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Synthesis of New Palladium(II) Complexes Containing Hemilabile *N*-(Alkylamino)pyrazole Ligands: Spectroscopic Analysis and Crystal Structure of [PdCl(ddae)]Cl·H_2O {ddae = Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine}

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Treatment of the tridentate (*NN′N*) *N*-alkylaminopyrazole ligands bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine (ddae), bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]isopropylamine (ddai) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]*tert*-butylamine (ddat) with $[PdCl_2(CH_3CN)_2]$ in a 1:1 M/L ratio in CH_2Cl_2 produces $[PdCl_2(NN'N)]$. Treatment of the corresponding ligand with $[PdCl_2(CH_3CN)_2]$ in a 1:2 M/L ratio in the presence of $AgBF_4$ in CH_2Cl_2/methanol (6:1) gives $[PdCl(NN'N)](BF_4)$. The complexes $[PdCl_2(NN'N)]$ were again obtained when the complexes $[PdCl(NN'N)](BF_4)$ were heated under reflux in a solution of NEt_4Cl in acetonitrile, which means that ligands ddae, ddai and ddat in complexes **1**–**6** are hemilabile. These Pd^{II} complexes have been characterised by elemental analyses, conductivity measurements and IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectroscopic studies for compounds $[PdCl_2(NN'N)]$ give evidence of $\kappa^2(N_{pz},N_{pz})$ coordination in acetonitrile and $\kappa^3(N_{pz},N_{amino},N_{pz})$ coordination in methanol. The X-ray structure of the complex [PdCl(ddae)]Cl·H_2O has been determined. The Pd^{II} is coordinated to the ddae ligand by two nitrogen atoms of the pyrazolyl groups and one nitrogen atom of the amine, along with one chlorine atom, in a slightly distorted square-planar geometry.

Introduction

In the course of a study of pyrazole-derived ligands we have studied and reported the synthesis and characterisation of ligands combining a pyrazolyl group with some other functions containing O (alcohol or ether),[1] S (thiol or thioether),[2] P (phosphane or phosphinite)[3] or N (amine)[4] as donor atoms. The synthesis of pyrazolyl-N(amine) ligands has been developed by Driessen et al. and, so far, the study of their coordinating ability has been mainly focused on the design of chelating systems to mimic metalloenzymes.[5]

In our group, we have investigated the reactivity of bi-(*NN′*) and tridentate (*NN′N*) *N*-(alkylamino)pyrazole ligands {1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole, 1-[2-(isopropylamino)ethyl]-3,5-dimethylpyrazole and bis[(3,5-dimethylpyrazolyl)methyl]ethylamine} with Rh^I and obtained the complexes $[Rh_2Cl_2(COD)_2(NN')]$,[4b] $[Rh(COD)(NN')](BF_4)$[4e] and $[Rh(CO)_2(NN'N)](BF_4)$, [4c] respectively. In a recent publication some of us have shown that bis[(3,5-dimethylpyrazolyl)methyl]ethylamine is a very flexible ligand with $\kappa^2(N,N)$ or $\kappa^3(N,N',N)$ bonding modes depending on the electronic configuration and the steric constrains around the metal.[4c] The hemilabile centre of the ligand is the nitrogen atom of the amine function.

Recently, we have synthesised the new Pd^{II} complexes $[PdCl_2(NN')]$,[6] and $[Pd(NN')_2](BF_4)_2$[7] {*NN′* = 1-[2-(ethylamino)ethyl]-3,5-dimethylpyrazole, 1-[2-(isopropylamino)-ethyl]-3,5-dimethylpyrazole and 1-[2-(*tert*-butylamino)-ethyl]-3,5-dimethylpyrazole}; the NMR studies of the complexes have shown the rigid conformation of the ligands when they are complexed.

This paper extends this work to a new family of *NN′N* ligands with Pd^{II}. We report the synthesis of the ligands bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine (ddae), bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]isopropylamine (ddai) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]*tert*-butylamine (ddat), and the study of their reactivity with Pd^{II}. The ligands contain two pyrazole nitrogens and one amine nitrogen as potential N-donor atoms (Scheme 1).

Results and Discussion

Synthesis and Spectroscopic Properties

Although bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine (ddae) has already been described,[5g] an alternative

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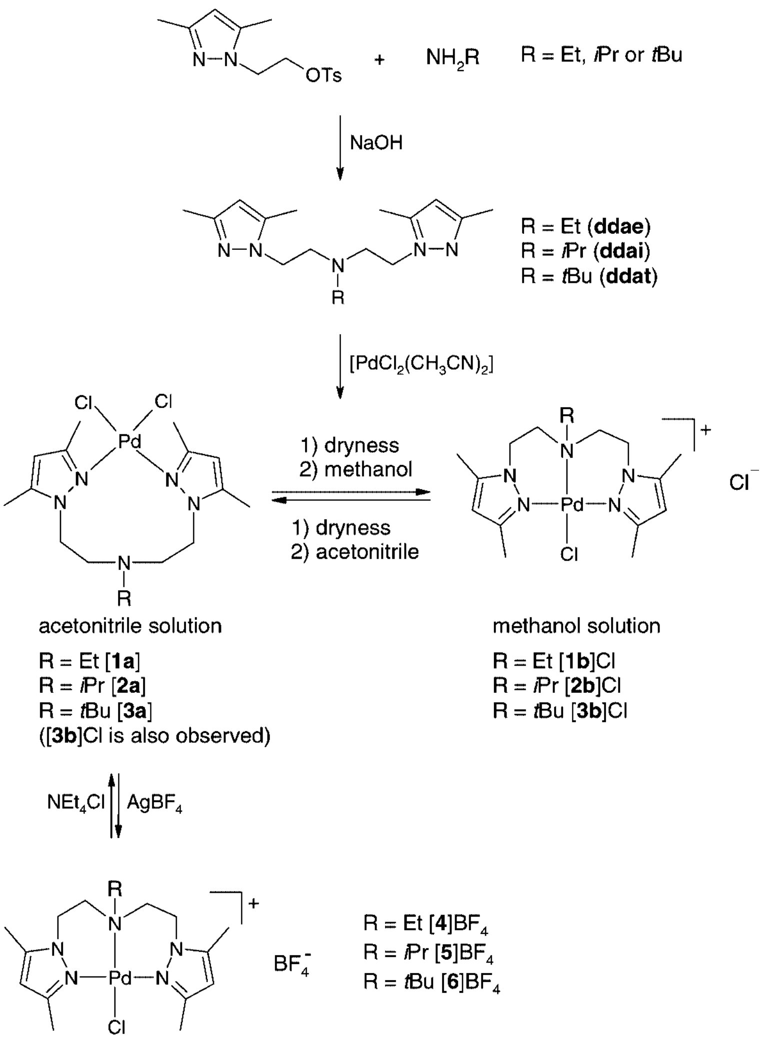

Scheme 1.

pathway for its synthesis is presented here. This new method is also useful to develop two new ligands that had not been described previously: bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]isopropylamino (ddai) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]*tert*-butylamino (ddat), neither of which could be synthesised by the same method that was used in the literature for ddae.

Synthesis of the three ligands consists of the treatment of 3,5-dimethyl-1-(2-toluene-*p*-sulfonyloxyethyl)pyrazole[8] with the appropriate primary amine (ddae: ethylamine; ddai: isopropylamine; ddat: *tert*-butylamine) in the presence of sodium hydroxide in water.

Each product was obtained as a yellow oil. This oil consists of a mixture of the mono- and bis(pyrazolyl)alkylamine ligands. The ligands were further purified by chromatography (silica gel 60) with ethyl acetate as eluent. The proportions of the bis(pyrazolyl)alkylamine/mono(pyrazolyl)alkylamine were 3:1 for ddae, 1:1 for ddai and 4:1 for ddat.

The ligands were characterised by elemental analysis, mass spectrometry and IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR signals were assigned by reference to the literature[9] and from DEPT, COSY and HMQC NMR experiments.

Complexes $[PdCl_2(NN'N)]$ [$NN'N$ = ddae (**1**), ddai (**2**) and ddat (**3**)] were obtained by treatment of the corresponding ligand with $[PdCl_2(CH_3CN)_2]$ in a 1:1 M/L ratio in CH_2Cl_2. Complexes $[PdCl(NN'N)](BF_4)$ [$NN'N$ = ddae (**4**), ddai (**5**) and ddat (**6**)] were obtained by reaction of the corresponding ligand with $[PdCl_2(CH_3CN)_2]$ in a 1:1 M/L ratio in the presence of $AgBF_4$ in CH_2Cl_2/methanol (6:1). When complexes **4**–**6** were heated under reflux in a solution of Et_4NCl in CH_3CN for 24 h complexes **1**–**3** were again obtained. The elemental analyses of products **1**–**3** are consistent with the formula $[PdCl_2(NN'N)]$ and those for compounds **4**–**6** with $[PdCl(NN'N)](BF_4)$.

Depending on the solvent used, different values of conductivity were found for complexes **1**–**3**. The conductivity values in methanol are 83–95 $\Omega^{-1}\,cm^2\,mol^{-1}$ (consistent with a 1:1 electrolyte), whereas those in acetonitrile are 78–80 $\Omega^{-1}\,cm^2\,mol^{-1}$ for **1** and **2** (in agreement with the non-electrolyte nature of the complexes) and 118 $\Omega^{-1}\,cm^2\,mol^{-1}$ for **3** (higher than for **1** and **2** due to the presence of a mixture of neutral and cationic isomers, as seen in the

NMR section). The conductivity values for complexes **4**–**6** in acetonitrile and methanol are in agreement with 1:1 electrolytes. The reported values for 10^{-3} M solutions of non-electrolyte complexes are lower than 120 Ω^{-1}cm^{2}mol^{-1} or 80 Ω^{-1}cm^{2}mol^{-1} in acetonitrile or methanol, respectively, while the range of conductivity values for 10^{-3} M solutions of 1:1 electrolyte compounds in methanol is between 80–115 Ω^{-1}cm^{2}mol^{-1} and in acetonitrile between 120 and 160 Ω^{-1}cm^{2}mol^{-1}.[10]

The IR spectra of all complexes are similar to those of the ligands, the most characteristic bands being those attributable to the pyrazolyl group: ν(C=C) and ν(C=N) between 1556 and 1554 cm^{-1} and δ(C–H)$_{oop}$ between 820 and 801 cm^{-1}. The ν(B–F) band between 1060–1053 cm^{-1} is characteristic for **4**–**6**.

The IR spectra of the complexes in the 500–100 cm^{-1} region were also recorded and show a well-defined band corresponding to ν(Pd–Cl) between 342 and 335 cm^{-1}. The number and energy of the bands is consistent with the presence of terminal chlorine. Bands attributable to ν(Pd–N) between 460 and 426 cm^{-1} are also present.[11]

The ^{1}H NMR, ^{13}C{^{1}H} NMR, HMQC and NOESY spectra were recorded in CD$_3$CN and methanol for **1**–**3**, and CD$_3$CN for **4**–**6**, and show the signals of the ligands (ddae, ddai, and ddat). NMR spectroscopic data are reported in the Exp. Sect.

The ^{1}H NMR spectra of **1** and **2** in acetonitrile at room temperature show the presence of one isomer (**1a** and **2a**, respectively), whereas the spectrum of **3** shows the presence of two isomers (**3a** and **3b**$^+$) in a 1:3 ratio (Scheme 1). The ^{1}H NMR spectra of **1**–**3** in methanol at room temperature show the presence of one isomer (**1b**$^+$, **2b**$^+$ and **3b**$^+$, respectively). The most significant feature for probing structural difference is provided by the N$_{pz}$CH$_2$CH$_2$N$_{amine}$ resonances: the CH$_2$ signals of the isomers **1b**$^+$–**3b**$^+$ are more deshielded than those of **1a**–**3a**. This observation suggests that the nitrogen of the amine group is bonded to palladium in **1b**$^+$–**3b**$^+$. For isomers **1a**–**3a**, at 298 K, the methylene protons appear as four poorly defined broad bands. This led us to record variable-temperature spectra for **1** in acetonitrile. At higher temperatures (313 K) only one signal can be observed for each CH$_2$ of the N$_{pz}$CH$_2$CH$_2$N$_{amine}$ chain, whereas lowering of the temperature induces a progressive broadening and splitting of the two signals corresponding to each CH$_2$. At 283 K, four well-defined bands are observed at δ = 4.95, 4.31, 3.09 and 2.72 ppm. This suggests that at 313 K there is a fluxional process in which, with ring-flipping, the two hydrogens of each CH$_2$ are interconverted and only one signal can be observed. This process would take place with a $\Delta G^{\ddagger}$ value of about 60 kJ mol^{-1}, as deduced from the coalescence behaviour of the methylene resonances.[12]

The ^{1}H NMR spectra at room temperature for **4**–**6** complexes in acetonitrile show the presence of one isomer (**4b**$^+$, **5b**$^+$ and **6b**$^+$, respectively).

The NMR spectra of complexes **1**–**3** in methanol and **4**–**6** in acetonitrile were studied in detail. 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 are consistent with the simulated spectra for compounds **1**–**6** obtained with the aid of the *g* NMR program.[13] All these results are reported in Tables 1 and 2. Figures 1 and 2 show the experimentally determined and simulated spectra for **2** and **5**, respectively. HMQC spectra were used to assign the signals of protons H-6 and H-7. The two protons of each CH$_2$ group in a N$_{pz}$CH$_2$CH$_2$N$_{amino}$ chain are diastereotopic and thus give rise to four groups of signals, each attributable to a single hydrogen atom of one N$_{pz}$CH$_2$CH$_2$N$_{amino}$ chain. Each group of signals can be assigned as a doublet of doublets of doublets for H-6 and H-7.

Table 1. Chemical shifts [ppm] and ^{1}H-^{1}H coupling constants [Hz] for **1b**$^+$–**3b**$^+$ in methanol.

Compound	[**1b**]$^+$	[**2b**]$^+$	[**3b**]$^+$
δ_H (6a)	4.68	4.71	4.71
δ_H (6b)	5.21	5.30	5.44
δ_H (7a)	3.26	3.22	3.19
δ_H (7b)	2.87	2.96	3.30
^2J(6a,6b)	15.71	15.75	15.82
^2J(7a,7b)	14.22	14.47	14.89
^3J(6a,7a)	3.33	3.78	3.80
^3J(6b,7b)	11.19	11.03	10.54
^3J(6a,7b)	2.54	2.04	1.60
^3J(6b,7a)	2.25	1.84	1.25

Table 2. Chemical shifts [ppm] and ^{1}H-^{1}H coupling constants [Hz] for **4b**$^+$–**6b**$^+$ in CD$_3$CN.

Compound	[**4b**]$^+$	[**5b**]$^+$	[**6b**]$^+$
δ_H (6a)	4.54	4.55	4.58
δ_H (6b)	5.10	5.17	5.22
δ_H (7a)	3.16	3.07	2.97
δ_H (7b)	2.78	2.85	3.08
^2J(6a,6b)	15.84	15.74	15.98
^2J(7a,7b)	14.30	14.01	14.86
^3J(6a,7a)	3.18	3.42	3.75
^3J(6b,7b)	11.22	11.01	11.22
^3J(6a,7b)	2.47	1.97	1.60
^3J(6b,7a)	2.63	1.60	1.25

In the NOESY spectra of compounds **1**–**3** in methanol and **4**–**6** in acetonitrile, it was observed that the methyl linked to the pyrazole at δ = 2.66 (**1b**$^+$), 2.63 (**2b**$^+$) 2.58 (**3b**$^+$), 2.63 (**4b**$^+$), 2.61 (**5b**$^+$) and 2.58 ppm (**6b**$^+$) shows an NOE with the doublet of doublets of doublets at δ = 4.58, 4.71, 4.71, 4.54, 4.55 and 4.48 ppm (**1b**$^+$–**6b**$^+$, respectively), but not with the ones at δ = 5.21, 5.30, 5.44, 5.10, 5.17 and 5.22 ppm (**1b**$^+$–**6b**$^+$, respectively). This allowed us to assign H-6a to the first set of doublet of doublets of doublets. From the NOESY spectra it can also be observed that the methyl groups from the ethylamino [δ = 1.65 (**1b**$^+$), 1.57 ppm (**4b**$^+$)], isopropylamino [δ = 1.55 (**2b**$^+$), 1.47 ppm (**5b**$^+$)] and *tert*-butylamino [δ = 1.22 (**3b**$^+$), 1.17 (**6b**$^+$)] moieties show NOEs with the doublet of doublets of doublets at δ = 2.87 (**1b**$^+$), 2.96 (**2b**$^+$), 3.30 (**3b**$^+$), 2.78 (**4b**$^+$), 2.85 (**5b**$^+$) and 3.08 ppm (**6b**$^+$). This information allowed us to assign H-7b to these signals. These assignments were possible thanks to the X-ray crystal structure of (**1b**)Cl·H$_2$O (Fig-

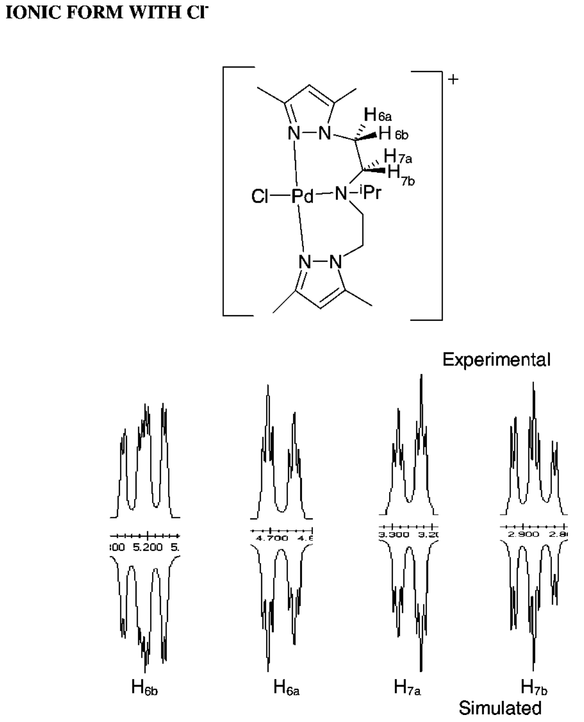

Figure 1. The experimental (250 MHz) and simulated (*g* NMR) ^{1}H NMR spectra for the H-6 and H-7 protons of the $N_{pz}CH_2$-CH_2N_{amino} fragment of [PdCl(ddai)]Cl ([**2b**]Cl).

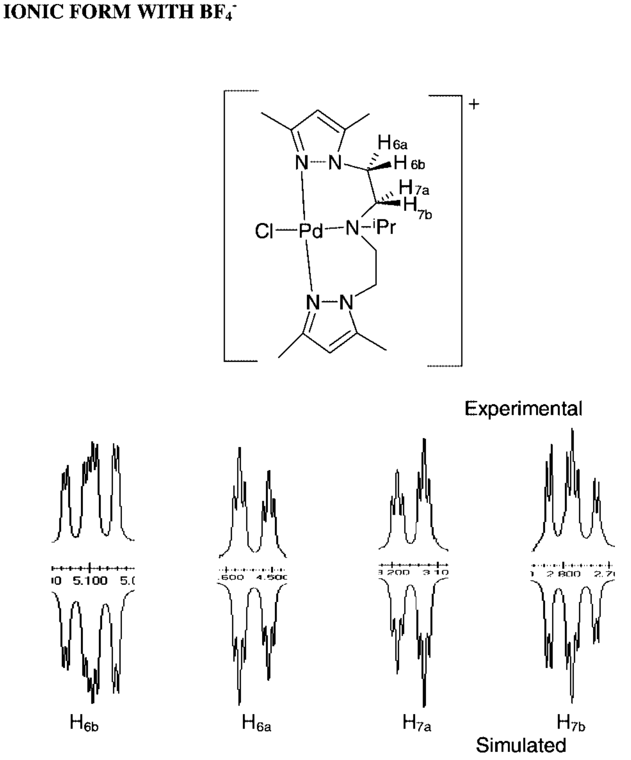

Figure 2. The experimental (250 MHz) and simulated (*g* NMR) ^{1}H NMR spectra for the H-6 and H-7 protons of the $N_{pz}CH_2$-CH_2N_{amino} fragment of [PdCl(ddai)]BF_4 ([**5b**]BF_4).

ure 3), which shows that the shortest distances are between the methyl linked to the pyrazole at δ = 2.66 ppm and the doublet of doublets of doublets at δ = 4.67 ppm (H6b···H5a = 2.03, H11a···H15a = 2.01 Å) and between the methyl group from the ethylamino group and H-7b (H10b···H9c = 2.09 Å).

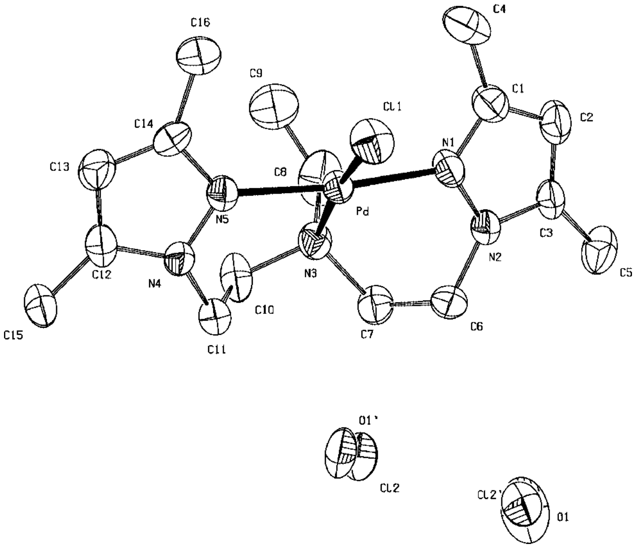

Figure 3. ORTEP drawing of [PdCl(ddae)]Cl·H_2O, showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Crystal Structure of [PdCl(ddae)]Cl·H_2O

The crystal structure consists of discrete [PdCl(ddae)]$^+$ units, chloride anions and solvent molecules (H_2O) (Figure 3). The H_2O and chloride ions are disordered.

The cation complex is mononuclear, and the Pd^{II} is coordinated to the ddae ligand by its three donor atoms (two nitrogen atoms of the pyrazolyl group and one nitrogen atom of the amine moiety), 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 (0.0045 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 N5–Pd–N3 and N1–Pd–N3 is 37.1(3)°. The ddae ligand acts as a tridentate chelate and forms two six-membered rings, with a boat conformation for Pd–N1–N2–C6–C7–N3 and a twist-boat conformation for Pd–N5–N4–C11–C10–N3, which share an edge (Pd–N_{amino}). The boat distortions in the six-membered rings are ΔC_s[(N3–C7)] = ΔC_s[(N1–N2)] = 19.4(6)° for Pd–N1–N2–C6–C7–N3 and ΔC_s[(N3–C10)] = ΔC_s[(N5–N4)] = 52.2(6)° for Pd–N5–N4–C11–C10–N3.

A PdN_3Cl core is present in 89 complexes in the literature.[14] Some selected bond lengths and bond angles for this complex are listed in Table 3. The Pd–N_{pz} bond lengths [2.019(6) and 2.027(6) Å], the Pd–N_{amino} bond length [2.113(5) Å] and the Pd–Cl bond length [2.2991(18) Å] can be regarded as normal compared with the distances found in the literature. For Pd–N_{pz}, the literature describes values between 1.979 and 2.141 Å,[1a,1b,1f,2a–2d,2g,6,15] for Pd–N_{amino} between 2.017 and 2.280 Å,[16] and for Pd–Cl between 2.280 and 2.341 Å.[1a,1b,1f,2a–2d,6,15b,15c]

Table 3. Selected bond lengths [Å] and angles [°] for [PdCl(ddae)]-Cl·H_2O.

Pd–N(1)	2.019(6)	Pd–N(3)	2.113(5)
Pd–N(5)	2.027(6)	Pd–Cl(1)	2.2991(18)
N(1)–Pd–N(5)	172.3(2)	N(1)–Pd–Cl(1)	90.44 (17)
N(1)–Pd–N(3)	87.3(2)	N(5)–Pd–Cl(1)	92.30(17)
N(5)–Pd–N(3)	90.8(2)	N(3)–Pd–Cl(1)	173.15(15)

The $N_{pyrazole}$–N_{amino} bite angles of the ligand are 87.3(2)° and 90.8(2)°, respectively, and are similar to the corresponding bite angles in the complexes [$PdCl_2$(*NN′*)] [*NN′* = deae, deat; 89.3(2)° and 88.16(18)°, respectively][6] and [Pd(*NN′*)$_2$](BF_4)$_2$ [*NN′* = deat; 87.3(2)°].[7]

Conclusion

The *N*-alkylaminopyrazole ligands ddae, ddai, and ddat can coordinate Pd^{II} centres in different ways. In complexes **1**–**3** these ligands show didentate coordination (*NN*) in acetonitrile and tridentate coordination (*NN′N*) in methanol. Furthermore, we have demonstrated the hemilabile properties of these ligands when coordinated to Pd^{II}.

Complexes **4**–**6**, where the ligand uses *NN′N* coordination, are obtained from **1**–**3** by treatment with $AgBF_4$. When complexes **4**–**6** are heated under reflux in a solution of Et_4NCl in CH_3CN, **1**–**3** are obtained once again. This could be considered as type-III hemilability.[17]

Experimental Section

General Details: 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 the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile and methanol, employing a CyberScan CON 500 (Eutech Instruments) conductimeter. Infrared spectra were run on a Perkin–Elmer FT spectrophotometer, series 2000 cm^{-1} as NaCl pellets, KBr pellets or polyethylene films in the range 4000–100 cm^{-1}. ^{1}H, ^{13}C{^{1}H}, DEPT, COSY, HMQC, and NOESY NMR spectra were recorded with an NMR-FT Bruker 250 MHz spectrometer in $CDCl_3$, CD_3CN or [D$_4$]methanol solutions at room temperature. 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 complex [$PdCl_2(CH_3CN)_2$][18] was synthesised according to published methods. The precursor 3,5-dimethyl-1-[2-(*p*-tosyloxy)ethyl]pyrazole was prepared as described in the literature.[8]

Synthesis of the Ligands Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine (ddae), Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]isopropylamine (ddai) and Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-*tert*-butylamine (ddat): The synthesis consists of the reaction between 3,5-dimethyl-1-[2-(*p*-tosyloxy)ethyl]pyrazole (6.17 g, 21 mmol), 11 mmol of the appropriate primary amine (ddae: 0.88 mL of 70% ethylamine; ddai: 0.98 mL of 97% isopropylamine; ddat: 1.18 mL of 98% *tert*-butylamine), and sodium hydroxide (0.96 g, 24 mmol). The reaction was carried out in 20 mL of water with continuous stirring at reflux for 4 h. The mixture was then cooled down to room temperature and extracted three times with 6 mL of CH_3Cl. The organic phase was collected and dried overnight with anhydrous $MgSO_4$. The solution was filtered off and the solvent removed under vacuum. Each product was obtained as a yellow oil. This oil consisted of a mixture of the mono- and bis(pyrazolylalkyl)amine ligands. The proportions of the bis(pyrazolylalkyl)amine and the mono(pyrazolylalkyl)amine were 3:1 for ddae, 1:1 for ddai and 1:4 for ddat.

In order to separate the two ligands, a silica gel column with ethyl acetate as eluent was used. The mono(pyrazolylalkyl)amine ligand stayed on top of the column whereas the bis(pyrazolylalkyl)amine ligand eluted. The solvent was removed under vacuum to give ddae as a pale-yellow oil, ddai as a pale-yellow solid (m.p. 25 °C) and ddat as a white solid (m.p. 30 °C).

ddae: Yield: 24% (0.76 g). $C_{16}H_{27}N_5$ (289.5): calcd. C 66.44, H 9.34, N 24.22; found C 66.01, H 9.35, N 24.50. MS (ESI): *m/z* (%) = 312.2(31) [MNa$^+$], 290.2 (100) [MH$^+$]. IR (NaCl): $\tilde{\nu}$ = 3120 cm^{-1} $\nu(C–H)_{ar}$, 2968, 2928 $\nu(C–H)_{al}$, 1552 [ν(C=C), ν(C=N)]$_{ar}$, 1462, 1424 [δ(C=C), δ(C=N)]$_{ar}$, 1092 $\delta(C–H)_{ip}$, 774 $\delta(C–H)_{oop}$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.66 [s, 2 H, C*H*(pz)], 3.77 (t, ^3J = 6.8 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.75 (t, ^3J = 6.8 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.50 (q, ^3J = 7.2 Hz, 2 H, NCH_2CH_3), 2.12 [s, 12 H, CH_3(pz)], 0.92 (t, ^3J = 7.2 Hz, 3 H, NCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 147.7 (CCH_3), 139.5 (CCH_3), 105.1 [CH(pz)], 54.8 ($N_{pz}CH_2CH_2N$), 49.1 (NCH_2CH_3), 47.8 ($N_{pz}CH_2CH_2N$), 13.8 (CCH_3), 12.5 (NCH_2CH_3), 11.4 (CCH_3) ppm.

ddai: Yield: 23% (0.77 g). $C_{17}H_{29}N_5$ (303.5): calcd. C 67.33, H 9.57, N 23.10; found C 67.09, H 9.76, N 22.80. MS (ESI): *m/z* (%) = 304.2 (100) [MH$^+$], 208.1 (5) [MH$^+$ – 3,5-dmpz]. IR (KBr): $\tilde{\nu}$ = 3114 cm^{-1} $\nu(C–H)_{ar}$, 2959, 2926 $\nu(C–H)_{al}$, 1552 [ν(C=C), ν(C=N)]$_{ar}$, 1460, 1425 [δ(C=C), δ(C=N)]$_{ar}$, 1089 $\delta(C–H)_{ip}$, 777 $\delta(C–H)_{oop}$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.66 [s, 2 H, C*H*(pz)], 3.66 (t, ^3J = 6.7 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.78 [sp, ^3J = 6.5 Hz, 1 H, $NCH(CH_3)_2$], 2.70 (t, ^3J = 6.7 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.12 [s, 12 H, CH_3(pz)], 0.90 [d, ^3J = 6.5 Hz, 6 H, $NCH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 147.7 (CCH_3), 139.6 (CCH_3), 105.0 [CH(pz)], 52.3 [$NCH(CH_3)_2$], 51.9 ($N_{pz}CH_2CH_2N$), 48.9 ($N_{pz}CH_2CH_2N$), 18.6 [$NCH(CH_3)_2$], 13.9 (CCH_3), 11.5 (CCH_3) ppm.

ddat: Yield: 21% (0.73 g). $C_{18}H_{31}N_5$ (317.5): calcd. C 68.14, H 9.78, N 22.08; found C 68.08, H 9.43, N 22.02. MS (ESI): *m/z* (%) = 340.2 (2) [MNa$^+$], 318.3 (100) [MH$^+$], 262.1 (76) [MH$^+$ – *t*Bu]. IR (KBr): $\tilde{\nu}$ = 3114 cm^{-1} $\nu(C–H)_{ar}$, 2975, 2915 $\nu(C–H)_{al}$, 1553 [ν(C=C), ν(C=N)]$_{ar}$, 1462, 1425 [δ(C=C), δ(C=N)]$_{ar}$, 1097 $\delta(C–H)_{ip}$, 776 $\delta(C–H)_{oop}$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.66 [s, 2 H, C*H*(pz)], 3.61 (t, ^3J = 6.4 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.79 (t, ^3J = 6.4 Hz, 4 H, $N_{pz}CH_2CH_2N$), 2.15 [s, 6 H, CH_3(pz)], 2.11 [s, 6 H, CH_3(pz)], 1.02 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 147.7 (CCH_3), 139.6 (CCH_3), 105.1 [CH(pz)], 55.8 [$NC(CH_3)_3$], 52.8 ($N_{pz}CH_2CH_2N$), 50.3 ($N_{pz}CH_2CH_2N$), 27.4 [$NC(CH_3)_3$], 13.9 (CCH_3), 11.6 (CCH_3).

Synthesis of the Complexes [$PdCl_2$(*NN′N*)] [*NN′N* = ddae (1), ddai (2), ddat (3)]: A solution of 0.27 mmol of the corresponding ligand (ddea: 0.078 g; ddai: 0.082 g; and ddat: 0.086 g) in 5 mL of dry CH_2Cl_2 was added to a solution of [$PdCl_2(CH_3CN)_2$] (0.070 g, 0.27 mmol) in 10 mL of dry CH_2Cl_2. After the mixture had been stirred for 12 h, most of the solvent was removed under vacuum. Diethyl ether (5 mL) was then added dropwise to induce precipitation. The orange solids were filtered off, washed twice with 5 mL of diethyl ether, and recrystallised from a dichloromethane/diethyl ether (1:1) mixture.

Key coupling constants for **1b**$^+$–**3b**$^+$ in methanol are given in Table 1.

1: Yield: 53% (0.067 g). $C_{16}H_{27}Cl_2N_5Pd$ (466.8): calcd. C 41.17, H 5.79, N 15.01; found C 41.05, H 5.94, N 14.86%. Conductivity (8.57×10^{-4} M in acetonitrile): 78 $\Omega^{-1}cm^2mol^{-1}$; (8.72×10^{-4} M in methanol): 95 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3129, 3085 cm^{-1} ν(C–H)$_{ar}$, 2965, 2915 ν(C–H)$_{al}$, 1554 [ν(C=C), ν(C=N)]$_{ar}$, 1465, 1422 [δ(C=C), δ(C=N)]$_{ar}$, 1093 δ(C–H)$_{ip}$, 801 δ(C–H)$_{oop}$; (polyethylene): $\tilde{\nu}$ = 458 cm^{-1} ν(Pd–N), 336 ν(Pd–Cl). ^{1}H NMR for isomer **1a** (CD$_3$CN, 250 MHz): δ = 6.12 [s, 2 H, C*H*(pz)], 5.02 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.68 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.16 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.88 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.63 [s, 6 H, C*H*$_3$(pz)], 2.38 [s, 6 H, C*H*$_3$(pz)], 2.17 (q, 2 H, C*H*$_2$CH$_3$), 1.57 (t, 3 H, CH$_2$C*H*$_3$) ppm; isomer **1b**$^+$ ([D$_4$]methanol, 250 MHz): δ = 6.16 [s, 2 H, C*H*(pz)], 5.21 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.67 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.26 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.87 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.66 [s, 6 H, C*H*$_3$(pz)], 2.42 [s, 6 H, C*H*$_3$(pz)], 2.18 (q, 2 H, C*H*$_2$CH$_3$), 1.65 (t, 3 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR for isomer **1a** (CD$_3$CN, 63 MHz): δ = 153.3 (*C*CH$_3$), 145.0 (*C*CH$_3$), 108.8 [*C*H(pz)], 60.8 (N*C*H$_2$CH$_3$), 60.6 (N$_{pz}$*C*H$_2$CH$_2$N), 48.6 (N$_{pz}$CH$_2$*C*H$_2$N), 14.8 (C*C*H$_3$), 14.2 (NCH$_2$*C*H$_3$), 11.2 (C*C*H$_3$) ppm; isomer **1b**$^+$ ([D$_4$]methanol, 63 MHz): δ = 153.5 (*C*CH$_3$), 144.8 (*C*CH$_3$), 108.7 [*C*H(pz)], 60.9 (N*C*H$_2$CH$_3$), 60.6 (N$_{pz}$*C*H$_2$CH$_2$N), 48.2 (N$_{pz}$CH$_2$*C*H$_2$N), 14.2 (C*C*H$_3$), 13.8 (NCH$_2$*C*H$_3$), 10.3 (C*C*H$_3$) ppm.

2: Yield: 46% (0.060 g). $C_{17}H_{29}Cl_2N_5Pd$ (480.8): calcd. C 42.47, H 6.04, N 14.57; found C 42.58, H 6.09, N 14.69. Conductivity (6.24×10^{-4} M in acetonitrile): 80 $\Omega^{-1}cm^2mol^{-1}$; (9.05×10^{-4} M in methanol): 83 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3125, 3077 cm^{-1} ν(C–H)$_{ar}$, 2963, 2922 ν(C–H)$_{al}$, 1554 [ν(C=C), ν(C=N)]$_{ar}$, 1468, 1424 [δ(C=C), δ(C=N)]$_{ar}$, 1093 δ(C–H)$_{ip}$, 807 δ(C–H)$_{oop}$; (polyethylene): $\tilde{\nu}$ = 460 cm^{-1} ν(Pd–N), 335 ν(Pd–Cl). ^{1}H NMR for isomer **2a** (CD$_3$CN, 250 MHz): δ = 6.11 [s, 2 H, C*H*(pz)], 5.13 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.60 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.15 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.87 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.61 [s, 6 H, C*H*$_3$(pz)], 2.38 [s, 6 H, C*H*$_3$(pz)], 2.27 [sp, 1 H, C*H*(CH$_3$)$_2$], 1.47 [d, 6 H, CH(C*H*$_3$)$_2$] ppm; isomer **2b**$^+$ ([D$_4$]methanol, 250 MHz): δ = 6.15 [s, 2 H, C*H*(pz)], 5.29 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.70 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.22 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.96 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.63 [s, 6 H, C*H*$_3$(pz)], 2.42 [s, 6 H, C*H*$_3$(pz)], 2.32 [sp, 1 H, C*H*(CH$_3$)$_2$], 1.55 [d, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR for isomer **2a** (CD$_3$CN, 63 MHz): δ = 153.2 (*C*CH$_3$), 144.9 (*C*CH$_3$), 108.7 [*C*H(pz)], 65.5 [N*C*H(CH$_3$)$_2$], 58.3 (N$_{pz}$*C*H$_2$CH$_2$N), 48.7 (N$_{pz}$CH$_2$*C*H$_2$N), 19.5 [NCH(*C*H$_3$)$_2$], 14.6 (C*C*H$_3$), 14.2 (NCH$_2$*C*H$_3$), 11.2 (C*C*H$_3$) ppm; isomer **2b**$^+$ ([D$_4$]methanol, 63 MHz): δ = 153.3 (*C*CH$_3$), 144.6 (*C*CH$_3$), 108.6 [*C*H(pz)], 65.8 [N*C*H(CH$_3$)$_2$], 58.5 (N$_{pz}$*C*H$_2$CH$_2$N), 48.2 (N$_{pz}$CH$_2$*C*H$_2$N), 19.0 [NCH(*C*H$_3$)$_2$], 14.1 (C*C*H$_3$), 10.4 (C*C*H$_3$) ppm.

3: Yield: 22% (0.029 g). $C_{18}H_{31}Cl_2N_5Pd$ (494.8): calcd. C 43.70, H 6.27, N 14.16; found C 43.91, H 6.24, N 13.81. Conductivity (1.12×10^{-3} M in acetonitrile): 118 $\Omega^{-1}cm^2mol^{-1}$; (6.07×10^{-4} M in methanol): 89 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3122, 3077 cm^{-1} ν(C–H)$_{ar}$, 2971, 2922 ν(C–H)$_{al}$, 1556 [ν(C=C), ν(C=N)]$_{ar}$, 1471, 1424 [δ(C=C), δ(C=N)]$_{ar}$, 1093 δ(C–H)$_{ip}$, 802 δ(C–H)$_{oop}$; (polyethylene): $\tilde{\nu}$ = 457 cm^{-1} ν(Pd–N), 336 ν(Pd–Cl). ^{1}H NMR for isomer **3a** (CD$_3$CN, 250 MHz): δ = 6.01 [s, 2 H, C*H*(pz)], 5.15 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.91 (m, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.60 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 3.12 (m, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.56 [s, 6 H, C*H*$_3$(pz)], 2.36 [s, 6 H, C*H*$_3$(pz)], 1.15 [s, 9 H, C(C*H*$_3$)$_3$] ppm; isomer **3b**$^+$: δ = 6.07 [s, 2 H, C*H*(pz)], 5.32 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.68 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.17 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 3.10 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.56 [s, 6 H, C*H*$_3$(pz)], 2.36 [s, 6 H, C*H*$_3$(pz)], 1.15 [s, 9 H, C(C*H*$_3$)$_3$] ppm; isomer **3b**$^+$ ([D$_4$]methanol, 250 MHz): δ = 6.10 [s, 2 H, C*H*(pz)], 5.44 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.71 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.30 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 3.19 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.58 [s, 6 H, C*H*$_3$(pz)], 2.41 [s, 6 H, C*H*$_3$(pz)], 1.22 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR for isomer **3a** (CD$_3$CN, 63 MHz): δ = 152.7 (*C*CH$_3$), 144.5 (*C*CH$_3$), 108.5 [*C*H(pz)], 69.3 [N*C*(CH$_3$)$_3$], 60.6 (N$_{pz}$*C*H$_2$CH$_2$N), 49.2 (N$_{pz}$CH$_2$*C*H$_2$N), 19.2 [NC(*C*H$_3$)$_3$], 14.3 (C*C*H$_3$), 10.8 (C*C*H$_3$) ppm; isomer **3b**$^+$: δ = 153.1 (*C*CH$_3$), 144.8 (*C*CH$_3$), 108.7 [*C*H(pz)], 69.4 [N*C*(CH$_3$)$_3$], 60.9 (N$_{pz}$*C*H$_2$CH$_2$N), 49.4 (N$_{pz}$CH$_2$*C*H$_2$N), 19.5 [NC(*C*H$_3$)$_3$], 14.5 (C*C*H$_3$), 11.0 (C*C*H$_3$) ppm; isomer **3b**$^+$ ([D$_4$]-methanol, 63 MHz): δ = 153.1 (*C*CH$_3$), 144.6 (*C*CH$_3$), 108.5 [*C*H(pz)], 69.7 [N*C*(CH$_3$)$_3$], 60.9 (N$_{pz}$*C*H$_2$CH$_2$N), 49.4 (N$_{pz}$CH$_2$*C*H$_2$N), 19.0 [NC(*C*H$_3$)$_3$], 14.0 (C*C*H$_3$), 10.3 (C*C*H$_3$) ppm.

Synthesis of the Complexes [PdCl(*NN′N*)](BF$_4$) [*NN′N* = ddae (4), ddai (5), ddat (6)]: AgBF$_4$ (0.052 g, 0.27 mmol) in 5 mL of methanol and 0.27 mmol of the corresponding ligand (ddae: 0.078 g; ddai: 0.082 g; ddat: 0.086 g) in 5 mL of dry CH$_2$Cl$_2$ were added to a solution of [PdCl$_2$(CH$_3$CN)$_2$] (0.070 g, 0.27 mmol) in 10 mL of dry CH$_2$Cl$_2$. The mixture was protected from the light and stirred at room temp. for 1 h. The yellow solution was then filtered through a pad of Celite. The solution was stirred for 30 min and then most of the solvent was removed under vacuum. Diethyl ether (5 mL) was then added dropwise to induce precipitation. The yellow solid was filtered off, washed twice with 5 mL of diethyl ether and dried under vacuum.

Key coupling constants for **4b**$^+$–**6b**$^+$ in CD$_3$CN are given in Table 2.

4: Yield: 81% (0.11 g). $C_{16}H_{27}BClF_4N_5Pd$ (517.7): calcd. C 37.09, H 5.22, N 13.52; found C 37.41, H 5.11, N 13.48. Conductivity (7.73×10^{-4} M in acetonitrile): 156 $\Omega^{-1}cm^2mol^{-1}$; (8.01×10^{-4} M in methanol): 93 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3132, 3078 cm^{-1} ν(C–H)$_{ar}$, 2975, 2938 ν(C–H)$_{al}$, 1555 [ν(C=C), ν(C=N)]$_{ar}$, 1466, 1422 [δ(C=C), δ(C=N)]$_{ar}$, 1053 ν(B–F), 820 δ(C–H)$_{oop}$; (polyethylene): $\tilde{\nu}$ = 426 cm^{-1} ν(Pd–N), 341 ν(Pd–Cl). ^{1}H NMR (CD$_3$CN, 250 MHz): δ = 6.12 [s, 2 H, C*H*(pz)], 5.10 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.54 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.16 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.78 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.63 [s, 6 H, C*H*$_3$(pz)], 2.36 [s, 6 H, C*H*$_3$(pz)], 2.14 (q, ^3J = 7.2 Hz, 2 H, NC*H*$_2$CH$_3$), 1.57 (t, ^3J = 7.2 Hz, 3 H, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (CD$_3$CN, 63 MHz): δ = 153.4 (*C*CH$_3$), 145.0 (*C*CH$_3$), 108.8 [*C*H(pz)], 60.8 (N*C*H$_2$CH$_3$), 60.7 (N$_{pz}$*C*H$_2$CH$_2$N), 48.1 (N$_{pz}$CH$_2$*C*H$_2$N), 14.7 (C*C*H$_3$), 14.1 (NCH$_2$*C*H$_3$), 11.0 (C*C*H$_3$) ppm.

5: Yield: 78% (0.11 g). $C_{17}H_{29}BClF_4N_5Pd$ (531.7): calcd. C 38.37, H 5.45, N 13.16; found C 38.38, H 4.77, N 12.56. Conductivity (7.52×10^{-4} M in acetonitrile): 154 $\Omega^{-1}cm^2mol^{-1}$; (9.28×10^{-4} M in methanol): 92 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3128, 3077 cm^{-1} ν(C–H)$_{ar}$, 2966, 2920 ν(C–H)$_{al}$, 1555 [ν(C=C), ν(C=N)]$_{ar}$, 1466, 1422 [δ(C=C), δ(C=N)]$_{ar}$, 1060 ν(B–F), 809 δ(C–H)$_{oop}$) ; (polyethylene): $\tilde{\nu}$ = 459 cm^{-1} ν(Pd–N), 342 ν(Pd–Cl). ^{1}H NMR (CD$_3$CN, 250 MHz): δ = 6.11 [s, 2 H, C*H*(pz)], 5.17 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 4.55 (ddd, 2 H, N$_{pz}$C*H*HCH$_2$N), 3.07 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.85 (ddd, 2 H, N$_{pz}$CH$_2$C*H*HN), 2.61 [s, 6 H, C*H*$_3$(pz)], 2.37 [s, 6 H, C*H*$_3$(pz)], 2.28 [sp, ^3J = 6.6 Hz, 1 H, C*H*(CH$_3$)$_2$], 1.47 [d, ^3J = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (CD$_3$CN, 63 MHz): δ = 153.2 (*C*CH$_3$), 144.9 (*C*CH$_3$), 108.7 [*C*H(pz)], 65.6 [N*C*H(CH$_3$)$_2$], 58.3 (N$_{pz}$*C*H$_2$CH$_2$N), 48.5 (N$_{pz}$CH$_2$*C*H$_2$N), 19.4 [NCH(*C*H$_3$)$_2$], 14.6 (C*C*H$_3$), 11.0 (C*C*H$_3$) ppm.

6: Yield: 73% (0.11 g). $C_{18}H_{31}BClF_4N_5Pd$ (545.7): calcd. C 39.58, H 5.68, N 12.83; found C 39.31, H 5.49, N 13.13. Conductivity (7.73×10^{-4} M in acetonitrile): 153 $\Omega^{-1}cm^2mol^{-1}$; (6.32×10^{-4} M in methanol): 92 $\Omega^{-1}cm^2mol^{-1}$. IR (KBr): $\tilde{\nu}$ = 3122, 3085 cm^{-1} $\nu(C–H)_{ar,}$ 2981, 2922 $\nu(C–H)_{al}$, 1555 $[\nu(C=C), \nu(C=N)]_{ar}$, 1473, 1424 $[\delta(C=C), \delta(C=N)]_{ar}$, 1060 $\nu(B–F)$, 809 $\delta(C–H)_{oop}$; (polyethylene): $\tilde{\nu}$ = 458 cm^{-1} $\nu(Pd–N)$, 335 $\nu(Pd–Cl)$. ^1H NMR (CD_3CN, 250 MHz): δ = 6.09 [s, 2 H, C*H*(pz)], 5.33 (ddd, 2 H, $N_{pz}CHHCH_2N$), 4.58 (ddd, 2 H, $N_{pz}CHHCH_2N$), 3.17 (ddd, 2 H, $N_{pz}CH_2CHHN$), 3.07 (ddd, 2 H, $N_{pz}CH_2CHHN$), 2.58 [s, 6 H, CH_3(pz)], 2.38 [s, 6 H, CH_3(pz)], 1.17 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (CD_3CN, 63 MHz): δ = 153.1 (CCH_3), 144.8 (CCH_3), 108.7 [*C*H(pz)], 69.5 [$NC(CH_3)_3$], 60.9 ($N_{pz}CH_2CH_2N$), 49.4 ($N_{pz}CH_2CH_2N$), 19.5 [$NC(CH_3)_3$], 14.5 (CCH_3), 11.0 (CCH_3) ppm.

X-ray Crystal Structure for Compound [PdCl(ddae)]Cl·H_2O: Crystals suitable for X-ray diffraction were obtained by crystallisation from methanol. A prismatic crystal was selected and mounted on a 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. Intensities were collected with graphite-monochromated Mo-K_α radiation using the $\omega/2\theta$ scan technique. 6425 Reflections were measured in the range $2.41 \leq \theta \leq 29.96°$, 6085 reflections of which were non-equivalent by symmetry [R_{int}(on I) = 0.031]. 4431 Reflections were assumed as observed by applying the condition $I > 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarisation but no absorption corrections were made. The structure was solved by direct methods using the SHELXS computer program,[19] and refined by full-matrix least-squares method with SHELX-97 [20] using 6425 reflections (very negative intensities were not assumed). The function minimised was $\Sigma w||F_o|^2 - |F_c|^2|^2$ where $\omega = [\sigma^2(I) + (0.0818P)^2 + 10.1890\ P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. All H-atoms were computed and refined using a riding model, with an overall temperature factor equal to 1.2-times the equivalent temperature factor of the atom to which they are 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 structure, are gathered in Table 4.

Table 4. Crystallographic data for [PdCl(ddae)]Cl·H_2O.

Formula	$C_{16}H_{29}Cl_2N_5OPd$
M	484.74
Temperature [K]	293(2)
Crystal System	monoclinic
Space group	$P2_1/a$
a [Å]	7.893(4)
b [Å]	31.437(5)
c [Å]	8.861(12)
α [°]	90
β [°]	107.31(7)
γ [°]	90
Z	4
D_{calc} [$g\,cm^{-3}$]	1.534
μ [mm^{-1}]	1.153
F(000)	992
Crystal size [mm]	0.2×0.1×0.1
θ range [°]	2.41 to 29.96
Index range	$-11 \leq h \leq 10, 0 \leq k \leq 44, 0 \leq l \leq 12$
Reflexions collected/unique	6425/6085 [R(int) = 0.0313]
Completeness to θ [%]	99.9
Absorption correction	none
Data/restraints/parameters	6085/0/245
Goodness-of-fit	1.080
Final R_1, ωR_2	0.0472, 0.1541
R_1 (all data), ωR_2	0.0864, 0.1898
Extinction coefficient	0.0020(2)
Residual electron density [$e\,Å^{-3}$]	0.858 and –0.737

CCDC-290469 contains 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.

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