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# Exploring the coordination chemistry and reactivity of hemilabile *N*-alkylaminopyrazole ligands towards Pd(II)

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### Abstract

Reaction of the *N*-alkylaminopyrazole (*NN'N*) ligands bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine (**bdmae**) and bis[(3,5-dimethyl-1-pyrazolyl)methyl]isopropylamine (**bdmai**) with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] in a 1:1 M/L ratio in CH<sub>2</sub>Cl<sub>2</sub> produces *cis*-[PdCl<sub>2</sub>(*NN'N*)] (*NN'N* = **bdmae** (1), **bdmai** (2)). The solid state structure of complex 1 was determined by X-ray diffraction studies. The **bdmae** ligand is coordinated through the two N<sub>pz</sub> atoms to the metal atom, which completes its coordination with two chlorine atoms in a *cis* disposition.

Treatment of the corresponding ligand with  $[PdCl_2(CH_3CN)_2]$  in 1:1 M/L ratio in the presence of AgBF<sub>4</sub> and metathesis with NaBPh<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (3:1) gave  $[PdCl(bdmae)](BPh_4)$  (3), and in the presence of NaBPh<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (3:1) gave  $[PdCl(bdmae)](BPh_4)$  (4). Complexes 1 and 2 were again obtained when complexes 3 and 4 were heated under reflux in a solution of Et<sub>4</sub>NCl in acetonitrile. These Pd(II) compounds were characterised by elemental analyses, conductivity measurements, IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, HMQC and NOESY spectroscopies. The NMR studies of the complexes prove the rigid conformation of the ligands when they are complexed.

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Keywords: Palladium(II); N-alkylaminopyrazole ligands; Hemilabile ligands; Pyrazole complexes; Crystal structures

# 1. Introduction

The *N*1-substituted pyrazolic ligands have been extensively investigated in our laboratory in recent years. In particular, we have reported the synthesis, spectroscopic studies and structural characterisation of new Rh(I) and Pd(II) compounds with *N*-alkylaminopyrazoles.

The synthesis of bidentate-(NN') and tridentate-(NN'N) pyrazole ligands was developed by Driessen et al., who described the synthesis and characterisation of the complexes [MX<sub>2</sub>(deae)] (M = Co(II), Zn(II); X = Cl<sup>-</sup>, NCS<sup>-</sup>) [1], [NiCl<sub>2</sub>(deae)]<sub>2</sub> [1], [CuCl<sub>3</sub>(deaeH)] [1] (deae = 1-[2-(eth-ylamino)ethyl]-3,5-dimethylpyrazole), [MX<sub>2</sub>(bdmae)] (M = Co(II), Ni(II), Cu(II), Zn(II); X = Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) [2],

We have previously reported the reactivity of bidentate-(*NN'*) ligands **deae**, 1-[2-(ethylamino)isopropyl]-3,5-dimethylpyrazole (**deai**), and 1-[2-(ethylamino)*tert*-butyl]-3,5dimethylpyrazole (**deat**) with Rh(I) and Pd(II), obtaining complexes with general formula [Rh<sub>2</sub>Cl<sub>2</sub>(COD)<sub>2</sub>(*NN'*)] (*NN'* = **deae**, **deai**) [5], [Rh(COD)(**deae**)](BF<sub>4</sub>) [6], [Rh<sub>2</sub>(CO)<sub>2</sub>(**deae**) [6] [PdCl<sub>2</sub>(**deae**)] [7], and [PdCl(**deae**)] (BF<sub>4</sub>) [8].

Moreover, with the tridentate-(NN'N) ligands, **bdmae** and bis[(3,5-dimethyl-1-pyrazolyl)methyl]isopropylamine (**bdmai**), we have reported the reactivity with Rh(I), obtaining the complexes [Rh<sub>2</sub>Cl<sub>2</sub>(COD)<sub>2</sub>(NN'N)](NN'N = **bdmae**,

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bdmai) [5],  $[Rh(COD)(bdmae)](BF_4)$  [9],  $[Rh(CO)_2-(bdmae)](BF_4)$  [9],  $[Rh(CO)_2(bdmae)](BPh_4)$  [9],  $[Rh(CO)-(bdmae)](BF_4)$  [9], and  $[Rh(CO)(bdmae)](BPh_4)$  [9].

In a previous work, we have synthesised the new Pd(II) complexes [PdCl<sub>2</sub>(NN'N)], [PdCl(NN'N)]Cl, and [PdCl-(NN'N)](BF<sub>4</sub>) [10] (NN'N = ddae, bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]isopropylamine (ddai), and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]*tert*-butylamine (ddat)). These ligands show bidentate coordination (NN') and tridentate coordination (NN'N) depending on the solvent. In these complexes, the hemilabile centre of the ligands is the nitrogen atom of the amine function.

This paper extends this work to the reactivity of a new family of NN'N ligands with Pd(II). We report the reactivity of the ligands **bdmae**, and **bdmai** with Pd(II). These ligands contain two pyrazole nitrogens and one amine nitrogen as potential N-donor atoms.

### 2. Experimental

### 2.1. General details

Standard Schlenk techniques were employed throughout the synthesis using a double manifold vacuum line with high purity dry nitrogen. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. The 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. The conductivity measurements were performed at room temperature (r.t.) in  $10^{-3}$  M in CH<sub>3</sub>CN or CH<sub>3</sub>OH employing a Crison, micro CM 2200 conductimeter. The infrared spectra were run on a Perkin-Elmer FT spectrophotometer series 2000 cm<sup>-1</sup> as KBr pellets or polyethylene films in the range  $4000-100 \text{ cm}^{-1}$  under a nitrogen atmosphere. The <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, HMQC and NOESY spectra were run on a NMR-FT Bruker 250 MHz instrument. <sup>1</sup>H NMR and <sup>13</sup>C $\{^{1}H\}$ NMR chemical shifts ( $\delta$ ) were determined relative to internal TMS and are given in ppm. The electrospray mass spectra were obtained on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics (ESI-IT).

The synthesis of bis[(3,5-dimethyl-1-pyrazolyl)methyl]-1-methylethylamine (**bdmae**) and bis[(3,5-dimethyl-1-pyrazolyl)methyl]-1-methylisopropylamine (**bdmai**), were prepared according to the published methods [5,11,12]. The samples of  $[PdCl_2(CH_3CN)_2]$  [13] were prepared as described in the literature.

## 2.2. Synthesis of the complexes

# 2.2.1. Synthesis of the complexes $[PdCl_2(NN'N)]$ (NN'N = bdmae (1), bdmai (2))

A solution of 0.27 mmol of the corresponding ligand (bdmae: 0.070 g; and bdmai: 0.074 g) in 5 ml of dry  $CH_2Cl_2$  was added to a solution of 0.27 mmol (0.070 g) of

 $[PdCl_2(CH_3CN)_2]$  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 yellow orange solids were filtered off, washed twice with 5 ml of diethyl ether, and recrystallised in a dichloromethane/diethyl ether (1:1) mixture.

Compound Yield: 64%. Anal. Calc. 1: for C<sub>14</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>5</sub>Pd (438.3): C, 38.33; H, 5.25; N, 15.97. Found: C, 39.06; H, 5.63; N, 15.60%. Conductivity  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, 9.82 \times 10^{-4} \text{ M})$ in CH<sub>3</sub>CN): 53:  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, 8.92 \times 10^{-4} \text{ M in CH}_3\text{OH})$ : 10. IR: (KBr, cm<sup>-1</sup>) 3131, 3045, v(C-H)<sub>ar</sub>, 2977, 2937 v(C-H)<sub>al</sub>, 1554  $(v(C=C), v(C=N))_{ar}, 1460, 1419 (\delta(C=C), \delta(C=N))_{ar},$ 1093  $\delta$ (C–H)<sub>ip</sub>, 800  $\delta$ (C–H)<sub>oop</sub>; (polyethylene, cm<sup>-1</sup>) 476, 443 v(Pd-N), 338, 322 v(Pd-Cl). <sup>1</sup>H NMR (CD<sub>3</sub>CN solution, 250 MHz)  $\delta$ : 6.78 [d, 2H, <sup>2</sup>J = 15.5 Hz, N<sub>pz</sub>CH*H*N], 5.85 [s, 2H, CH(pz)], 5.32 [d, 2H,  ${}^{2}J = 15.5$  Hz,  $N_{pz}CHHN$ ], 2.74 [q, 2H, <sup>3</sup>J = 7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>], 2.63 [s, 6H,  $CH_3(pz)$ ], 2.24 [s, 6H,  $CH_3(pz)$ ], 0.68 [t, 3H,  ${}^{3}J = 7.2$  Hz, NCH<sub>2</sub>CH<sub>3</sub>].  ${}^{13}C$  NMR (CD<sub>3</sub>CN solution, 63 MHz) δ: 151.0 [CCH<sub>3</sub>], 144.4 [CCH<sub>3</sub>], 108.1 [CH(pz)], 68.8 [N<sub>pz</sub>CH<sub>2</sub>N], 44.2 [NCH<sub>2</sub>CH<sub>3</sub>], 14.9 [NCH<sub>2</sub>CH<sub>3</sub>], 12.7 [CCH<sub>3</sub>], 11.6 [CCH<sub>3</sub>].

Compound 2: Yield: 57%. Anal. Calc. for C15H25Cl2N5Pd (452.3): C, 39.79; H, 5.53; N, 15.48. Found: C, 40.33; H, 5.43; N, 15.52%. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 8.11×  $10^{-4}$  M in CH<sub>3</sub>CN): 36; ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, 9.03 × 10<sup>-4</sup> M in CH<sub>3</sub>OH): 24. IR: (KBr, cm<sup>-1</sup>) 3124, 3084, v(C-H)<sub>ar</sub>, 2971, 2938 v(C-H)<sub>al</sub>, 1555 (v(C=C), v(C=N))<sub>ar</sub>, 1462, 1417  $(\delta(C=C), \delta(C=N))_{ar}, 1083 \delta(C-H)_{ip}, 807 \delta(C-H)_{oop}; (poly$ ethylene, cm<sup>-1</sup>) 472, 448 v(Pd–N), 337, 320 v(Pd–Cl). <sup>1</sup>H NMR (CD<sub>3</sub>CN solution, 250 MHz)  $\delta$ : 6.75 [d, 2H,  $^{2}J = 15.4$  Hz, N<sub>pz</sub>CHHN], 5.87 [s, 2H, CH(pz)], 5.41 [d, 2H,  ${}^{2}J = 15.4$  Hz, N<sub>pz</sub>CHHN], 3.28 [sp, 1H,  ${}^{3}J = 6.8$  Hz, NCH(CH<sub>3</sub>)<sub>2</sub>], 2.65 [s, 6H, CH<sub>3</sub>(pz)], 2.27 [s, 6H, CH<sub>3</sub>(pz)], 0.78 [d, 6H,  ${}^{3}J = 6.8$  Hz, NCH(CH<sub>3</sub>)<sub>2</sub>].  ${}^{13}C$  NMR (CD<sub>3</sub>CN solution, 63 MHz) *δ*: 151.3 [CCH<sub>3</sub>], 144.1 [CCH<sub>3</sub>], 108.4 [CH(pz)], 68.4  $[N_{pz}CH_2N]$ , 53.2  $[NCH(CH_3)_2]$ , 20.2 [NCH(CH<sub>3</sub>)<sub>2</sub>], 15.2 [CCH<sub>3</sub>], 11.6 [CCH<sub>3</sub>].

# 2.2.2. Synthesis of the complexes [PdCl(NN'N)](BPh<sub>4</sub>) (NN'N = bdmae (3), bdmai (4))

2.2.2.1. Synthesis of the complex  $[PdCl(bdmae)](BPh_4)$ (3). To a solution of 0.27 mmol (0.070 g) of  $[PdCl_2(CH_3CN)_2]$  in 10 ml of dry  $CH_2Cl_2$ , 0.27 mmol (0.052 g) of AgBF<sub>4</sub> in 5 ml of CH<sub>3</sub>OH and 0.27 mmol (0.070 g) of the ligand bdmae in 5 ml of dry  $CH_2Cl_2$  were added. The mixture was stirred at r.t. and light-protected for 40 min. The yellow solution was then filtered through a pad of Celite. The solution was stirred for 6 h and concentrated on a vacuum line to one-fifth of the initial volume. 0.27 mmol (0.092 g) of NaBPh<sub>4</sub> was added; then the solution was cooled down to 0° and 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*.

*Compound* **3**: Yield: 34%. Anal. Calc. for C<sub>38</sub>H<sub>43</sub>BClN<sub>5</sub>Pd (721.7): C, 63.18; H, 5.96; N, 9.76. Found: C. 62.82; H. 5.87; N. 9.96%. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.  $4.16 \times 10^{-4} \text{ M}$  in CH<sub>3</sub>CN): 146;  $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ .  $9.18 \times 10^{-4}$  M in CH<sub>3</sub>OH): 100. IR: (KBr, cm<sup>-1</sup>) 3054, 3035 v(C–H)<sub>ar</sub>, 2983 v(C–H)<sub>al</sub>, 1579, 1555 (v(C=C),  $v(C=N))_{ar}$ , 1467, 1425 ( $\delta(C=C)$ ,  $\delta(C=N))_{ar}$ , 1067  $\delta(C-N)$ H)<sub>ip</sub>, 802  $\delta$ (C–H)<sub>oop</sub>; 612 (B–C); (polyethylene, cm<sup>-1</sup>) 480, 411 v(Pd-N), 343 v(Pd-Cl). MS (%) = 403 (100%) [PdCl(bdmae)]<sup>+</sup>. <sup>1</sup>H NMR (acetone- $d_6$  solution, 250 MHz)  $\delta$ : 6.04 [s, 2H, CH(pz)], 5.50 [d, 2H,  $^{2}J = 11.7$  Hz, N<sub>pz</sub>CH*H*N], 5.03 [d, 2H,  $^{2}J = 11.7$  Hz,  $N_{pz}CHHN$ ], 2.98 [q, 2H,  ${}^{3}J = 7.3$  Hz, NCH<sub>2</sub>CH<sub>3</sub>], 2.32 [s, 12H,  $CH_3(pz)$ ], 1.04 [t, 3H,  ${}^{3}J = 7.3$  Hz,  $NCH_2CH_3$ ].  ${}^{13}C$ NMR (acetone- $d_6$  solution, 63 MHz)  $\delta$ : 155.6 [CCH<sub>3</sub>], 144.4 [CCH<sub>3</sub>], 108.6 [CH(pz)], 70.1 [N<sub>pz</sub>CH<sub>2</sub>N], 54.6 [NCH<sub>2</sub>CH<sub>3</sub>], 13.2 [NCH<sub>2</sub>CH<sub>3</sub>], 11.7 [CCH<sub>3</sub>], 11.3 [CCH<sub>3</sub>].

2.2.2.2. Synthesis of the complex  $[PdCl(bdmai)](BPh_4)$ (4). To a solution of 0.27 mmol (0.070 g) of  $[PdCl_2(CH_3CN)_2]$  and 0.27 mmol (0.074 g) of the ligand bdmai in 15 ml of dry  $CH_2Cl_2$  and with continuous stirring, 0.27 mmol (0.10 g) of NaBPh<sub>4</sub> solved in 5 ml of dry  $CH_3CN$  were added. After 5 min stirring, the solution becomes turbid because of the formation of NaCl. The solution is stirred for 1 h, and then, it is filtered through a pad of Celite. The resultant yellow solution is concentrated under vacuum to 4 ml and cooled down to 0°C. Diethyl ether (5 ml) is then added dropwise with continuous stirring until a pale yellow precipitate is observed. Finally, the precipitate is filtered off, washed twice with 4 ml of cool dry diethyl ether and dried under vacuum.

*Compound* **4**: Yield: 61%. Anal. Calc. for C<sub>39</sub>H<sub>45</sub>BClN<sub>5</sub>Pd (735.7): C, 63.61; H, 6.12; N, 9.51. Found: C, 63.43; H, 5.98; N, 9.37 %. Conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $5.20 \times 10^{-4}$  M in CH<sub>3</sub>CN): 131; ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $3.12 \times 10^{-4}$  M in CH<sub>3</sub>OH): 98. IR: (KBr, cm<sup>-1</sup>) 3054, 3035 v(C–H)<sub>ar</sub>, 2982 v(C–H)<sub>al</sub>, 1579, 1557 (v(C=C),  $v(C=N))_{ar}$ , 1466, 1425 ( $\delta(C=C)$ ,  $\delta(C=N))_{ar}$ , 1065  $\delta(C-D)$ H)<sub>ip</sub>, 802  $\delta$ (C–H)<sub>oop</sub>, 612 v(B–C); (polyethylene, cm<sup>-1</sup>) 468, 419 v(Pd–N), 352 v(Pd–Cl). MS (%) = 417 (100%) [PdCl(bdmai)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN solution, 250 MHz) δ: 6.05 [s, 2H, CH(pz)], 5.22 [d, 2H,  ${}^{2}J$  = 12.5 Hz, N<sub>pz</sub>CHHN], 4.78 [d, 2H,  ${}^{2}J$  = 12.5 Hz, N<sub>pz</sub>CHHN], 3.42  $[sp, 1H, {}^{3}J = 7.6 \text{ Hz}, \text{ NCH}(\text{CH}_{3})], 2.43 [s, 6H, CH_{3}(\text{pz})],$ 2.32 [s, 6H,  $CH_3(pz)$ ], 1.15 [d, 6H,  ${}^3J = 7.6$  Hz, NCH(CH<sub>3</sub>)]. <sup>13</sup>C NMR (CD<sub>3</sub>CN solution, 63 MHz)  $\delta$ : 165.1 [CCH<sub>3</sub>], 144.8 [CCH<sub>3</sub>], 108.9 [CH(pz)], 68.0 [N<sub>pz</sub>CH<sub>2</sub>N], 59.9 [NCH(CH<sub>3</sub>)<sub>2</sub>], 19.1 [NCH(CH<sub>3</sub>)<sub>2</sub>], 14.0 [CCH<sub>3</sub>], 12.6 [CCH<sub>3</sub>].

# 2.3. X-ray crystal structure for compound $cis[PdCl_2(bdmae)] \cdot CH_2Cl_2(1)$

Suitable crystals for X-ray diffraction of compound *cis*-[PdCl<sub>2</sub>(bdmae)]  $\cdot$  CH<sub>2</sub>Cl<sub>2</sub> were obtained through crystallisation from ethanol/dichloromethane (1:1). A prismatic crystal was selected and mounted on a MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from 9384 reflections  $(3 \le \theta \le 31^\circ)$  and refined by least-squares method. Intensities were collected with graphite monochromatized Mo K $\alpha$  radiation. 9945 reflections were measured in the range  $2.25 \le \theta \le 30^\circ$ . 5628 of which were non-equivalent by symmetry ( $R_{int}$ (on I) = 0.023). 5390 reflections were assumed as observed applying the condition  $I \ge 2\sigma(I)$ . Lorentz-polarization but no absorption corrections were made.

The structure was solved by Direct methods, using SHELXS computer program, and refined by full-matrix least-squares method with shelx97 computer programs [14] using 9945 reflections (very negative intensities were The function minimised not assumed). was  $\sum w ||F_o||^2 - |F_c|^2|^2$  where  $\omega = [\sigma^2(I) + (0.0628P)^2 + 2.7870]$  $\overline{P}$ ]<sup>-1</sup>, and  $P = (|F_0|^2 + 2|F_c|^2)/3$ . Twenty-two H atoms were located from a difference synthesis and refined with overall isotropic temperature factor and three H atoms were located from a difference synthesis and refined, using a riding model, with an isotropic temperature factor equal to 1.2 the equivalent temperature factor of the atom which 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 1.

10010 1	Table	1
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C (11) 1.1 1.4	C [D 1C]	(1 1 · · · · ) 1	CII CI	(1)
Crystallographic data	a for  PaCl <sub>2</sub>	(bamae)   ·	$CH_2CI_2$	$(\mathbf{I})$

	==2 (=)
Formula	C <sub>15</sub> H <sub>27</sub> Cl <sub>4</sub> N <sub>5</sub> Pd
M	525.60
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.5350(10)
b (Å)	18.1020(10)
c (Å)	13.4940(10)
α (°)	90
β (°)	91.280(10)
γ (°)	90
$U(\text{\AA}^3)$	2084.3(3)
Ζ	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.669
$\mu (\mathrm{mm}^{-1})$	1.412
<i>F</i> (000)	1056
Crystal size	$0.2 \times 0.1 \times 0.1$
$\theta$ Range (°)	2.25-30.00
Index range	$0 \leqslant h \leqslant 12$ ,
	$-25 \leqslant k \leqslant 25$ ,
	$-18 \leqslant l \leqslant 18$
Reflections collected/unique $(R_{int})$	9945/5628 (0.02381)
Completeness to $\theta = 30^{\circ}$	92.7%
Absorption correction	none
Data/restraints/parameters	5628/0/242
Goodness-of-fit	1.344
Final $R_1$ , $\omega R_2$	0.0478 and 0.1420
$R_1$ (all data), $\omega R_2$	0.0511 and 0.1476
Largest difference in peak and hole (e $Å^{-3}$ )	0.977 and -0.987

### 3. Results and discussion

### 3.1. Synthesis and spectroscopic properties

The *N*-alkylaminopyrazole ligands (bis[(3,5-dimethyl-1pyrazolyl)methyl]ethylamine (**bdmae**), and bis[(3,5dimethyl-1-pyrazolyl)methyl]isopropylamine (**bdmai**)) (Scheme 1) used for the synthesis of the Pd(II) complexes were prepared according to the literature procedures [5,11,12].

Complexes  $[PdCl_2(NN'N)]$  (NN'N = (bdmae) (1), and (bdmai) (2)) were obtained by treatment of the corresponding ligand with  $[PdCl_2(CH_3CN)_2]$  in a 1:1 M/L ratio in CH<sub>2</sub>Cl<sub>2</sub>. Complexes  $[PdCl(NN'N)](BPh_4)$  (NN'N = (bdmae) (3), and (bdmai) (4)) 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<sub>4</sub> and metathesis with NaBPh<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (3:1) for complex 3, and in the presence of NaBPh<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (3:1) for complex 4. When complexes 3 and 4 were heated under reflux in a solution of Et<sub>4</sub>NCl in CH<sub>3</sub>CN for 24 h, complexes 1 and 2 were again obtained. The elemental analyses

of compounds 1 and 2 are consistent with the formula  $[PdCl_2(NN'N)]$  and those for compounds 3 and 4 with  $[PdCl(NN'N)](BPh_4)$ .

Complexes 3 and 4 decompose when they are left in solution (for this reason, the obtaining of suitable monocrystals for X-ray diffraction was not possible). This kind of instability had already been observed in a preceding paper for NSSN ligands 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh) and 1,7-bis(3,5-dimethyl-1-pyrazolvl)-2,6-dithiaheptane (bddhp), which are not able to tetracoordinate Pd(II) centres. In this case. the tetracoordination of **bddh** and **bddhp** ligands would involve the formation of unstable five-membered PdNNCS rings similar to the PdNNCN rings obtained for 3 and 4 [15,16] and presented in this paper. To confirm the existence of 3 and 4 complexes, electrospray mass spectra were recorded. The positive ionisation spectrum of 3 and 4 when measured gave peaks with m/z values of 403 and 417, respectively (molecular peak of the cation).

The conductivity values in  $CH_3CN$  and  $CH_3OH$  for compounds 1 and 2, are in agreement with non-electrolyte natures. The conductivity values in  $CH_3CN$  and  $CH_3OH$ 



[4]BPh<sub>4</sub>

for compounds **3** and **4** are in agreement with 1:1 electrolytes. The reported values for  $10^{-3}$  M solutions of non-electrolyte complexes are lower than  $120 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$  or  $80 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$  in CH<sub>3</sub>CN or CH<sub>3</sub>OH, respectively, while the range of conductivity values for  $10^{-3}$  M solutions of 1:1 electrolyte compounds in CH<sub>3</sub>OH is between 80 and  $115 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$  and in CH<sub>3</sub>CN between 120 and  $160 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$  [17,18].

The IR spectra of complexes 1–4 in the range 4000– 400 cm<sup>-1</sup> show that the ligands are coordinated to Pd(II). The v(C=C), v(C=N) and  $\delta(C-H)_{oop}$  bands of the pyrazolic ligands increase its frequency when they are part of the complexes [5,11,12]. The IR spectra of 3 and 4 present bands that were assigned to v(B-C) at 612 cm<sup>-1</sup> [19].

The IR spectra of complexes 1–4 in the region 600–100 cm<sup>-1</sup> were also studied. The presence of bands between 480 and 411 cm<sup>-1</sup> assigned to v(Pd-N) confirms the coordination of the ligand to the metallic atom. The complexes 1 and 2 display two well-defined v(Pd-Cl) bands at 338, 322 cm<sup>-1</sup> (1) and 337, 320 cm<sup>-1</sup> (2). These bands clearly indicate that the chlorine atoms are coordinated to the Pd(II) in a *cis* disposition. In compounds 3 and 4 only one band attributable to v(Pd-Cl) (343 cm<sup>-1</sup> (3), 340 cm<sup>-1</sup> (4)) was observed [20].

<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, HMQC, and NOESY NMR spectra of compounds **1** and **2** were recorded in CD<sub>3</sub>CN and for compounds **3** and **4** in acetone- $d_6$  and CD<sub>3</sub>CN, respectively, and they show the signals of the ligands (**bdmae**, **bdmai**). The NMR spectroscopic data are reported in the Section 2.

No significant differences between  ${}^{13}C{}^{1}H$  NMR spectra of free and coordinated ligands were observed. In the

<sup>1</sup>H NMR spectra of 1–4 at room temperature, the methylene hydrogens appear as narrow AB spectra. The two protons of the CH<sub>2</sub> group in the N<sub>pz</sub>-CH<sub>2</sub>-N<sub>amine</sub> chain are diastereotopic thus giving rise to two 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. In this way, each group of signals can be assigned as a doublet for H<sub>6</sub> and H<sub>7</sub> (Scheme 1).

In the NOESY spectra of the compounds 1 and 2 it can be seen that the methyl(pyrazole) group at  $\delta = 2.63$  (1), and 2.65 (2) ppm shows NOE interaction with the doublet at  $\delta = 5.32$  (1), and 5.41 (2) ppm but not with the one at  $\delta = 6.78$  (1), and 6.75 (2) ppm. This information leads us to assign H-6a to the doublet at 5.32 (1), and 5.41 (2) ppm, and H-6b to the one at  $\delta = 6.78$  (1), and 6.75 (2) ppm, because according to the X-ray crystal structure of 1, H-6a has the shortest distance to the methyl(pyrazole) group at 2.63 ppm (2.895 Å) (Fig. 1).

### 3.2. Crystal and molecular structure of complex 1

The crystal structure of complex 1 consists of monomeric *cis*-[PdCl<sub>2</sub>(**bdmae**)] molecules and solvent molecules (CH<sub>2</sub>Cl<sub>2</sub>) linked by van der Waals forces (Fig. 1).

The palladium centre has a square planar geometry (with a slight tetrahedral distortion, in which the metallic atom lies 0.004 Å out of the coordination plane).

The environment consists of two chlorine atoms in *cis* disposition to the metal and two nitrogen atoms of the pyrazolic rings. **Bdmae** behaves as a bidentate ligand and only uses two of its three donor nitrogen atoms, forming a eight-membered metallocycle. The *cis*-PdCl<sub>2</sub>( $N_{pz}$ )<sub>2</sub> *core* 



Fig. 1. ORTEP drawing of [PdCl<sub>2</sub>(bdmae)] (1), showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Table 2 Selected bond lengths (Å) and bond angles (°) for  $[PdCl_2(\textit{bdmae})]\cdot CH_2Cl_2$  (1)

Pd–N(1)	2.012(3)	Pd–N(4)	2.012(3)
Pd–Cl(1)	2.2876(10)	Pd–Cl(2)	2.2917(10)
N(1)-Pd-N(4)	88.45(13)	N(4)-Pd-Cl(1)	177.62(9)
N(1)-Pd-Cl(1)	89.36(10)	N(4)-Pd-Cl(2)	88.94(10)
N(1)-Pd-Cl(2)	177.35(9)	Cl(1)-Pd-Cl(2)	93.25(4)

(containing terminal chlorine atoms) is already found in the literature as a part of nine crystal structures [7,21– 27]. The Pd–Cl (2.2876(10) and 2.2917(10) Å) distances in complex **1** are typical of palladium square-planar complexes (Pd–Cl from 2.276 to 2.326 Å [7,28–33]). Moreover, the Pd–N<sub>pz</sub> (2.012(3) Å) bond lengths are of the same order as those reported in the literature (Pd–N<sub>pz</sub> from 1.971 to 2.141 Å [7,8,10,28,31,34,35]). All the complexes described above have a *cis* disposition of the pyrazolic ligands therefore; the angles N–Pd–N and Cl–Pd–Cl are also likely to be compared. In most of the cases, the Cl–Pd–Cl angle appears to be wider than the N–Pd–N angle, often by more than 2°. In structure **1**, *cis* N–Pd–N angles deviate 1.55° (88.45(13)°). Other bond lengths and angle data of interest are gathered in Table 2.

## 4. Conclusion

The *N*-alkylaminopyrazole ligands (**bdmae**, and **bdmai**) can coordinate Pd(II) centres in different ways. In complexes **1** and **2** these ligands show bidentate coordination  $(N_{pz}, N_{pz})$  and in complexes **3** and **4** shows tridentate coordination  $(N_{pz}, N_{amino}, N_{pz})$ . Furthermore, we have demonstrated the hemilabile properties of these ligands when coordinated to Pd(II). When complexes **3** and **4** are heated under reflux in solution of Et<sub>4</sub>NCl in CH<sub>3</sub>CN, **1** and **2** are obtained once again. This could be considered as type III hemilability [36].

#### 5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 604072 for compound [1]  $\cdot$  CH<sub>2</sub>Cl<sub>2</sub>. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ. UK; fax: +44 1223336033; e-mail: deposit@ccdc.cam.acuk or www.htpp://ccdc.cam.ac.uk.

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