR experiments.

The elemental analyses for complexes **1**–**4** are in agreement with the formula $[MCl_2(NN')]$. Electrospray ionization mass spectrometry (MS-ESI+) spectra of compounds **1**–**4** give peaks with *m/z* values of 396 (100%) for **1**, 480 (100%) for **2**, 484 (76%) for **3**, and 568 (100%) for **4**, attributable to $[MCl_2(NN')–HCl–Cl]^+$. Moreover, for compound **3**, a peak with *m/z* value of 580 (100%), attributable to $[PtCl_2(dpea) + Na]^+$, is observed.

These peaks are observed with the same isotopic distribution as the theoretical one.

Conductivity values for 10^{-3} M solutions of **1**–**4**, in acetonitrile, are in agreement with a non-electrolyte nature of the complexes (1.8–12.7 Ω^{-1} cm^2 mol^{-1}).[15]

The IR spectra of complexes **1**–**4**, in the range 4000–400 cm^{-1}, show signals corresponding to the coordinated ligands. The most characteristic bands are those attributable to the pyrazolyl group: ν(C=C), ν(C=N), and δ(C–H)$_{oop}$. Another relevant band is the one attributable to ν(N–H). The IR spectra of complexes **1**–**4** in the 600–100 cm^{-1} region were also recorded. Complexes **1** and **2** show one band corresponding to ν(Pd–N) at 398 and 405 cm^{-1}, respectively, and two well-defined ν(Pd–Cl) bands at 335, 326 cm^{-1} and 330, 318 cm^{-1}, for **1** and **2** respectively, which are typical of compounds with a *cis* disposition of the chlorine atoms around Pd^{II}. Likewise, complexes **3** and **4** show one band corresponding to ν(Pt–N) at 404 and 407 cm^{-1}, respectively, and two ν(Pt–Cl) bands at 337, 328 cm^{-1}, and 336, 329 cm^{-1}, respectively, typical of compounds with a *cis* disposition of the chlorine atoms around the Pt^{II}.[16]

The ^{1}H, ^{13}C{^{1}H}, DEPT, COSY, HMQC, and NOESY NMR spectra were recorded in $CDCl_3$ for **1** and **2**, and in CD_3CN for **3** and **4**. The ^{1}H{^{195}Pt} and ^{195}Pt{^{1}H} NMR spectra for **3** and **4** were also recorded. NMR spectroscopic data are reported in the Experimental section. ^{1}H{^{195}Pt}NMR spectra of complexes **3** and **4** show the same signals (chemical shift and multiplicity) as the ^{1}H NMR spectra, suggesting that no coupling between the Pt^{II} atom and the hydrogens of the ligands takes place.

In the ^{1}H NMR spectra of complexes **1**–**4**, the two protons of each CH_2 group of the N_{pz}–CH_2–CH_2–N_{amino} chain are diastereotopic, thus giving rise to four groups of signals, each one attributable to a single hydrogen atom. This happens because of the rigid conformation of the ligand once it has been complexed. These signals appeared as four poorly defined signals and could not be further studied. HMQC spectra were useful in order to assign the protons that correspond to the same CH_2 group.

Additional ^{195}Pt{^{1}H} NMR experiments for complexes **3** and **4** at 298 K were also recorded in CD_3CN and displayed only one signal for each complex, at $\delta = -2008$ ppm for **3** and -2106 ppm for **4**. These values appear in the range described in the literature for complexes with a [$PtCl_2N_2$] core (between -2447 and -1198 ppm).[9,17,18]

Crystal structures of [**1**]·CH_2Cl_2 and [**3**]·CH_2Cl_2 consist of discrete [MCl_2(dpea)] (M = Pd^{II}, **1**; M = Pt^{II}, **3**) units and solvent molecules (CH_2Cl_2) linked by van der Waals forces (Figs 1 and 2, respectively).

The metal atom (Pd^{II} or Pt^{II}) is surrounded by an identical core composed of the N_{pz} and an N_{amino} of one dpea ligand and two chlorine atoms in a slightly distorted square-planar geometry, with the chlorine atoms in *cis* disposition. The tetrahedral distortion can be observed from the bond angles and from the largest deviation to the mean plane (0.054(3) Å (**1**) and 0.050(4) Å (**3**)) of the atoms coordinated to Pd^{II} (**1**) or Pt^{II} (**3**). In both complexes, the dpea ligand acts as a bidentate chelate, forming a six-membered metallacycle ring, with twist-boat conformation for M–N(1)–N(2)–C(16)–C(17)–N(3) (M = Pd^{II}, **1**; Pt^{II}, **3**). Selected bond lengths and bond angles for both structures are listed in Table 1.

The $PdCl_2N_{pz}N_{amino}$ (terminal chlorine, aliphatic amine) core is found in the literature as part of five crystal structures.[19] We recently published three of these structures: [$PdCl_2$(deae)],

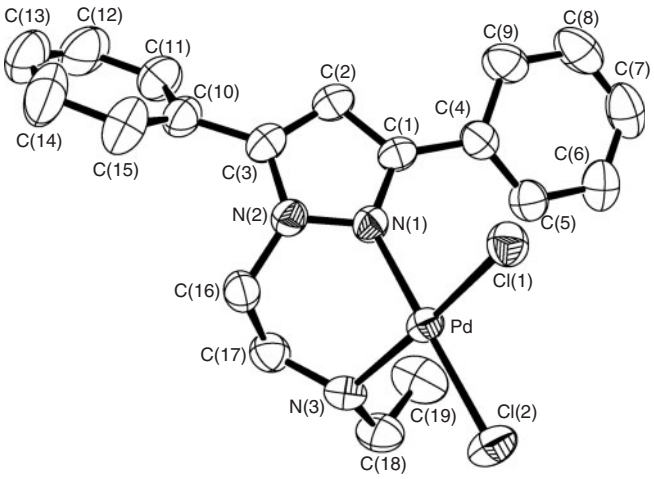

Fig. 1. *ORTEP* drawing of [$PdCl_2$(dpea)]·CH_2Cl_2, showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

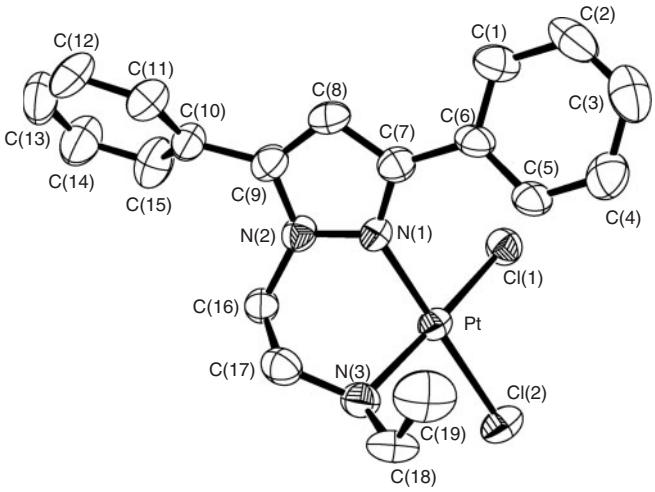

Fig. 2. *ORTEP* drawing of [$PtCl_2$(dpea)]·CH_2Cl_2, showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Table 1. Selected bond lengths [Å] and bond angles [°] for [MCl_2(dpea)]·CH_2Cl_2 (M = Pd^{II} [1**]·CH_2Cl_2, M = Pt^{II} [**3**]·CH_2Cl_2) and for [**5**]$(BF_4)_2$**

1		**3**	
Pd–N(1)	2.021(3)	Pt–N(1)	2.014(7)
Pd–N(3)	2.062(4)	Pt–N(3)	2.074(8)
Pd–Cl(1)	2.3119(12)	Pt–Cl(1)	2.309(2)
Pd–Cl(2)	2.2864(12)	Pt–Cl(2)	2.299(2)
N(1)–Pd–N(3)	89.85(14)	N(1)–Pt–N(3)	90.7(3)
N(1)–Pd–Cl(1)	90.19(10)	N(1)–Pt–Cl(1)	90.1(2)
N(1)–Pd–Cl(2)	176.88(10)	N(1)–Pt–Cl(2)	177.8(2)
N(3)–Pd–Cl(1)	171.69(10)	N(3)–Pt–Cl(1)	172.8(2)
N(3)–Pd–Cl(2)	88.86(10)	N(3)–Pt–Cl(2)	88.5(2)
Cl(1)–Pd–Cl(2)	91.50(5)	Cl(1)–Pt–Cl(2)	91.04(10)
[5]$(BF_4)_2$			
Pd–N(1)	2.033(2)	Pd–N(3)	2.078(2)
N(1)–Pd–N(3)	90.70(11)	N(1)#–Pd–N(3)	171.36(9)
N(1)#–Pd–N(1)	89.14(13)	N(3)#–Pd–N(3)	90.74(14)

[$PdCl_2$(deat)] (deae = 1-(2-(ethylamino)ethyl)-3,5-dimethylpyrazole; deat = 1-(2-(*tert*-butylamino)ethyl)-3,5-dimethylpyrazole)[8a] and [$PdCl_2$(L1)] (L1 = 1-(2-(diethylamino)ethyl)-3,5-diphenylpyrazole).[12a] The Pd–N_{pz} (2.021(3) Å), Pd–N_{amino} (2.062(4) Å), and Pd–Cl (2.3119(12) and 2.2864(12) Å) bond lengths for complex **1** lie in the interval of distances found for other structures described in the literature with the same environment: 1.979–2.141 Å (Pd–N_{pz}),[12a,20] 2.017–2.280 Å (Pd–N_{amino}),[8a,8d,12a,21] and 2.280–2.341 Å (terminal Pd–Cl).[8a,8d,12a,21a–j] The Pd–N_{amino} bond length for **1** is clearly shorter than the same distance for [$PdCl_2$(L1)] (2.114(6) Å). This could indicate that ligands with only one terminal alkyl chain form stronger chelated structures than ligands with two terminal alkyl chains, giving rise to the different behavior of these kind of ligands when they coordinate Pd^{II}.[12a]

The $PtCl_2N_{pz}N_{amino}$ (terminal chlorine, aliphatic amine) core is found in the literature as part of two crystal structures.[19] Our group has recently published one of these structures: [$PtCl_2$(deae)].[11]

The Pt–N_{pz} (2.021(3) Å), Pt–N_{amino} (2.062(4) Å), and Pt–Cl (2.2863(12) and 2.3118(12) Å) bond lengths for complex **3** can be regarded as normal compared with the distances found in the literature. For Pt–N_{pz}, the literature describes values between 1.981 and 2.138 Å,[18,20b,22,23] for Pt–N_{amino} between 1.848 and 2.147 Å,[24] and for terminal Pt–Cl between 2.253 and 2.329 Å.[18,20b,22,23] No significant differences are observed between Pt–N_{amino} bond lengths in structure **3** and [$PtCl_2$(deae)] (2.073(10), 2.092(11) Å),[11] as happened with Pd^{II} complexes. In this way, the change of methyl groups to phenyl groups in these positions does not appear to have any remarkable effect on the coordination features toward Pt^{II}.

The N_{pz}–M–N_{amino} bite angles are 89.85(14)° for **1** and 90.7(3)° for **3**. The bite angles for these complexes can also be regarded as normal compared with those reported in the literature for [$PdCl_2$(deae)] (89.3(2)°),[8a] [$PdCl_2$(deat)] (88.16(18)°),[8a] [$PtCl_2$(deae)] (90.3(4)°),[11] and [$PdCl_2$(L1)] (90.3(2)°).[12a]

The N_{amino}–H bonds are intermolecularly hydrogen-bridged to a chlorine atom (Cl(1)). For complex **1**, the N(3)–H(3N) bond length is 0.894(11) Å and the contact parameters between N(3)–H(3N) and Cl(1) are 2.497(12) Å for H(3N)···Cl(1), 3.339(4) Å for N(3)···Cl(1), and 157.2(14)° for N(3)–H(3N)···Cl(1). For complex **3**, the N(3)–H(3N) bond length has been geometrically fixed in refinement (0.91 Å) and the contact parameters between N(3)–H(3N) and Cl(1) are 2.52 Å for H(3N)···Cl(1), 3.358(9) Å for N(3)···Cl(1), and 153° for N(3)–H(3N)···Cl(1). The symmetry code for **1** and **3** is $-x, 1/2+y, 1/2-z$.

Synthesis and Characterization of the Complexes [Pd(NN′)$_2$](BF$_4$)$_2$

Complexes [Pd(*NN′*)$_2$](BF_4)$_2$ (*NN′* = dpea, [**5**](BF_4)$_2$; dpoa, [**6**](BF_4)$_2$) were obtained by treatment of the corresponding ligand with [$PdCl_2(CH_3CN)_2$] in a 1:2 M:NN′ molar ratio in acetonitrile and in the presence of $NaBF_4$ in order to provoke the precipitation of the chloride ions. Note that the same stoichiometric conditions (1:2 M:NN′ molar ratio) without the presence of $NaBF_4$ led to the formation of molecular complexes [$PdCl_2$(*NN′*)] (*NN′* = dpea, **1**; dpoa, **2**).

Several techniques were used for the characterization of the complexes: elemental analyses, mass spectrometry, conductivity measurements, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray diffraction methods. The NMR signals were assigned from DEPT, COSY, HMQC, and NOESY NMR experiments.

The elemental analyses for compounds [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$ are consistent with the formula [Pd(*NN′*)$_2$](BF_4)$_2$. MS-ESI+ spectra of compounds [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$ give peaks with *m/z* values of 344 (100%) and 428 (100%), respectively, attributable to [Pd(*NN′*)$_2$]$^{2+}$. These peaks are observed with the same isotopic distribution as the theoretical one.

Conductivity values for 10^{-3} M solutions of complexes [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$ in acetonitrile are in agreement with 1:2 electrolyte compounds (270.4 and 296.3 Ω^{-1} cm^2 mol^{-1}, respectively).[15]

The IR spectra of complexes [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$, in the range 4000–400 cm^{-1}, show signals corresponding to the coordinated ligands. The most characteristic bands are ν(N–H), ν(C=C), ν(C=N), δ(C–H)$_{oop}$, and ν(B–F).[16] The IR spectra of complexes [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$ in the 600–100 cm^{-1} region were also recorded. There is only one significant band in this region corresponding to ν(Pd–N).[16]

The crystal structure of compound [**5**](BF_4)$_2$ consists of discrete [Pd(dpea)$_2$]$^{2+}$ cations and BF_4^- anions (Fig. 3).

The [Pd(dpea)$_2$]$^{2+}$ cation presents two dpea ligands in a *cis* disposition, bonded to the Pd^{II} centre in a bidentate coordination mode by the N_{pz} and N_{amino} atoms in a square-planar geometry, forming two six-membered metalocyclic rings with twist-boat conformation. Selected bond lengths and bond angles for this structure are listed in Table 1.

This coordination mode, which involves a [Pd(N_{amino})$_2$(N_{pz})$_2$]$^{2+}$ core, is found in one single structure in the literature, [Pd(deat)$_2$](BF_4)$_2$.[8c]

The metal–ligand bond distances for [**5**](BF_4)$_2$ are 2.033(2) Å (Pd–N_{pz}) and 2.078(2) Å (Pd–N_{amino}). These values are consistent with those described in the literature: 1.979–2.140 Å for Pd–N_{pz}[12a,20] and 2.017–2.280 Å for Pd–N_{amino}.[8a,8d,12a,21] The value for the N_{amino}–Pd–N_{pz} bite angle (90.70(11)°) is greater than that found for [Pd(deat)$_2$](BF_4)$_2$ (87.47(6)°), which presents the same core.[8c] The main difference between the structure of complex [**5**](BF_4)$_2$ and [Pd(deat)$_2$](BF_4)$_2$ lies in the disposition of the two ligands. For [Pd(deat)$_2$](BF_4)$_2$,[8c] the ligands are in a *trans* disposition, while for complex [**5**](BF_4)$_2$, the dpea ligands are in a *cis* disposition and the ligands adopt an *anti* disposition of the terminal chains to minimize steric hindrance.

The phenyl groups of the dpea ligand are able to arrange themselves in a way that allows the π–π interaction between a phenyl ring of one ligand and the pyrazole ring of the other ligand in the same cation. The centroid$_{pz}$–centroid$_{ph}$ distance is 3.7 Å and the angle between the phenyl plane and the pyrazole plane is 21.6° (Fig. 4). These parameters are in agreement with those described in the literature for π–π interactions.[25]

Moreover, the N_{amino}–H bonds are intermolecularly hydrogen-bridged to a fluorine atom (F(1)) of a BF_4^- anion. The N(3)–H(3N) bond length is 0.90(4) Å and the contact parameters between N(3)–H(3N) and F(1) are 2.22(4) Å for H(3N)···F(1), 2.09 (4) Å for H(3N)···F(1′), 3.043(17) Å for N(3)···F(1), 2.932(18) Å for N(3)···F(1′), 153(4)° for N(3)–H(3N)···F(1) and 156(4)° for N(3)–H(3N)···F(1′). The symmetry code is $1-x, y, -z+1/2$.

NMR spectroscopic data are reported in the Experimental section. ^1H NMR spectra of [**5**]$^{2+}$ and [**6**]$^{2+}$ at variable temperatures (338–233 K) in CD_3CN did not show any splitting or broadening of the signals.

For complexes [**5**](BF_4)$_2$ and [**6**](BF_4)$_2$, both ligands in each one of the complexes are equivalent. ^1H NMR spectra were studied in detail. If we focus our attention on the protons of the

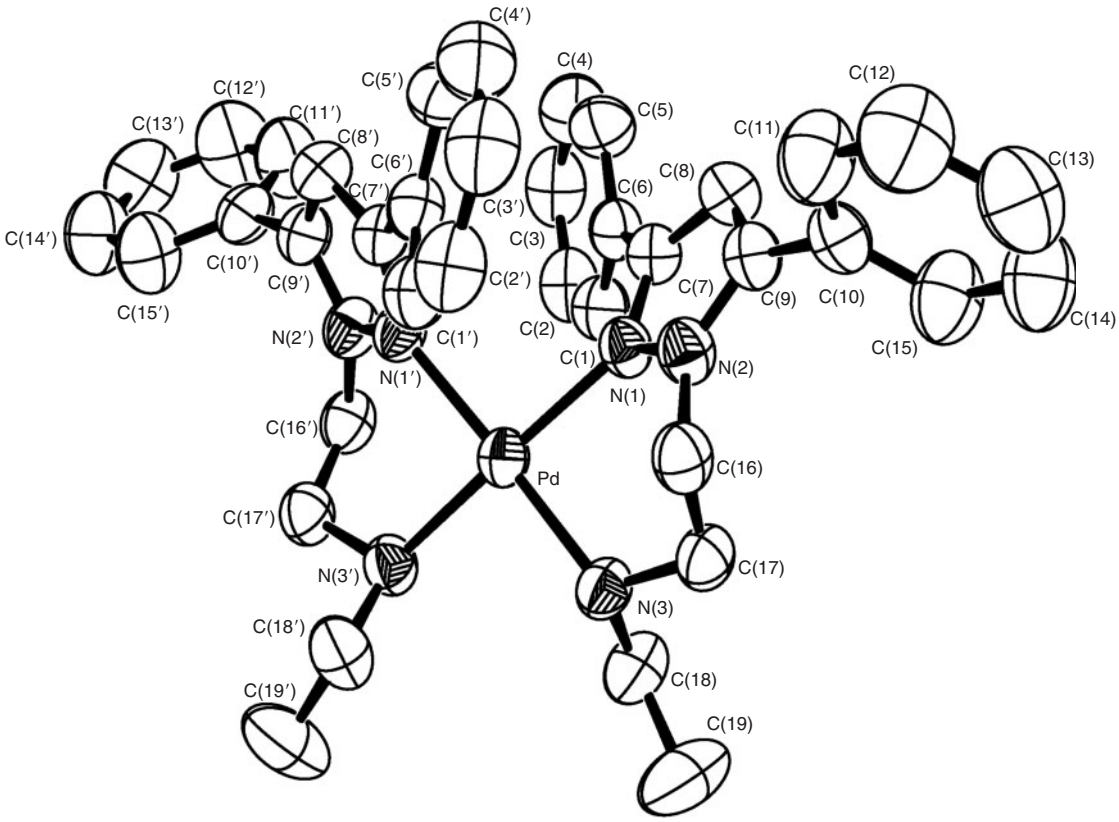

Fig. 3. *ORTEP* drawing of $[Pd(dpea)_2]^{2+}$, showing all non-hydrogen atoms and the atoms numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

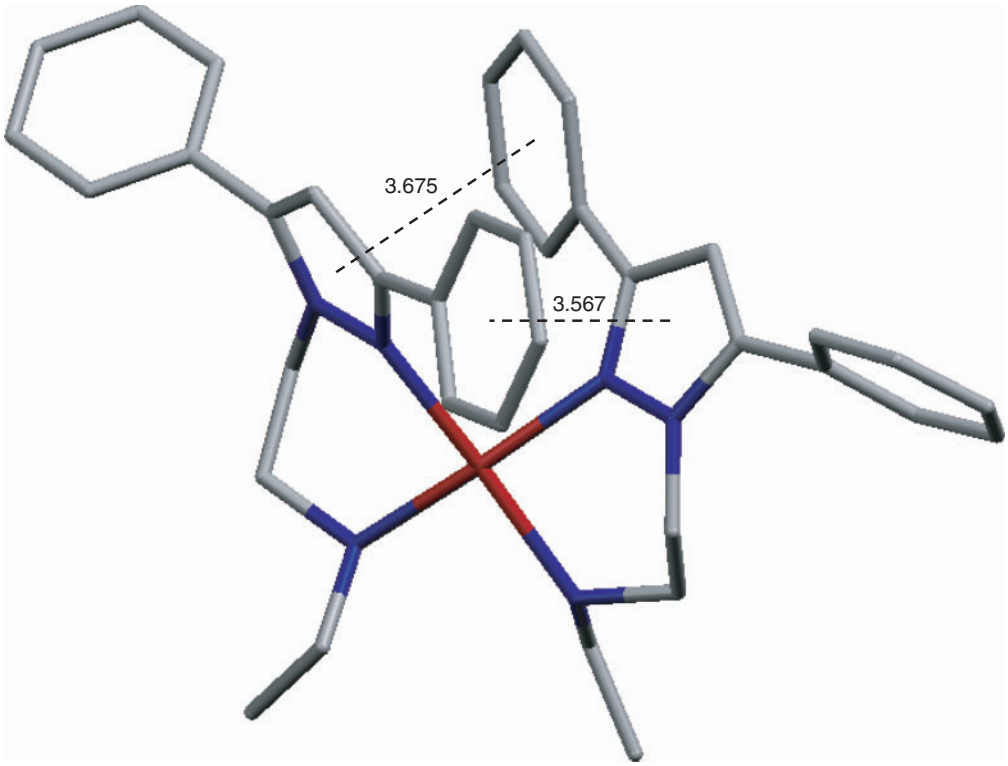

Fig. 4. View of the π–π stacking interactions between the pyrazole ring and the phenyl ring in $[Pd(dpea)_2]^{2+}$.

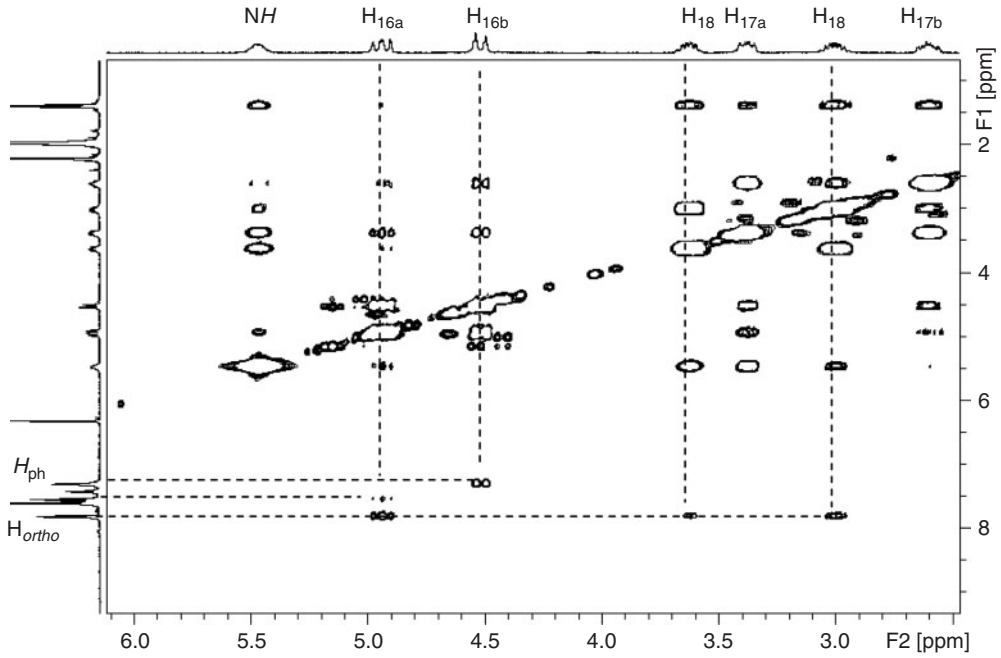

Fig. 5. The 250-MHz 2D NOESY spectrum of $[Pd(dpea)_2]^{2+}$ in CD_3CN at 298 K.

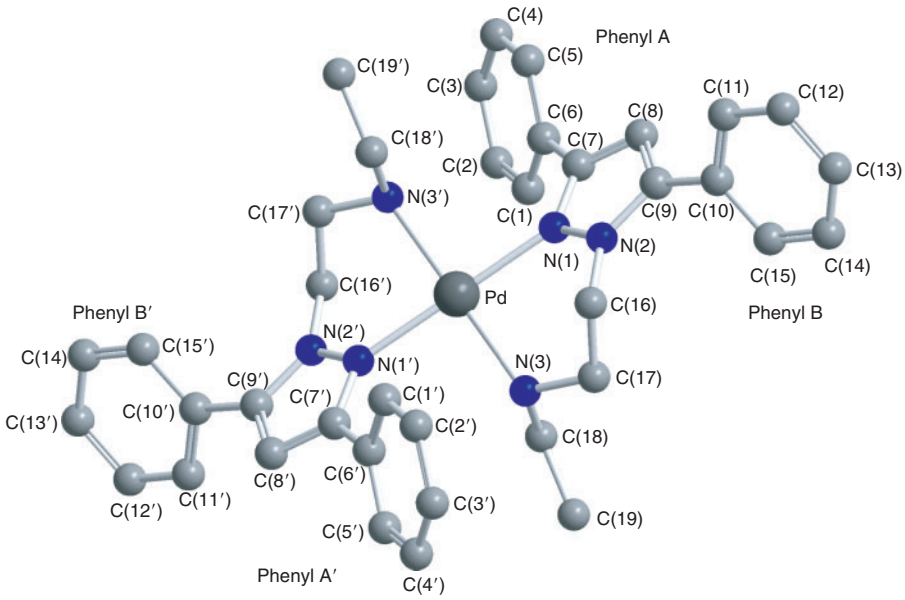

Fig. 6. Optimized structure of the *trans* isomer of $[Pd(dpea)_2]^{2+}$. Hydrogen atoms have been omitted for clarity.

terminal alkyl chains, protons C(18)–H (Fig. 3) appear as two multiplets at $\delta = 3.64$, 2.99 ($[\mathbf{5}]^{2+}$) and 3.36, 2.60 ppm ($[\mathbf{6}]^{2+}$). However, protons C(19)–H, corresponding to the methyl group of the terminal alkyl chain for $[\mathbf{5}]^{2+}$ and the rest of the protons of the octyl chain for $[\mathbf{6}]^{2+}$ appear as a single signal for each CH_2 or CH_3 (for the octyl chain, most of them appear to overlap) at $\delta = 1.40$ ($[\mathbf{5}]^{2+}$) and 1.34, 0.90 ppm ($[\mathbf{6}]^{2+}$).

NOESY spectra of these compounds were also studied (Fig. 5). Complexes $[\mathbf{5}](BF_4)_2$ and $[\mathbf{6}](BF_4)_2$ show NOE interactions between protons C(18)–H/C(19)–H and the protons of Ph(A) groups. These effects do not seem compatible with the *cis* disposition obtained from the X-ray structure previously described (Fig. 3). In fact, in the crystal structure, the shortest distances between protons of the terminal alkyl chain and protons of the phenyl groups are between C(18)–H and C1–H protons (3.643 and 4.055 Å), and between C(19)–H and C1–H protons (5.917, 5.840, and 6.169 Å).

However, these NOE interactions would be possible if the two ligands in complexes $[\mathbf{5}](BF_4)_2$ and $[\mathbf{6}](BF_4)_2$ are in the *trans* disposition. For this reason, we have optimized the geometries of the *cis* and *trans* isomers of $[\mathbf{5}]^{2+}$ and $[\mathbf{5}](BF_4)_2$. The structure of the optimized *trans* isomer of $[\mathbf{5}]^{2+}$ is shown in Fig. 6.

In the *trans* isomer, the shortest distances between the protons of the terminal chain and the protons at the phenyl groups are

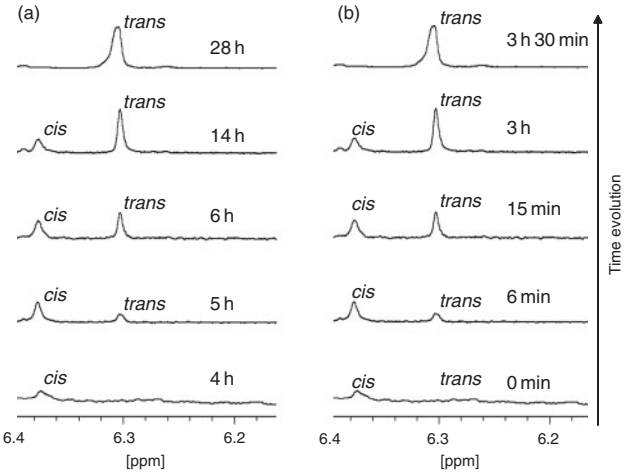

Fig. 7. Evolution of the pyrazolic protons of the *cis* and *trans* isomers of $[Pd(dpea)_2]^{2+}$ with time at (a) 298 K, (b) and 313 K.

between C(18)–H and C1–H (3.099 and 3.816 Å), and between C(19)–H and C(5′)–H (3.083, 4.523, and 4.792 Å). These distances are consistent with the NOESY data obtained in solution, so that we may conclude that the complexes observed in acetonitrile solution correspond to the *trans* isomers of $[\mathbf{5}]^{2+}$ and $[\mathbf{6}]^{2+}$ cations.

Theoretical studies show that for the $[\mathbf{5}]^{2+}$ cation, the *trans* isomer is more stable than the *cis* by 12.5 kJ mol^{-1} ($\Delta G°$ at 298.15 K in acetonitrile). This difference leads to a predicted *trans*:*cis* ratio of 99.4:0.6. However, the relative stabilities are reversed when the $[Pd(dpea)_2](BF_4)_2$ complexes are considered and the *cis* isomer becomes the most stable by 48.5 kJ mol^{-1} ($\Delta G°$ at 298.15 K in acetonitrile). The dissociation of these complexes into $[Pd(dpea)_2]^{2+} + 2\ BF_4^-$ is thermodynamically favourable in acetonitrile solution. The computed Gibbs reaction energies at 298.15 K are −84.8 and −23.8 kJ mol^{-1} for the *trans* and *cis* isomers, respectively. As we can observe, there is a notable difference in the values of the Gibbs dissociation energies for *cis* and *trans* isomers. This difference is directly related to the charge distribution of the cations. In the *cis* isomer, the positive charge is more polarized than in the *trans* one, so that the interaction with the BF_4^- counteranions becomes favoured.

An additional experiment was performed in order to obtain information about the presence of *cis* or *trans* isomers in solution. The reaction was carried out in an NMR tube in CD_3CN at 298 K (conditions described in Experimental section). The evolution of the synthesis of complex $[\mathbf{5}](BF_4)_2$ (up to 28 h) was monitored by ^{1}H NMR spectroscopy.

Fig. 7a shows the evolution of the pyrazole proton (CH_{pz}) of the *cis* and *trans* isomers of $[\mathbf{5}]^{2+}$ with time at 298 K. Up to 4 h after the reaction begins, only one peak corresponding to CH_{pz} at 6.39 ppm is observed. This signal is assigned to the *cis* isomer. From that time on, a second peak at 6.32 ppm, corresponding to the *trans* isomer, begins to grow. As the time goes by, the peak corresponding to the *cis* isomer decreases and finally disappears 28 h after the beginning of the reaction. Therefore, the kinetic *cis* isomer is completely transformed into the *trans* isomer, which is the thermodynamically most stable one.

The same kind of experiment was also performed at 313 K. In this case, the presence of the *trans* isomer is detected from the beginning of the reaction, and the *cis*–*trans* conversion is completed in 3.5 h (Fig. 7b). The isomerization rate constants, determined at both temperatures, lead to an activation energy of ∼80 kJ mol^{-1}.

Table 2. ^{1}H NMR results: chemical shifts [ppm] and ^{1}H, ^{1}H coupling constants [Hz] for $[\mathbf{5}](BF_4)_2$ and $[\mathbf{6}](BF_4)_2$ in CD_3CN

Compound	$[\mathbf{5}](BF_4)_2$	$[\mathbf{6}](BF_4)_2$
δ H_{amino}	5.71	5.55
δ H (16a)	4.93	4.95
δ H (16b)	4.52	4.54
δ H (17a)	3.36	2.97
δ H (17b)	2.61	1.89
^2J(16a,16b)	15.6	15.3
^2J(17a,17b)	13.6	12.0
^2J(17a, H_{amino})	7.5	9.9
^2J(17b, H_{amino})	6.1	5.6
^3J(16a,17a)	2.7	3.3
^3J(16b,17b)	2.2	2.0
^3J(16a,17b)	11.7	11.0
^3J(16b,17a)	2.4	3.2

In addition to the detailed study of the terminal chains, the N_{pz}–CH_2–CH_2–N_{amino} fragment of compounds $[\mathbf{5}](BF_4)_2$ and $[\mathbf{6}](BF_4)_2$ was also studied. The two protons of each CH_2 group in the N_{pz}–CH_2–CH_2–N_{amino} chain are diastereotopic, thus giving rise to four groups of signals, each one attributable to a single hydrogen atom. Each group of signals can be assigned as two doublets of doublets of doublets for C(16)–H and two doublets of doublets of doublets of doublets for C(17)–H owing to the additional coupling of this proton to H_{amino}. Treatment of the N_{pz}–CH_2–CH_2–N_{amino} fragment as an AA′XX′ system gave a set of coupling constants for each compound. These constants were consistent with the simulated spectra obtained with the aid of the g*NMR* program.[26] All the results are reported in Table 2. Fig. 8 shows experimental and simulated ^{1}H NMR spectra for complex $[\mathbf{5}](BF_4)_2$.

In the NOESY spectra of $[\mathbf{5}]^{2+}$ (Fig. 6) and $[\mathbf{6}]^{2+}$ in CD_3CN, one of the *ortho* hydrogens of the Ph(A′) groups ($\delta = 7.81$ ($[\mathbf{5}]^{2+}$) or 7.80 ppm ($[\mathbf{6}]^{2+}$)) shows NOE interaction with the doublet of doublets of doublets at $\delta = 4.93$ ($[\mathbf{5}]^{2+}$) or 4.95 ppm ($[\mathbf{6}]^{2+}$), but not with the ones at $\delta = 4.52$ ($[\mathbf{5}]^{2+}$) or 4.54 ppm ($[\mathbf{6}]^{2+}$). This allowed us to assign H–16a to the first set of doublet of doublets of doublets at 4.93 ($[\mathbf{5}]^{2+}$) or 4.95 ppm ($[\mathbf{6}]^{2+}$) (Fig. 8). These assignments were done thanks to the *trans* structure obtained by computational studies, which shows that the shortest distances are between the H_{ortho} of Ph(A′) group at $\delta = 7.81$ ppm and the doublet of doublets of doublets at $\delta = 4.93$ ppm (C(16a)–H···C1′–H = 3.046 Å, Fig. 6) and between the H_{meta} of the Ph(A′) group (appearing as a part of the overlapped phenyl signals in the ^{1}H NMR spectrum of $[\mathbf{5}]^{2+}$) and the same doublet of doublets of doublets at 4.93 ppm (C(16a)–H···C2′–H = 3.374 Å, Fig. 6).

Therefore, C(16)–Hb was assigned to the set of doublet of doublets of doublets at $\delta = 4.52$ ($[\mathbf{5}]^{2+}$) or 4.54 ppm ($[\mathbf{6}]^{2+}$) and presents NOE interaction with C(15)–H of the Ph(B) (C(16b)–H···C(15)–H = 2.548 Å).

Coupling constants (obtained from the g*NMR*-generated[17] ^{1}H NMR simulated spectra, Fig. 8, Table 2) helped us to differentiate between C(17)–Ha and C(17)–Hb. These coupling constants agree with the conformation of the N_{pz}–CH_2–CH_2–N_{amino} chains as seen in Fig. 8, which was corroborated by the computational studies.

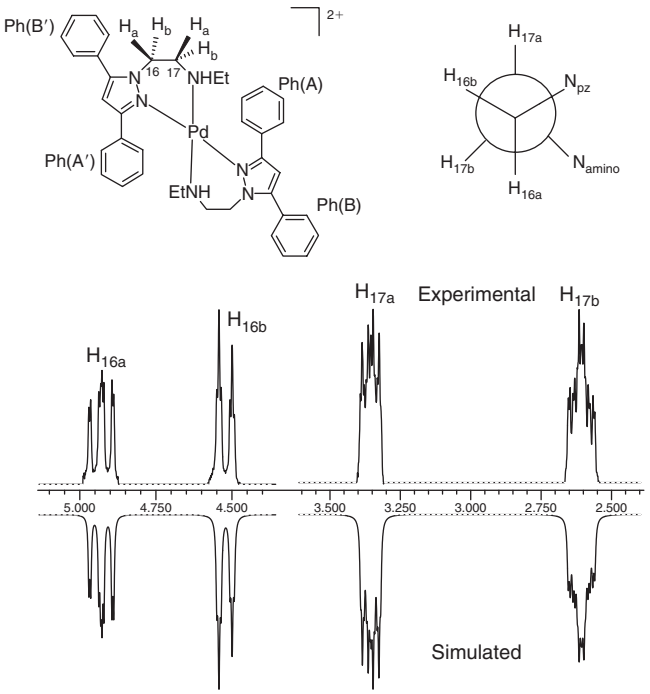

Fig. 8. The 250-MHz ^{1}H NMR and the simulated *g*NMR spectra for the H-16 and H-17 protons of the N_{pz}–CH_2–CH_2–N_{amino} fragment of $[Pd(dpea)_2]^{2+}$ in CD_3CN at 298 K.

Geminal ^2J and ∼180° ^3J coupling constants have significantly higher values than ∼30° and ∼60° ^3J coupling constants (Fig. 8, Table 2). Thus, C(17)–Ha should correspond to the doublet of doublets of doublets of doublets at 3.36 ([**5**]$^{2+}$) and 2.97 ppm ([**6**]$^{2+}$) and C(17)–Hb to the ones at 2.61 ([**5**]$^{2+}$) and 1.89 ppm ([**6**]$^{2+}$).

Conclusions

The *N*-alkylamino-3,5-diphenylpyrazole ligands dpea and dpoa act as bidentate ligands (N_{pz}, N_{amino}) forming chelated compounds with *cis*-[MCl_2(*NN′*)] (M = Pd^{II} (**1**, **2**) and Pt^{II} (**3**, **4**)) stoichiometry. Complexes [Pd(*NN′*)$_2$]$(BF_4)_2$ ([**5**–**6**]$(BF_4)_2$) have also been synthesized.

In complexes **1**–**4**, the ligands show the same behaviour as the complexes with ligands containing methyl moieties in positions 3 and 5 of the pyrazole ring,[8a,9] chelating the metallic centre through the N_{pz} and N_{amino} atoms. However, complexes **1**–**4** do not further react to form zwitterionic or cyclopalladated complexes as happened with the *N*-dialkylamino-3,5-diphenylpyrazole ligands.[12a]

For complexes [**5**–**6**]$(BF_4)_2$, we studied the *cis–trans* isomerization by NMR spectroscopy. The crystal structure of complex [**5**]$(BF_4)_2$ shows that dpea ligands are in a *cis* disposition in the solid state. However, ^{1}H NMR experiments show that the *trans* isomer is the isomer present in acetonitrile solution. Furthermore, we have shown by ^{1}H NMR experiments that the thermodynamically favoured *trans* isomer of $[Pd(dpea)_2]^{2+}$ is formed from the kinetic *cis* isomer in acetonitrile solution (28 h at 298 K and 3.5 h at 313 K). These experiments served to calculate the activation energy of the process, which was estimated to be ∼80 kJ mol^{-1}. The NOESY spectra for [**5**]$^{2+}$ and [**6**]$^{2+}$ were also consistent with the presence of *trans* species of these compounds in solution.

In addition to the experimental results, theoretical calculations have shown that the *trans* isomer of the $[Pd(dpea)_2]^{2+}$ cation is thermodynamically more stable than the *cis* one. If we study $[Pd(dpea)_2](BF_4)_2$ aggregates, the *cis* isomer becomes the most stabilized one. The same calculations show that the dissociation of $[Pd(dpea)_2](BF_4)_2$ into $[Pd(dpea)_2]^{2+} + 2\ BF_4^-$ is predicted to be thermodynamically favourable in acetonitrile solution.

Experimental

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 Euro Vector 3011 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile solution employing a Cyber Scan CON 500 (Euthech Instruments) conductimeter. Infrared spectra were run on a Perkin–Elmer Fourier-transform (FT) spectrophotometer, series 2000, as NaCl disks, KBr pellets or polyethylene films in the range of 4000–100 cm^{-1}. ^{1}H, ^{13}C{^{1}H}, COSY, HMQC, and NOESY NMR spectra were recorded with an NMR-FT Bruker 250 MHz spectrometer in $CDCl_3$ or CD_3CN solutions at room temperature. ^{195}Pt{^{1}H} NMR spectra were recorded at 298 K and 77.42 MHz on a DPX-360 Bruker spectrometer using aqueous solution of $[PtCl_6]^{2-}$ (0 ppm) as an external reference and a 0.01 s delay time. All chemical shift values (δ) are given in ppm. Mass spectra were obtained with an Esquire 3000 ion-trap mass spectrometer from Bruker Daltonics. The complexes $[PdCl_2(CH_3CN)_2]$[27] and $[PtCl_2(CH_3CN)]$[28] were synthesized according to published methods. The precursor 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole was prepared as described in the literature.[13]

Synthesis of the Ligands 1-(2-(Ethylamino)ethyl)-3,5-diphenylpyrazole (dpea) and 1-(2-(Octylamino)ethyl)-3,5-diphenylpyrazole (dpoa)

The synthesis of the ligands consists of the reaction between 1-(2-toluene-*p*-sulfonyloxyethyl)-3,5-diphenylpyrazole (1.45 g, 3.47 mmol) and the appropriate primary amine (dpea, 1.47 g of 70% ethylamine, 22.9 mmol; dpoa, 2.99 g of 99% octylamine, 22.9 mmol) with sodium hydroxide (0.82 g of 98% purity, 20.1 mmol). The reaction was carried out in a solution of THF:water (dpea, 4:1; dpoa, 7:3) (20 mL) with continuous stirring and under reflux for 48 h. The mixture was cooled down to room temperature and extracted three times with chloroform (3 × 10 mL). 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. Each product was obtained as pale-yellow oil. In order to purify the ligand dpoa, a silica-gel column (60 Å) with ethyl acetate as eluent was used. The fractions containing pure dpoa ligand were gathered and the solvent was removed under vacuum. After evaporation, a pale-yellow oil was obtained.

dpea: (0.71 g, 70%) (Found: C 78.45, H 7.44, N 14.71. $C_{19}H_{21}N_3$ (291.1) requires C 78.32, H 7.26, N 14.41%.) ν_{max}(NaCl)/cm^{-1} ν(N–H) 3306, ν(C–H)$_{ar}$ 3060, ν(C–H)$_{al}$ 2963–2870, δ(N–H) 1680, ν(C=C)$_{ph}$ 1605, (ν(C=C)$_{pz}$, ν(C=N)$_{pz}$) 1549, (δ(C=C)$_{ar}$, δ(C=N)$_{ar}$) 1461, δ(C–H)$_{oop\ ph}$

761, δ(C–H)$_{oop\ pz}$ 695. δ_H (250 MHz, $CDCl_3$, 298 K) 7.85 (d, 2H, ^3J 7.0, $H_{ortho\text{-}3\text{-}ph}$), 7.41 (m, 8H, H_{ph}), 6.60 (s, 1H, CH_{pz}), 4.27 (t, 2H,^3J 6.1, $N_{pz}CH_2CH_2NH$), 3.09 (t, 2H, ^3J 6.1, $N_{pz}CH_2CH_2NH$), 2.59 (q, 2H, ^3J 7.1, $NHCH_2CH_3$), 1.58 (br, 1H, $NHCH_2CH_3$), 1.09 (t, 3H, ^3J 7.1, $NHCH_2CH_3$). δ_C (63 MHz, $CDCl_3$, 298 K) 151.2, 145.8, 133.9, 131.1 (C_{pz}, C_{ph}), 129.5–126.0 (C_{ph}), 103.8 (C$H_{(pz)}$), 49.8 ($N_{pz}CH_2CH_2NH$), 49.4 ($N_{pz}CH_2CH_2NH$), 44.1 ($NHCH_2CH_3$), 15.7 ($NHCH_2CH_3$). *m/z* (ESI+) 314 (12%, $[M + Na]^+$), 298 (64%, $[M + Li]^+$), 292 (100%, $[M + H]^+$).

dpoa: (0.77 g, 59%) (Found: C 80.18, H 8.95, N 11.24. $C_{25}H_{33}N_3$ (375.3) requires C 79.90, H 8.90, N 11.20%.) ν_{max}(NaCl)/cm^{-1} ν(N–H) 3310, ν(C–H)$_{ar}$ 3061, ν(C–H)$_{al}$ 2926–2853, δ(N–H) 1679, ν(C=C)$_{ph}$ 1606, [ν(C=C)$_{pz}$, ν(C=N)$_{pz}$] 1549, [δ(C=C)$_{ar}$, δ(C=N)$_{ar}$] 1480, 1463, δ(C–H)$_{oop\ ph}$ 761, δ(C–H)$_{oop\ pz}$ 695. δ_H (250 MHz, $CDCl_3$, 298 K) 7.77 (d, 2H, ^3J 7.0, $H_{ortho\text{-}3\text{-}ph}$), 7.35 (m, 8H, H_{ph}), 6.52 (s, 1H, CH_{pz}), 4.20 (t, 2H, ^3J 6.0, $N_{pz}CH_2CH_2NH$), 3.00 (t, 2H, ^3J 6.0, $N_{pz}CH_2CH_2NH$), 2.46 (t, 2H, ^3J 7.0, $NHCH_2(CH_2)_6CH_3$), 1.76 (br, 1H, $NHCH_2(CH_2)_6CH_3$), 1.17 (br, 12H, $NHCH_2(CH_2)_6CH_3$), 0.80 (t, 3H, ^3J 6.9, $NHCH_2(CH_2)_6CH_3$). δ_C (63 MHz, $CDCl_3$, 298 K) 151.0, 145.6, 134.1, 131.4 (C_{pz}, C_{ph}), 129.5–126.0 (C_{ph}), 103.7 (C$H_{(pz)}$), 55.2 ($N_{pz}CH_2CH_2NH$), 54.4 ($N_{pz}CH_2CH_2NH$), 48.7 ($NHCH_2(CH_2)_6CH_3$), 32.2–23.1 ($NHCH_2(CH_2)_6CH_3$), 14.5 ($NHCH_2(CH_2)_6CH_3$). *m/z* (ESI+) 398 (6%, $[M + Na]^+$), 376 (100%, $[M + H]^+$).

*Synthesis of Complexes [PdCl$_2$(NN′)] (NN′ = dpea **1**; dpoa **2**)*

A solution of the corresponding ligand (0.27 mmol: dpea, 0.079 g; dpoa, 0.101 g) in dry dichloromethane (10 mL) was added to a solution of [$PdCl_2(CH_3CN)_2$] (0.070 g, 0.27 mmol) in the same solvent (10 mL). The mixture was stirred at room temperature for 12 h. Then, most of the solvent was removed under vacuum (5 mL). Cool diethyl ether (5 mL) was added to induce precipitation. The resulting brown-orange precipitate was filtered off, washed twice with cool diethyl ether (3 mL), and recrystallized from a dichloromethane/diethyl ether (4:1) mixture.

Compound ***1*** (0.105 g, 71%) (Found: C 43.50, H 4.33, N 7.87. $C_{19}H_{21}Cl_2N_3Pd{\cdot}CH_2Cl_2$ (551.0) requires C 43.39, H 4.19, N 7.59%.) Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.0×10^{-3} M in acetonitrile) 12.7. ν_{max}(KBr)/cm^{-1} ν(N–H) 3164, ν(C–H)$_{ar}$ 3056, ν(C–H)$_{al}$ 2976–2932, ν(C=C)$_{ph}$ 1620, (ν(C=C)$_{pz}$, ν(C=N)$_{pz}$) 1551, 1482, (δ(C=C)$_{ar}$, δ(C=N)$_{ar}$) 1466, δ(C–H)$_{ip}$ 1015, δ(C–H)$_{oop\ ph}$ 762, δ(C–H)$_{oop\ pz}$ 696. ν_{max}(polyethylene)/cm^{-1} ν(Pd–N) 398, ν(Pd–Cl) 335, 326. δ_H (250 MHz, $CDCl_3$, 298 K) 8.36 (d, 2H, ^3J 7.2, $H_{ortho\text{-}3\text{-}ph}$), 7.35 (m, 8H, H_{ph}), 6.60 (s, 1H, CH_{pz}), 5.90 (m, 1H, $N_{pz}CHHCH_2NH$), 5.71 (br, 1H, $NHCH_2CH_3$), 4.50 (m, 1H, $N_{pz}CHHCH_2NH$), 3.30 (br, 1H, $N_{pz}CH_2CHHNH$), 3.06 (m, 2H, $NHCH_2CH_3$), 2.10 (m, 1H, $N_{pz}CH_2CHHNH$), 1.42 (t, 3H, ^3J 7.4, $NHCH_2CH_3$). δ_C (63 MHz, $CDCl_3$, 298 K) 157.4–148.3 (C_{pz}, C_{ph}), 131.3–128.7 (C_{ph}), 107.5 (C$H_{(pz)}$), 51.6 ($NHCH_2CH_3$), 50.0 ($N_{pz}CH_2CH_2NH$), 49.2 ($N_{pz}CH_2CH_2NH$), 14.4 ($NHCH_2CH_3$). *m/z* (ESI+) 396 (100%, [$PdCl_2$(dpea)–HCl–Cl]$^+$).

Compound ***2*** (0.100 g, 67%) (Found: C 54.15, H 6.04, N 7.90. $C_{25}H_{33}Cl_2N_3Pd$ (551.1) requires C 54.31, H 6.02, N 7.60%.) Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.1×10^{-3} M in acetonitrile) 1.8. ν_{max}(KBr)/cm^{-1} ν(N–H) 3162, ν(C–H)$_{ar}$ 3055, ν(C–H)$_{al}$ 2925–2853, ν(C=C)$_{ph}$ 1609, (ν(C=C)$_{pz}$, ν(C=N)$_{pz}$) 1552, (δ(C=C)$_{ar}$, δ(C=N)$_{ar}$) 1482, 1466, δ(C–H)$_{ip}$ 1016, δ(C–H)$_{oop\ ph}$ 762, δ(C–H)$_{oop\ pz}$ 695. ν_{max}(polyethylene)/cm^{-1} ν(Pd–N) 405, ν(Pd–Cl) 330, 318. δ_H (250 MHz, $CDCl_3$, 298 K) 8.38 (d, 2H, ^3J 7.8, $H_{ortho\text{-}3\text{-}ph}$), 7.54 (m, 8H, H_{ph}), 6.63 (s, 1H, C$H_{(pz)}$), 5.90 (m, 1H, $N_{pz}CHHCH_2NH$), 5.63 (br, 1H, $NHCH_2(CH_2)_6CH_3$), 4.53 (m, 1H, $N_{pz}CHHCH_2NH$), 3.32 (br, 1H, $N_{pz}CH_2CHHNH$), 3.12 (br, 1H, $NHCHH(CH_2)_6CH_3$), 2.90 (br, 1H, $NHCHH(CH_2)_6CH_3$), 2.10 (br, 1H, $N_{pz}CH_2CHHNH$), 1.96 (br, 1H, $NHCH_2CHH(CH_2)_5CH_3$), 1.73 (br, 1H, $NHCH_2CHH(CH_2)_5CH_3$), 1.28 (br, 10H, $NHCH_2CH_2(CH_2)_5CH_3$), 0.89 (t, 3H, ^3J 6.9, $NH(CH_2)_7CH_3$). δ_C (63 MHz, $CDCl_3$, 298 K) 155.3, 147.9, 131.1, 130.2 (C_{pz}, C_{ph}), 129.5–125.4 (C_{ph}), 107.2 (C$H_{(pz)}$), 55.5 ($N_{pz}CH_2CH_2NH$), 51.5 ($N_{pz}CH_2CH_2NH$), 49.6 ($NHCH_2(CH_2)_6CH_3$), 31.9–22.7 ($NHCH_2(CH_2)_6CH_3$), 14.2 ($NHCH_2(CH_2)_6CH_3$). *m/z* (ESI+) 480 (100%, [$PdCl_2$(dpoa)–HCl–Cl]$^+$).

*Synthesis of Complexes [PtCl$_2$(NN′)] (NN′ = dpea **3**; dpoa **4**)*

A solution of the corresponding ligand (0.14 mmol: dpea, 0.041 g; dpoa, 0.053 g) in dry acetonitrile (10 mL) was added to a solution of [$PtCl_2(CH_3CN)_2$] (0.050 g, 0.14 mmol) in the same solvent (10 mL). The mixture was stirred at reflux for 48 h. Then, all the solvent was removed under vacuum. Dichloromethane (5 mL) was added to dissolve the solid, and then cool diethyl ether (5 mL) was added to induce precipitation. The resulting pale-yellow precipitate was filtered off, washed twice with diethyl ether (3 mL), and recrystallized from a dichloromethane/diethyl ether (4:1) mixture.

Compound ***3*** (0.058 g, 67%) (Found: C 37.61, H 3.85, N 6.33. $C_{19}H_{21}Cl_2N_3Pt{\cdot}CH_2Cl_2$ (640.0) requires C 37.40, H 3.61, N 6.54%.) Conductivity (Ω^{-1} cm^2 mol^{-1}, 9.0×10^{-4} M in acetonitrile) 10.6. ν_{max}(KBr)/cm^{-1} ν(N–H) 3129, ν(C–H)$_{ar}$ 2963, ν(C–H)$_{al}$ 2921–2841, ν(C=C)$_{ph}$ 1595, (ν(C=C)$_{pz}$, ν(C=N)$_{pz}$) 1554, (δ(C=C)$_{ar}$, δ(C=N)$_{ar}$) 1480, 1466, δ(C–H)$_{ip}$ 1021, δ(C–H)$_{oop\ ph}$ 762, δ(C–H)$_{oop\ pz}$ 696. ν_{max}(polyethylene)/cm^{-1} ν(Pt–N) 404, ν(Pt–Cl) 337, 328. δ_H (250 MHz, CD_3CN, 298 K) 8.37 (d, 2H, ^3J 6.7, $H_{ortho\text{-}3\text{-}ph}$), 7.46 (m, 8H, H_{ph}), 6.61 (s, 1H, C$H_{(pz)}$), 6.33 (br, 1H, $NHCH_2CH_3$), 5.88 (m, 1H, $N_{pz}CHHCH_2NH$), 4.32 (m, 1H, $N_{pz}CHHCH_2NH$), 3.41 (br, 1H, $N_{pz}CH_2CHHNH$), 3.28 (m, 1H, $NHCHHCH_3$), 3.09 (m, 1H, $NHCHHCH_3$), 2.15 (m, 1H, $N_{pz}CH_2CHHNH$), 1.36 (t, 3H, ^3J 7.1, $NHCH_2CH_3$). δ_C (63 MHz, CD_3CN, 298 K) 154.4–130.2 (C_{pz}, C_{ph}), 129.4–128.0 (C_{ph}), 107.3 (C$H_{(pz)}$), 51.2, 51.0 ($N_{pz}CH_2CH_2NH$, $NHCH_2CH_3$), 49.5 ($N_{pz}CH_2CH_2NH$), 13.6 ($NHCH_2CH_3$). δ_{Pt} (77.42 MHz, CD_3CN, 298 K) −2008. *m/z* (ESI+) 580 (100%, [$PtCl_2$(dpea) + Na]$^+$), 484 (76%, [$PtCl_2$(dpea)–HCl–Cl]$^+$).

Compound ***4*** (0.014 g, 16%) (Found: C 46.67, H 5.09, N 6.53. $C_{25}H_{33}Cl_2N_3Pt$ (640.2) requires C 46.80, H 5.18, N 6.55%.) Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.0×10^{-3} M in acetonitrile) 7.7. ν_{max} (KBr)/cm^{-1} ν(N–H) 3163, ν(C–H)$_{ar}$ 3055, ν(C–H)$_{al}$ 2952–2853, ν(C=C)$_{ph}$ 1591, (ν(C=C)$_{pz}$, ν(C=N)$_{pz}$) 1551, (δ(C=C)$_{ar}$, δ(C=N)$_{ar}$) 1482, 1463, δ(C–H)$_{ip}$ 1021, δ(C–H)$_{oop\ ph}$ 760, δ(C–H)$_{oop\ pz}$ 695. ν_{max}(polyethylene)/cm^{-1} ν(Pt–N) 407, ν(Pt–Cl) 336, 329. δ_H (250 MHz, CD_3CN, 298 K) 8.35 (d, 2H, ^3J 6.8, $H_{ortho\text{-}3\text{-}ph}$), 7.50 (m, 8H, H_{ph}), 6.61 (s, 1H, CH_{pz}), 5.85 (m, 1H, $N_{pz}CHHCH_2NH$), 5.53 (br, 1H, $NHCH_2(CH_2)_6CH_3$), 4.50 (m, 1H, $N_{pz}CHHCH_2NH$), 3.29 (br, 1H, $N_{pz}CH_2CHHNH$), 3.08 (m, 1H, $NHCHH(CH_2)_6CH_3$), 2.87 (m, 1H, $NHCHH(CH_2)_6CH_3$), 2.09 (m, 1H, $N_{pz}CH_2CHHNH$), 1.94 (br, 1H, $NHCH_2CHH(CH_2)_5CH_3$), 1.72 (br, 1H, $NHCH_2$

$CH\mathit{H}(CH_2)_5CH_3$), 1.25 (br, 10H, $NHCH_2CH_2(C\mathit{H}_2)_5CH_3$), 0.87 (br, 3H, $NH(CH_2)_7C\mathit{H}_3$). δ_C (63 MHz, CD_3CN, 298 K) 152.3–130.5 (C_{pz}, C_{ph}), 129.8–128.7 (C_{ph}), 107.5 ($C\mathit{H}_{(pz)}$), 55.9 ($N_{pz}CH_2\mathit{C}H_2NH$), 51.6 ($N_{pz}\mathit{C}H_2CH_2NH$), 49.8 ($NH\mathit{C}H_2(CH_2)_6CH_3$), 32.1–23.0 ($NHCH_2(\mathit{C}H_2)_6CH_3$), 14.5 ($NHCH_2(CH_2)_6\mathit{C}H_3$). δ_{Pt} (77.42 MHz, CD_3CN, 298 K) −2106. *m/z* (ESI+) 568 (100%, $[PtCl_2(dpoa)–HCl–Cl]^+$).

*Synthesis of Complexes $[Pd(NN')_2](BF_4)_2$ (NN′ = dpea [**5**](BF4)2; dpoa [**6**](BF4)2)*

A solution of the corresponding ligand (0.31 mmol: dpea, 0.090 g; dpoa, 0.116 g) in dry dichloromethane (10 mL) was added to a solution of $[PdCl_2(CH_3CN)_2]$ (0.041 g, 0.16 mmol) in the same solvent (10 mL). Then, $NaBF_4$ (0.035 g, 0.31 mmol) was added to the solution. A white precipitate appeared instantaneously. The mixture was stirred for 30 min and then the precipitate was filtered off. The solvent was reduced under vacuum to 5 mL. Diethyl ether (3 mL) was added to induce precipitation. The resulting pale-yellow precipitate was filtered off, washed twice with diethyl ether (5 mL), and recrystallized from a dichloromethane/diethyl ether (4:1) mixture.

*Compound [**5**](BF4)2*: (0.084 g, 63%) (Found: C 53.09, H 4.99, N 9.64. $C_{38}H_{42}B_2F_8N_6Pd$ (862.8) requires C 52.90, H 4.91, N 9.74%.) Conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$, 1.0×10^{-3} M in acetonitrile) 270.4. ν_{max}(KBr)/cm^{-1} ν(N–H) 3222, $\nu(C–H)_{ar}$ 3129, $\nu(C–H)_{al}$ 2975–2848, $\nu(C{=}C)_{ph}$ 1626, ($\nu(C{=}C)_{pz}$, $\nu(C{=}N)_{pz}$) 1552, 1481, ($\delta(C{=}C)_{ar}$, $\delta(C{=}N)_{ar}$) 1470, ν(B–F) 1083, $\delta(C–H)_{oop\ ph}$ 764, $\delta(C–H)_{oop\ pz}$ 698. ν_{max}(polyethylene)/cm^{-1} ν(Pd–N) 520. δ_H (250 MHz, CD_3CN, 298 K) 7.81 (d, 2H, ^3J 7.2, $H_{ortho\text{-}3\text{-}ph}$), 7.61 (m, 8H, H_{ph}), 6.32 (s, 1H, $C\mathit{H}_{(pz)}$), 5.71 (br, 1H, $N_{pz}CH_2CH_2N\mathit{H}$), 4.93 (ddd, 1H, $N_{pz}C\mathit{H}HCH_2NH$), 4.52 (ddd, 1H, $N_{pz}CH\mathit{H}CH_2NH$), 3.64 (m, 2H, $NHC\mathit{H}_2CH_3$), 3.36 (dddd, 1H, $N_{pz}CH_2C\mathit{H}HNH$), 2.99 (m, 2H, $NHC\mathit{H}_2CH_3$), 2.61 (dddd, 1H, $N_{pz}CH_2CH\mathit{H}NH$), 1.40 (t, 3H, ^3J 7.2, $NHCH_2C\mathit{H}_3$). δ_C (63 MHz, CD_3CN, 298 K) 148.4–127.9 (C_{pz}, C_{ph}), 107.1 ($C\mathit{H}_{(pz)}$), 51.9, 50.1 ($N_{pz}CH_2\mathit{C}H_2NH$, $NH\mathit{C}H_2CH_3$), 48.1 ($N_{pz}\mathit{C}H_2CH_2NH$), 13.0 ($NHCH_2\mathit{C}H_3$). *m/z* (ESI+) 344 (100%, $[Pd(dpea)_2]^{2+}$).

*Compound [**6**](BF4)2*: (0.086 g, 54%) (Found: C 58.02, H 6.18, N 8.03. $C_{50}H_{66}B_2F_8N_6Pd$ (1030.4) requires C 58.24, H 6.45, N 8.15%.) Conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$, 1.1×10^{-3} M in acetonitrile) 296.3. ν_{max}(KBr)/cm^{-1} ν(N–H) 3223, $\nu(C–H)_{ar}$ 3133–3062, $\nu(C–H)_{al}$ 2950–2856, $\nu(C{=}C)_{ph}$ 1629, ($\nu(C{=}C)_{pz}$, $\nu(C{=}N)_{pz}$) 1551, 1483, ($\delta(C{=}C)_{ar}$, $\delta(C{=}N)_{ar}$) 1470, ν(B–F) 1083, $\delta(C–H)_{oop\ ph}$ 763, $\delta(C–H)_{oop\ pz}$ 698. ν_{max}(polyethylene)/cm^{-1} ν(Pd–N) 520. δ_H (250 MHz, CD_3CN, 298 K) 7.80 (d, 2H, ^3J 7.5, $H_{ortho\text{-}3\text{-}ph}$), 7.60 (m, 8H, H_{ph}), 6.32 (s, 1H, $C\mathit{H}_{(pz)}$), 5.55 (br, 1H, $N_{pz}CH_2CH_2N\mathit{H}$), 4.95 (ddd, 1H, $N_{pz}C\mathit{H}HCH_2NH$), 4.54 (ddd, 1H, $N_{pz}CH\mathit{H}CH_2NH$), 3.36 (m, 1H, $NHC\mathit{H}H(CH_2)_6CH_3$), 2.97 (dddd, 1H, $N_{pz}CH_2C\mathit{H}HNH$), 2.60 (m, 1H, $NHCH\mathit{H}(CH_2)_6CH_3$), 1.89 (dddd, 1H, $N_{pz}CH_2CH\mathit{H}NH$), 1.34 (br, 12H, $NHCH_2(\mathit{C}H_2)_6CH_3$), 0.90 (br, 3H, $NHCH_2CH_2(CH_2)_5\mathit{C}H_3$). δ_C (63 MHz, CD_3CN, 298 K) 154.1–134.3 (C_{pz}, C_{ph}), 130.4–127.0 (C_{ph}), 107.2 ($C\mathit{H}_{(pz)}$), 57.0 ($N_{pz}CH_2\mathit{C}H_2NH$), 50.1 ($NH\mathit{C}H_2(CH_2)_6CH_3$), 48.9 ($N_{pz}\mathit{C}H_2CH_2NH$), 31.5–22.3 ($NHCH_2(\mathit{C}H_2)_6CH_3$), 13.4 ($NHCH_2(CH_2)_6\mathit{C}H_3$). *m/z* (ESI+) 428 (100%, $[Pd(dpoa)_2]^{2+}$).

*Additional Experiments for Monitoring [**5**](BF4)2 Synthesis by ^{1}H NMR Spectroscopy*

A solution of dpea ligand (0.0079 g, 0.027 mmol) in CD_3CN (0.5 mL) was added to a solution of $[PdCl_2(CH_3CN)_2]$ (0.0035 g, 0.014 mmol) in the same solvent (0.5 mL). The mixture was placed in the NMR tube and $NaBF_4$ (0.0030 g, 0.027 mmol) was added. The reaction was monitored by ^{1}H NMR spectroscopy at 298 K during 28 h, and at 313 K during 3.5 h.

X-ray Crystallographic Study

Suitable crystals for X-ray diffraction experiments of **1**, **3**, and [**5**](BF4)2 were obtained by crystallization from a mixture of dichloromethane and diethyl ether (4:1). Prismatic crystals were selected and mounted on an MAR345 diffractometer with an image plate detector. Unit-cell parameters were determined from 765 (**1**), 1159 (**3**), or 697 ([**5**](BF4)2) reflections ($3 < \theta < 31°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. 15961 (**1**), 18232 (**3**) or 17469 ([**5**](BF4)2) reflections were measured in the range $2.59 \le \theta \le 32.14$ (**1**); $2.58 \le \theta \le 30.00$ (**3**); or $2.73 \le \theta \le 30.84$ ([**5**](BF4)2). 5422 (**1**), 5852 (**3**), or 5274 ([**5**](BF4)2) of these reflections were non-equivalent by symmetry (R_{int}(on I) = 0.048 (**1**), 0.053 (**3**), or 0.048 ([**5**](BF4)2)). 5160 (**1**), 5374 (**3**), or 5040 ([**5**](BF4)2) reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but no absorption corrections were made. The structures were solved by direct methods, using the *SHELXS-97* computer program,[29] and refined by full-matrix least-squares method with *SHELXL-97*[30] using 15930 (**1**), 18232 (**3**), or 17469 ([**5**](BF4)2) reflections (very negative intensities were not assumed). The function minimized was $\Sigma w||F_O|^2 - |F_C|^2|^2$, where $w = [\sigma^2(I) + (0.0933P)^2 + 2.9515P]^{-1}$ (**1**), $w = [\sigma^2(I) + (0.0904P)^2 + 21.1342P]^{-1}$ (**3**), or $w = [\sigma^2(I) + (0.08504P)^2 + 3.2509P]^{-1}$ ([**5**](BF4)2) and $P = (|F_O|^2 + 2|F_C|^2)/3$. Thirteen H atoms for [**5**](BF4)2 were located from a difference synthesis and refined with an overall isotropic temperature factor. All H atoms of **1** and **3** and seven H atoms of [**5**](BF4)2 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 that is linked. The final $R(F)$ factor and $R_w(F^2)$ values, as well as the number of parameters and other details concerning the refinement of the crystal structures are gathered in Table 3.

CCDC-731090 (**1**), 731091 (**3**) and 731092 ([**5**](BF4)2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

Calculations were done using the *Gaussian-03* program.[31] Geometries were optimized using the M05[32] density functional method with a LANL2DZ[33] basis set supplemented with d polarization functions for B, C, N, O, and F.

Harmonic vibrational frequencies have been computed to verify that the obtained structures are energy minima. Energies in acetonitrile solution have been computed for geometries optimized in the gas phase using the Conductor-like Polarizable Continuum Model method.[34] In this case, the basis set has been supplemented with sp diffuse functions for B, C, N, O, and F.

Kinetic Studies

Rate constants for the *cis–trans* isomerization at 298 and 313 K were obtained from the five-point linear regressions of ln[*cis*] versus t. The activation energy was obtained using the Arrhenius equation for both temperatures.

Table 3. Crystallographic data for $[MCl_2(dpea)]\cdot CH_2Cl_2$ (M = Pd^{II} [1]·CH_2Cl_2; M = Pt^{II} [3]·CH_2Cl_2) and [5]$(BF_4)_2$

	1	3	[5]$(BF_4)_2$
Formula	$C_{20}H_{23}Cl_4N_3Pd$	$C_{20}H_{23}Cl_4N_3Pt$	$C_{38}H_{42}B_2F_8N_6Pd$
M	553.61	642.30	862.60
Temperature [K]	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
Unit cell dimensions			
a [Å]	12.420(5)	12.420(5)	21.938(7)
b [Å]	7.945(2)	7.950(5)	14.936(4)
c [Å]	24.040(8)	24.067(11)	15.023(4)
β [°]	99.90(2)	99.46(3)	128.23(2)
Z	4	4	4
U [Å^3]	2336(2)	2344(2)	3867(2)
D_{calc} [g cm^{-3}]	1.574	1.820	1.482
μ [mm^{-1}]	1.262	6.453	0.555
F(000)	1112	1240	1760
Crystal size (mm)	0.2 × 0.1 × 0.1	0.09 × 0.05 × 0.05	0.2 × 0.1 × 0.1
θ range [°]	2.59 to 32.14	2.58 to 30.00	2.73 to 30.84
Index range	$-18 \le h \le 16, -11 \le k \le 9, -32 \le l \le 32$	$-16 \le h \le 15, -10 \le k \le 10, -32 \le l \le 32$	$-31 \le h \le 31, -20 \le k \le 20, -20 \le l \le 20$
Reflections collected/unique	15961/5422 [R(int) = 0.0489]	18232/5852 [R(int) = 0.0539]	17469/5274 [R(int) = 0.0483]
Completeness to θ [%]	92.6	92.2	98.6
Absorption correction	None	None	None
Data/restraints/parameters	5422/5/259	5852/0/254	5274/0/342
Goodness-of-fit	1.204	1.089	1.172
Final R_1, wR_2	0.0565, 0.1597	0.0540, 0.1532	0.0557, 0.1470
R_1 (all data), wR_2	0.0621, 0.1700	0.0625, 0.1761	0.0591, 0.1545
Extinction coefficient	0.044(2)	0.045(5)	0.0261(16)
Residual electron density [e Å^{-3}]	1.343 and −1.300	0.923 and −0.086	1.264 and −0.622

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