Synthesis of New Pd^{II} Complexes Containing Thioether−Pyrazole Hemilabile Ligands − Structural Analysis by ^1H and ^{13}C NMR Spectroscopy and Crystal Structures of $[PdCl_2(bddo)]$ and $[Pd(bddo)](BF_4)_2$ [bddo = 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane]

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Treatment of the ligands 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh), 1,7-bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (bddhp), 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) with $[PdCl_2(CH_3CN)_2]$ produces $[PdCl_2(L)]$ or $[Pd_2Cl_4(L)]$ complexes, depending on the stoichiometry. Treatment of the complexes $[PdCl_2(bddo)]$ and $[PdCl_2(bddn)]$ with $AgBF_4$ gives $[Pd(bddo)](BF_4)_2$ and $[Pd(bddn)](BF_4)_2$. These Pd^{II} complexes have been characterised by elemental analyses, conductivity measurements, IR and ^1H and ^{13}C NMR spectroscopy where possible. The X-ray structures of the complexes $[PdCl_2(bddo)]$ and $[Pd(bddo)](BF_4)_2$ have been determined. In $[PdCl_2(bddo)]$ the thioether–pyrazole ligand is coordinated through the azine nitrogen atoms to the metal atom, which completes its coordination with two chloride ions in a *trans* disposition. In $[Pd(bddo)](BF_4)_2$ the metal atom is tetracoordinated by the two thioether sulfur atoms and the two azine nitrogen atoms of the pyrazole rings. Complexes $[PdCl_2(bddo)]$ and $[PdCl_2(bddn)]$ were obtained again when the complexes $[Pd(bddo)](BF_4)_2$ and $[Pd(bddn)](BF_4)_2$ were heated under reflux in a solution of Et_4NCl in CH_2Cl_2/MeOH (1:1).
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Introduction

The chemistry of hemilabile ligands has been widely studied in recent years.[1] The term "hemilabile ligand", introduced in 1979 by Jeffrey and Rauchfuss,[2] refers to polydentate chelates containing at least two types of bonding groups displaying different properties in substitution reactions (one labile and one inert). Thus, one group bonds strongly to a metal centre and the other group is weakly bonded and easily displaced by coordinating ligands. This makes them very attractive for catalytic purposes.

In recent years, we have studied and reported on the properties of hemilabile ligands based on the pyrazolyl group and on some other groups, containing N,[3] P[4] or O[5] atoms. This article is the initial part of a study of ligands containing pyrazolyl and thioether groups.

The literature describes the use of low molecular mass coordination compounds (with cations such as Ni^{II}, Cu^I, Cu^{II}, Co^{II}, Zn^{II}, Cd^{II} and Ag^I) with ligands of this kind for the modelling of metalloprotein-active centres in the bioinorganic field.[6−9] Our goal is to extend these studies to include the potential hemilabile capability of ligands that coordinate Pd^{II}.

Here we report the synthesis of the ligand 1,7-bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (bddhp). We have also studied the reactivity towards Pd^{II} of the previously described ligands 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh),[6] 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo)[7] and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn)[8] (Scheme 1). We have isolated the following complexes: $[PdCl_2L]$ with L = bddh (**1**), L = bddhp (**2**), L = bddo (**3**) and L = bddn (**4**), and $[Pd_2Cl_4L]$ with L = bddhp (**5**), L = bddo (**6**) and L = bddn (**7**). Treatment of **3** and **4** with $AgBF_4$ affords $[Pd(bddo)](BF_4)_2$ (**8**) and $[Pd(bddn)](BF_4)_2$ (**9**). NMR studies and the X-ray crystal structures of **3** and **8** are also presented.

Results and Discussion

The pyrazole ligands bddh, bddo and bddn were synthesised as described in the literature.[6−8] The bddh ligand was further purified by chromatography (silica gel 60) with methanol/dichloromethane (1:9) as eluent; bddo and bddn were purified by extraction ($CHCl_3/H_2O$/NaOH).

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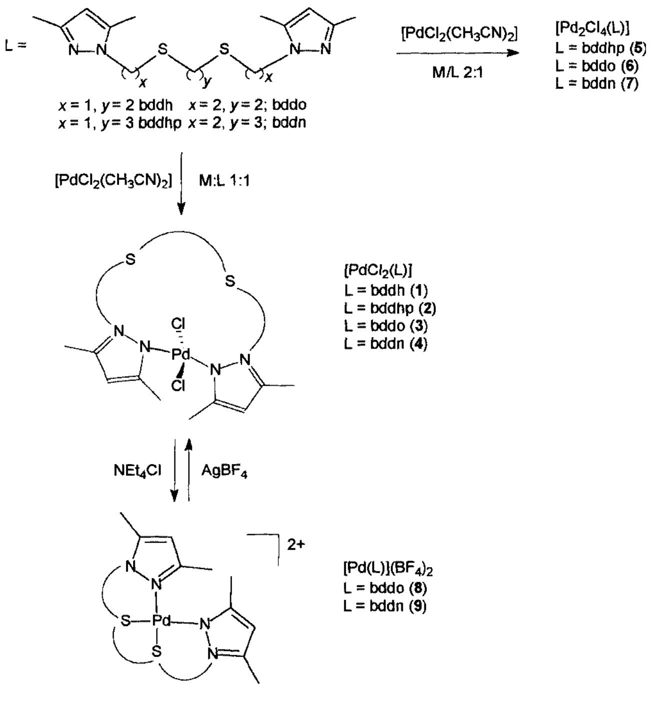

Scheme 1

Ligand bddhp, not previously reported in the literature, was prepared by a synthetic route similar to that used for the ligand bddh.[6a] Treatment of 2-(hydroxymethyl)-3,5-dimethylpyrazole with thionyl chloride gave 2-(chloromethyl)-3,5-pyrazolium chloride. This compound, on treatment with 1,3-propanedithiol in the presence of sodium hydroxide, yielded the desired product. The ligand bddhp was characterised by elemental analysis, mass spectrometry and IR, ^{1}H and ^{13}C NMR spectroscopy.

Complexes [$PdCl_2L$] [L = bddh (**1**), bddhp (**2**), bddo (**3**) and bddn (**4**)] were obtained by treatment of the corresponding ligand either with [$PdCl_2(CH_3CN)_2$] or with [$PdCl_2(COD)$] in a 1:1 M/L ratio. Complexes [Pd_2Cl_4L] [L = bddhp (**5**), bddo (**6**) and bddn (**7**)] were obtained by use of a 2:1 M/L ratio.

Treatment of **3** and **4** with $AgBF_4$ gave compounds of formula [PdL]$(BF_4)_2$ [L = bddo (**8**) and bddn (**9**)]. In contrast, use of the same reaction conditions with complexes **1** and **2** gave decomposition products. When complexes **8** and **9** were heated under reflux in a solution of Et_4NCl in CH_2Cl_2/MeOH (1:1) for 24 h, complexes **3** and **4** were obtained again.

The elemental analyses of products **5**, **6** and **7** are consistent with the formulas [Pd_2Cl_4L]. The low solubilities of the complexes were sufficient for their conductivity and ^{1}H NMR spectra to be measured, but their ^{13}C NMR spectra could not be recorded.

Conductivity values in acetonitrile for complexes **1−4**, and in DMSO for complexes **5−7**, are in agreement with non-electrolyte natures (Table 4). Conductivity values in methanol for complexes **8** and **9** are in agreement with 2:1 electrolytes. The reported values for 10^{-3} M solutions of non-electrolyte complexes are lower than 120 $\Omega^{-1}cm^2mol^{-1}$ or 50 $\Omega^{-1}cm^2mol^{-1}$ in acetonitrile or DMSO, respectively, while the range of conductivity values for 10^{-3} M solutions of 2:1 electrolyte compounds in methanol is between 160 and 220 $\Omega^{-1}cm^2mol^{-1}$.[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 1564−1554 cm^{-1} and δ(C−H)$_{oop}$ between 820 and 778 cm^{-1}. The ν(B−F) band at 1061 cm^{-1} is characteristic for **8** and **9**.[11]

The IR spectra of the complexes in the 500−100 cm^{-1} region were also studied. Complexes [$PdCl_2L$] (**1−4**) show two well-defined bands corresponding to ν(Pd−Cl) at 340−326 cm^{-1} and ν(Pd−N) at 473−448 cm^{-1}. For the [Pd_2Cl_4L] complexes **5−7**, three bands can be observed. One of these can be assigned to ν(Pd−N) at 459−452 cm^{-1}. The number and energy of the other two bands are consistent with the presence of terminal (366−360 cm^{-1}) and bridging (335−299 cm^{-1}) Pd−Cl bonds. For complexes **8** and **9** the ν(Pd−N) and ν(Pd−S) bands can be attributed to the signals appearing between 461−456 and 238−247 cm^{-1}, respectively.[12]

NMR Experiments

The ^{1}H and ^{13}C NMR spectra of complexes **1−4**, **8** and **9** show the signals of coordinated ligands. NMR spectroscopic data are shown in the Exp. Sect. NMR spectra of compounds **3**, **4**, **8** and **9** were studied in more detail.

Study of the S−CH$_2$−CH$_2$−N fragment (in **3** and **4**) as an AA′XX′ system gave a set of coupling constants for each compound. These constants were consistent with the simulated spectra for compounds **3** and **4**, obtained with the aid of the *g* NMR program.[13] All these results are reported in Table 1. Figure 1 shows the experimentally determined and simulated spectra for **3**.

Table 1. ^{1}H NMR results: chemical shifts (ppm) and ^{1}H,^{1}H coupling constants (Hz) for **3** and **4** in $CDCl_3$

Compound	**3**	**4**
δ(CH$_2$) (6)	4.93	4.89
δ(CH$_2$) (7)	3.08	3.14
^2J(6a,6b)	−12.28	−12.87
^2J(7a,7b)	−12.28	−14.32
^3J(6a,7a) = ^3J(6b,7b), ^3J(6a,7b) = ^3J(6b,7a)	4.81, 13.01	4.87, 12.39

The Karplus equation cannot be used directly to calculate the dihedral angle between adjacent hydrogen atoms if the ethylenic fragments are α-substituted by heteroatoms (O, S, NR). In such cases, coupling constants are dependent on the electronegativity of the α-heteroatom substituent as well as on the dihedral angle.[14] Here, we have used a program based on the Karplus equation but which takes account of the electronegativity of the fragments connected

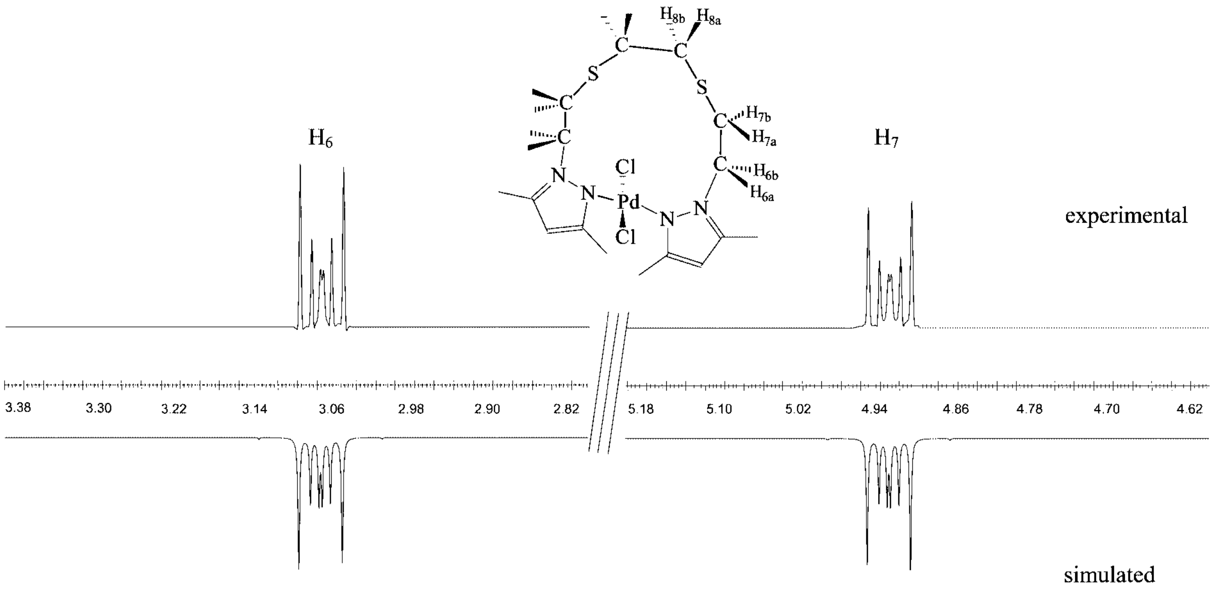

Figure 1. The 400-MHz ^{1}H NMR and the simulated *g* NMR spectra for the NCH_2CH_2S fragment of [PdCl$_2$(bddo)] (**3**)

to the two carbon atoms involved.[15] Although this program was designed for organic molecules, in our case it works correctly when our ligands are coordinated to Pd^{II}. By use of this program, the dihedral angles corresponding to the observed adjacent coupling constants ($^3J_{6a,7a}$ = 4.81 and 4.87 Hz for **3** and **4**, respectively) are 51° and 52° for **3** and **4**, respectively. These values are in both cases consistent with an *anti* conformation (Figure 2).

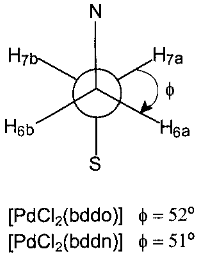

Figure 2. Dihedral angles for the NCH_2CH_2S fragment of [PdCl$_2$(bddo)] (**3**)

The two different chains [S−(CH$_2$)$_2$−N and S−(CH$_2$)$_x$−S; x = 2 for **8** and x = 3 for **9**] were studied separately. HMQC spectra were used to assign the signals of protons H$_6$, H$_7$ and H$_8$ for **8** and H$_6$, H$_7$, H$_8$ and H$_9$ for **9** (Figure 3). Simulated ^{1}H NMR spectra of both chains were obtained by use of the *g* NMR program.[13] The coupling constants are reported in Table 2.

Because of the symmetry of **8**, the two CH$_2$ units in the S−CH$_2$−CH$_2$−S fragment are equivalent. The two protons of each CH$_2$, though, are diastereotopic and can be assigned to the two doublets found at δ = 3.52 and 4.04 ppm. The signal of H$_8$ for the S−(CH$_2$)$_3$−S chain in compound **9** is superposed on that of H$_7$ and could not be further studied.

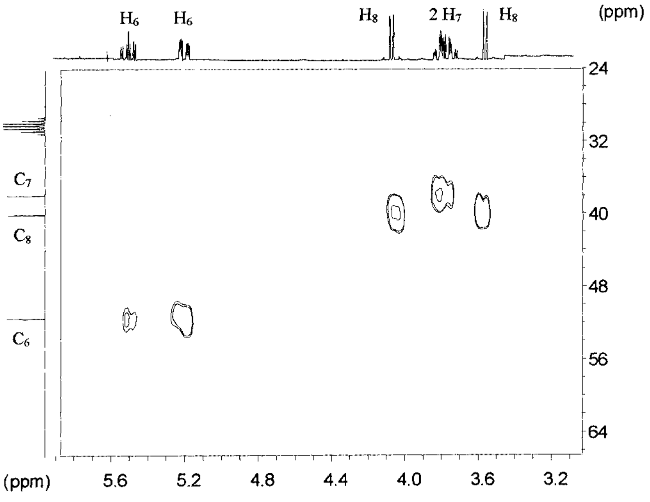

Figure 3. The 250-MHz 2D HMQC spectrum of [Pd(bddo)](BF$_4$)$_2$ (**8**)

Table 2. ^{1}H NMR results: chemical shifts (ppm) and ^{1}H,^{1}H coupling constants (Hz) for **8** and **9** in [D$_6$]acetone

Compound	8	9
δ(H) (6*R*), δ(H) (6*S*)	5.19, 5.50	5.23, 5.58
δ(H) (7*S*), δ(H) (7*R*)	3.72, 3.78	3.52, 3.92
δ(H) (8*R*), δ(H) (8*S*)	3.52, 4.04	3.53
δ(H) (9*R*), δ(H) (9*S*)	−	2.70
^2J(6*R*,6*S*)	−13.56	−8.80
^2J(7*R*,7*S*)	−13.70	−4.40
^3J(6*R*,7*R*), ^3J(6*S*,7*S*),	2.11, 3.17,	2.92, 10.28,
^3J(6*R*,7*S*), ^3J(6*S*,7*R*)	3.84, 12.45	15.24, 15.52
^2J(8*R*,8*S*)	−8.04	−

For complexes **8** and **9**, the two protons of each CH_2 group in the $S-CH_2-CH_2-N$ chain are diastereotopic, thus giving rise to four groups of signals, each attributable to a single hydrogen atom. This happens because of the rigid conformation of the ligand when it is complexed. In this way, each group of signals can be assigned as a double double doublet. In **8**, the two signals of lower δ value appear partially superimposed. Figure 4 shows the experimental and the simulated spectra for **8**.

Crystal Structure of $[PdCl_2(bddo)]$ (3)

The structure of **3** (Figure 5) consists of discrete $[PdCl_2(bddo)]$ units. The palladium atom is coordinated by two pyrazole nitrogen and two chlorine atoms in a distorted square-planar geometry. The tetrahedral distortion can be observed in the mean separation [±0.174(3)] of the atoms coordinated to the Pd atom in relation to the mean plane. Tetrahedral distortion of the square-planar geometry can

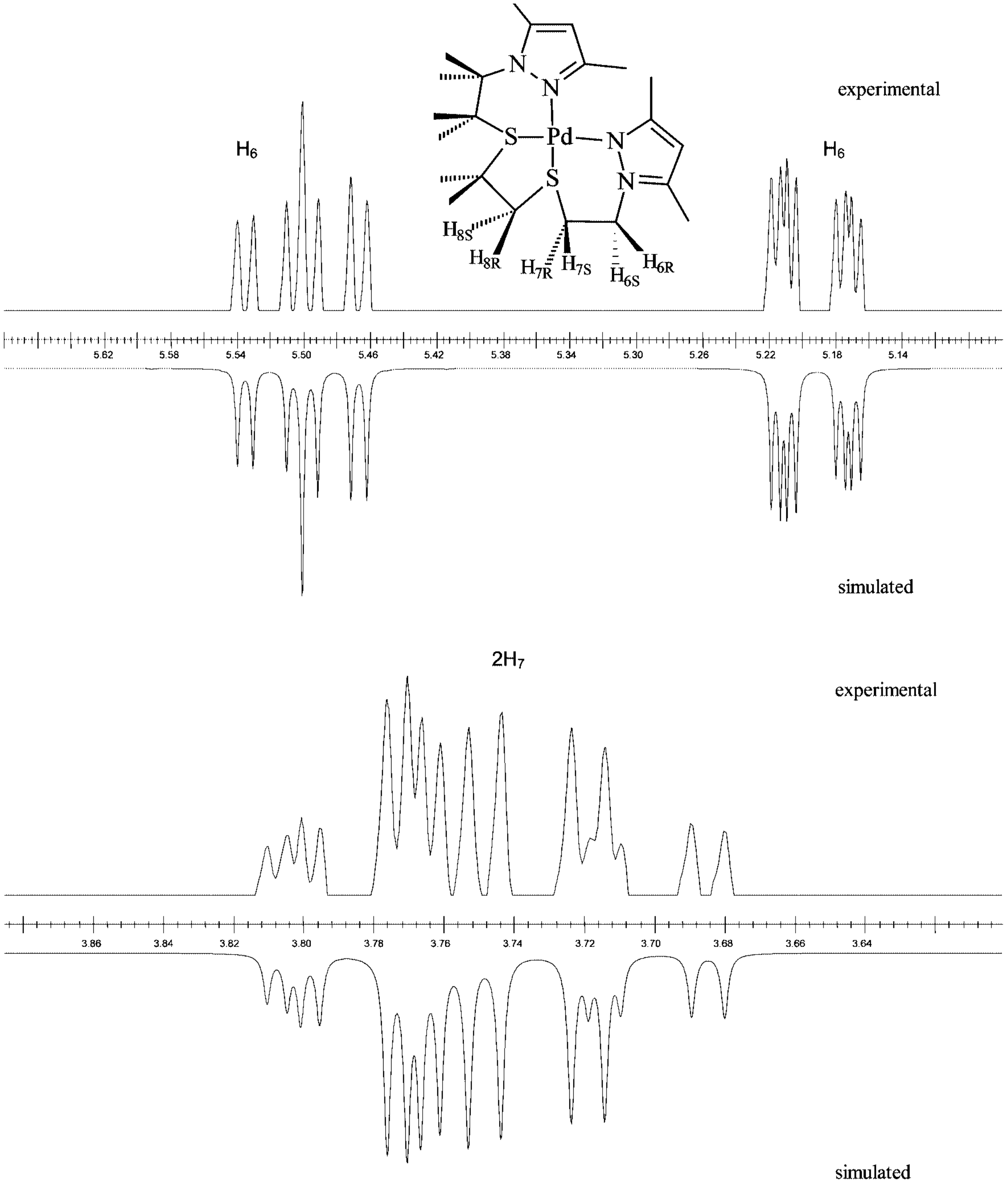

Figure 4. The 400-MHz ^1H NMR and the simulated *g* NMR spectra for the H_6 and H_7 protons of the NCH_2CH_2S fragment of $[Pd(bddo)](BF_4)_2$ (**8**)

also be observed in the angles Cl(1)−Pd−Cl(2) and N(1)−Pd−N(3), of 172.47(4) and 168.65(9)°, respectively. The dihedral angle between the planes N(1)−Pd−Cl(1) and N(3)−Pd−Cl(2) is 13.5(1)°.

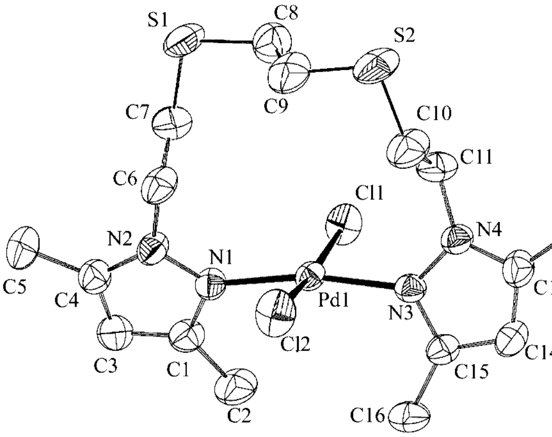

Figure 5. ORTEP drawing of $[PdCl_2(bddo)]$ (**3**, 273 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

The pyrazolyl groups are *trans* to each other. The PdN_2Cl_2 core (containing pyrazole nitrogen atoms and terminal chloride ions) is found in 11 complexes described in the literature (seven of the complexes found had *trans* geometry and five were *cis*).[16] Both the Pd−N and the Pd−Cl bond lengths in **3** are of the same order as those found in the literature.[17] The palladium atom does not interact with the sulfur atoms, the Pd−S distances being 5.02(8) and 5.16(8) Å, respectively. The SCH_2CH_2S bridging segment is disordered in the crystal.

The structure of **3** is similar to that found for the complex $[CuCl_2(bddo)]$,[7b] but the copper complex shows greater distortion of the square-planar geometry. This can be observed in the dihedral angle between the planes N(1)−Cu−Cl(1) and N(3)−Cu−Cl(2), which is 27°. Table 3 lists some selected bond lengths and angles for this complex.

Table 3. Selected bond lengths (Å) and angles (°) for **3** and **8**, with estimated standard deviations (e.s.d.) in parentheses

3		**8**	
Pd(1)−N(1)	2.027(3)	Pd(1)−N(1)	2.027(4)
Pd(1)−N(3)	2.017(3)	Pd(1)−N(4)	2.030(4)
Pd(1)−Cl(1)	2.292(1)	Pd(1)−S(1)	2.246(1)
Pd(1)−Cl(2)	2.287(1)	Pd(1)−S(2)	2.247(1)
N(1)−Pd(1)−Cl(1)	90.98(9)	N(1)−Pd(1)−N(4)	97.4(2)
N(1)−Pd(1)−Cl(2)	90.03(9)	N(1)−Pd(1)−S(2)	86.2(1)
N(3)−Pd(1)−Cl(1)	91.38 (9)	N(4)−Pd(1)−S(1)	86.8(1)
N(3)−Pd(1)−Cl(2)	89.08(9)	S(1)−Pd(1)−S(2)	89.78(6)
N(1)−Pd(1)−N(3)	168.65(9)	N(1)−Pd(1)−S(1)	175.4(1)
Cl(1)−Pd(1)−Cl(2)	172.47(4)	N(4)−Pd(1)−S(2)	175.2(1)

Crystal Structure of $[Pd(bddo)](BF_4)_2{\cdot}H_2O$ (8)

The structure of **8** (Figure 6) consists of cationic units of $[Pd(bddo)]^{2+}$, BF_4^- anions and solvent molecules (H_2O). Two nitrogen atoms of the pyrazolyl groups and two thioether groups coordinate the palladium atom in a slightly distorted square-planar geometry. The pyrazolyl groups are *cis* to each other. The tetrahedral distortion of the square-planar geometry can be observed in the mean separation of the atoms linked to Pd from the mean plane, which is ±0.050(3) Å. The dihedral angle between the planes N(1)−Pd−N(4) and S(1)−Pd−S(2) is 3.79(9)°. Some selected bond lengths and bond angles for this complex are listed in Table 3.

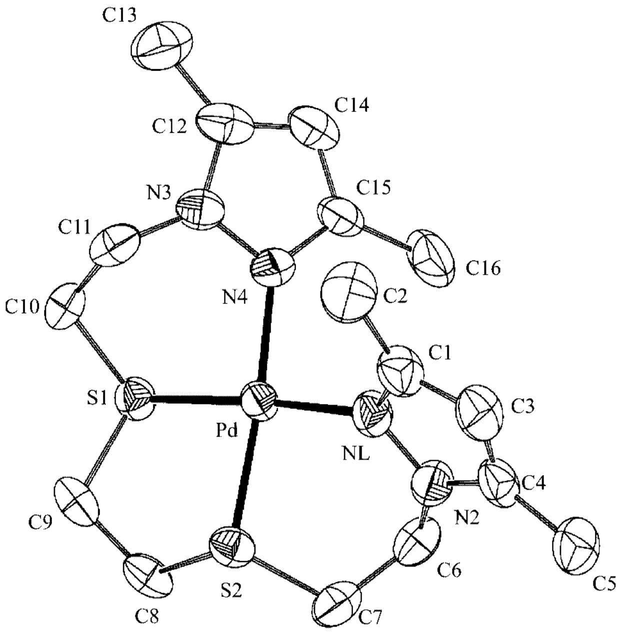

Figure 6. ORTEP drawing of $[Pd(bddo)]\ (BF_4)_2$ (**8**, 273 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

The PdN_2S_2 core (N in aromatic amine and S thioether) is found in five complexes in the literature.[18] The Pd−N and Pd−S distances in complex **8** are of the same order as those found in the literature for this kind of complexes.[17]

Ligand bddo acts as a tetradentate chelate and forms two Pd−N−N−C−C−S six-membered rings and one Pd−S−C−C−S five-membered ring. All of these have half-chair configurations. For the six-membered rings the N(4)−Pd−S(1) and N(1)−Pd−S(2) bite angles are 86.8(1) and 86.2(1)°, respectively. For the five-membered ring, the S(1)−Pd−S(2) bite angle is 89.75(6)°. These bite angles are similar to those reported in the literature for $[Pd(pdto)](ClO_4)_2$ [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane] (N−Pd−S bite angles are 86.9 and 87.2° and the S−Pd−S bite angle is 89.4°).[18d] This is the only compound with a PdN_2S_2 core similar to that presented in this paper, with two six-membered rings and one five-membered ring.

The half-chair distortions in the six-membered rings are ΔC_S(Pd) = 10.9(4)° and 17.0(4)° and ΔC_S[S(1)−C(10)] = 11.95(5)°, ΔC_S[S(2)−C(7)] = 14.0(6)° for Pd−S(1)−C(10)−C(11)−N(3)−N(4) and Pd−S(2)−C(7)−C(6)−N(2)−N(1), respectively.

Conclusion

We have shown that thioether−pyrazole N_2S_2 ligands can coordinate Pd^{II} centres in different ways. Treatment of [PdCl$_2$(CH$_3$CN)$_2$] with these ligands gave complexes in which the Pd^{II} centre is bonded to two pyrazole rings and two chloride ions in a *trans* disposition. Abstraction of the chloride components in **3** and **4** with AgBF$_4$ gave complexes **8** and **9** with the Pd^{II}N$_2$S$_2$ core. These kinds of complexes were not obtained with bddh and bddhp ligands, probably because of the imposed geometry of the hypothetical PdNNCS metallacycle, which would induce steric hindrance between the methyl groups of the pyrazole rings. The Cl$_2$N$_2$ and N$_2$S$_2$ coordination modes of Pd^{II} can be interconverted. Thus, if **8** and **9** are heated under reflux in solutions with Et$_4$NCl, **3** and **4** are formed again. This reactivity is confirmation of the hemilabile behaviour of these thioether−pyrazole ligands in the complexation of Pd^{II}.

Experimental Section

Generals Remarks: Preparations were performed by use of conventional vacuum line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. Acetonitrile and dichloromethane were dried and distilled by standard methods and deoxygenated in the vacuum line in advance. Samples of [PdCl$_2$(CH$_3$CN)$_2$][19] and [PdCl$_2$(COD)][20] were prepared as described in the literature. 1,6-Bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh),[6a] 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo)[7a] and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn)[8] were prepared according to the published methods. Analyses (C, H, N, S) were performed in our analytical laboratory with a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile, DMSO or methanol solutions, with the aid of a Crison micro CM 2200 conductimeter. Infrared spectra were recorded as KBr pellets or polyethylene mulls under nitrogen over the 4000−100 cm^{-1} range. The ^{1}H, ^{13}C{^{1}H} NMR and HMQC spectra were obtained either with Bruker 250-MHz or 400-MHz instruments. Chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Mass spectra were obtained with an HP 5989A apparatus.

1,7-Bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (bddhp): 2-(Chloromethyl)-3,5-pyrazolium chloride[6a] (720 mg, 3.98 mmol) and 1,3-propanedithiol (0.20 mL, 1.97 mmol) were dissolved in dry DMF (6 mL) and the mixture was then heated to 90 °C. After the mixture had been maintained at this temperature for 15 min, sodium hydroxide (500 mg, 12.1 mmol), dissolved in water (7 mL), was added dropwise. Heating was stopped; after 15 min, additional water (7 mL) was added. After cooling to room temperature, the reaction mixture was extracted four times with CHCl$_3$ (15 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed under vacuum. The product was purified by chromatography (silica gel 60) with methanol/dichloromethane (1:9) as eluent to give a white solid. Yield: 0.46 g (72%). M.p. 30−32 °C. IR (NaCl, cm^{-1}): $\tilde{\nu}$ = 2918 [ν(C−H)$_{al}$], 1558 [ν(C=C), ν(C=N)], 1455 [δ(CH$_3$)$_{as}$], 1378 [δ(CH$_3$)$_s$], 779 [δ(C−H)$_{oop}$]. ^{1}H NMR (250 MHz, CDCl$_3$ solution): δ = 1.76 (q, ^3J = 7 Hz, 2 H, CH$_2$−$\mathit{CH_2}$−CH$_2$), 2.22 (s, 6 H, *Me*), 2.31 (s, 6 H, *Me*), 2.67 (t, ^3J = 7 Hz, 4 H, S−$\mathit{CH_2}$−CH$_2$), 5.05 (s, 4 H, pz-$\mathit{CH_2}$−S), 5.86 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$ solution, 63 MHz): δ = 11.6 (*Me*), 13.9 (*Me*), 29.4 (CH$_2$−$\mathit{CH_2}$−CH$_2$), 30.3 (S-$\mathit{CH_2}$−CH$_2$), 50.3 (pz-$\mathit{CH_2}$−S), 106.9 (pz-CH), 139.4 (pz-C), 148.1 (pz-C) ppm. MS (CI, NH$_3$): *m/z* (%) = 325 (100) [MH$^+$]. C$_{15}$H$_{24}$N$_4$S$_2$ (324): calcd. C 55.52, H 7.45, N 17.27, S 19.76; found C 55.21, H 7.25, N 16.96, S 19.71.

Synthesis of the Pd^{II} Complexes

Complexes [PdCl$_2$L] with L = bddh (1), bddhp (2), bddo (3) and bddn (4): A solution of [PdCl$_2$(CH$_3$CN)$_2$] or [PdCl$_2$(COD)] (0.36 mmol) in dichloromethane (30 mL) was added to a solution of the appropriate ligand (0.36 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 12 h, most of the solvent was removed under vacuum. Diethyl ether was then added to induce precipitation. The resulting precipitate was then filtered and washed with diethyl ether, yielding the desired compound.

Complex 1: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2951 [ν(C−H)$_{al}$], 1562 [ν(C=C), ν(C=N)], 1462 [δ(CH$_3$)$_{as}$], 1380 [δ(CH$_3$)$_s$], 778 [δ (C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 459 [ν(Pd−N)$_{as}$], 326 [ν(Pd−Cl)]. ^{1}H NMR (400 MHz, CDCl$_3$ solution): δ = 2.35 (s, 6 H, *Me*), 2.85 (s, 6 H, *Me*), 3.96 (s, 4 H, S−CH$_2$−$\mathit{CH_2}$−S), 5.96 (s, 2 H, pz-CH), 5.98 (s, 4 H, pz-$\mathit{CH_2}$−S) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$ solution): δ = 12.5 (*Me*), 16.3 (*Me*), 31.6 (S−CH$_2$−$\mathit{CH_2}$−S), 48.8 (pz-$\mathit{CH_2}$−S), 108.9 (pz-CH), 144.8, 152.5 (pz-C) ppm.

Complex 2: IR (KBr, cm^{-1}): $\tilde{\nu}$ =3130 [ν(C−H)$_{ar}$], 2923 [ν(C−H)$_{al}$], 1559 [ν(C=C), ν(C=N)], 1464 [δ(CH$_3$)$_{as}$], 1381 [δ(CH$_3$)$_s$], 800 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 448 [ν(Pd−N)$_{as}$], 338 [ν(Pd−Cl)]. ^{1}H NMR (400 MHz, CDCl$_3$ solution): δ = 2.38 (s, 6 H, *Me*), 3.01 (s, 6 H, *Me*), 3.13 (m, 2 H, CH$_2$−$\mathit{CH_2}$−CH$_2$), 3.22 (m, 4 H, S−$\mathit{CH_2}$−CH$_2$), 5.84 (s, 4 H, pz-$\mathit{CH_2}$−S), 6.02 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$ solution): δ = 12.7 (*Me*), 16.4 (*Me*), 27.2 (CH$_2$−$\mathit{CH_2}$−CH$_2$), 31.4 (S−$\mathit{CH_2}$−CH$_2$), 48.3 (pz-$\mathit{CH_2}$−S), 109.7 (pz-CH), 144.6, 151.4 (pz-C) ppm.

Complex 3: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3129 [ν(C−H)$_{ar}$], 2918 [ν(C−H)$_{al}$], 1557 [ν(C=C), ν(C=N)], 1469 [δ(CH$_3$)$_{as}$], 1393 [δ(CH$_3$)$_s$], 820 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 453 [ν(Pd−N)$_{as}$], 340 [ν(Pd−Cl)]. ^{1}H NMR (400 MHz, CDCl$_3$ solution): δ = 2.28 (s, 6 H, *Me*), 2.95 (s, 6 H, *Me*), 3.08 (m, 4 H, CH$_2$−$\mathit{CH_2}$−S), 3.20 (s, 4 H, S−$\mathit{CH_2}$−$\mathit{CH_2}$−S), 4.93(m, 4 H, pz-$\mathit{CH_2}$−CH$_2$), 5.94 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$ solution): δ = 12.1 (*Me*), 15.5 (*Me*), 30.8 (S-$\mathit{CH_2}$−$\mathit{CH_2}$−S), 34.0 (CH$_2$−$\mathit{CH_2}$−S), 51.1 (pz-$\mathit{CH_2}$−CH$_2$), 108.8 (pz-CH), 142.9, 150.6 (pz-C) ppm.

Complex 4: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3126 [ν(C−H)$_{ar}$], 2917 [ν(C−H)$_{al}$], 1554 [ν(C=C), ν(C=N)], 1469 [δ(CH$_3$)$_{as}$], 1390 [δ(CH$_3$)$_s$], 789 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 473 [ν(Pd−N)$_{as}$], 335 [ν(Pd-Cl)]. ^{1}H NMR (400 MHz, CDCl$_3$ solution): δ = 2.28 (s, 6 H, *Me*), 2.97 (s, 6 H, *Me*), 1.72 (q, 2 H, CH$_2$−$\mathit{CH_2}$−CH$_2$), 2.84 (t, 4 H, $\mathit{CH_2}$−CH$_2$-$\mathit{CH_2}$), 3.14 (m, 4 H, CH$_2$−$\mathit{CH_2}$−S), 4.89 (m, 4 H, pz-$\mathit{CH_2}$−CH$_2$), 5.94 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$ solution): δ = 12.1 (*Me*), 15.6 (*Me*), 29.5, 29.6, 30.6 (pz-CH$_2$−$\mathit{CH_2}$−S, $\mathit{CH_2}$−CH$_2$−$\mathit{CH_2}$, CH$_2$−$\mathit{CH_2}$−CH$_2$), 50.7 (pz-$\mathit{CH_2}$−CH$_2$), 108.8 (pz-CH), 143.1, 150.9 (pz-C) ppm.

Complexes [Pd$_2$Cl$_4$L] with L = bddhp (5), bddo (6) and bddn (7): A solution of [PdCl$_2$(CH$_3$CN)$_2$] (0.36 mmol) in dichloromethane

(30 mL) was added to a solution of the appropriate ligand (0.18 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 12 h, a precipitate had formed. This precipitate was filtered off, washed with diethyl ether and dried under vacuum, yielding the desired compound. No Pd^{II} complex of this stoichiometry with bddh as ligand could be isolated.

Complex 5: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3129 [ν(C−H)$_{ar}$], 2967 [ν(C−H)$_{al}$], 1564 [ν(C=C)], 1463 [ν(C=N), $\delta(CH_3)_{as}$], 1392 [$\delta(CH_3)_s$], 808 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 452 [ν(Pd−N)$_{as}$], 366 [ν(Pd−Cl)], 335 [ν_B(Pd−Cl)]. ^{1}H NMR (400 MHz, [D$_6$]DMSO solution): δ = 2.16 (s, 6 H, *Me*), 2.34 (s, 6 H, *Me*), 2.69 (br, 2 H, CH_2-*CH_2*$-CH_2$), 2.97 (br, 4 H, S−*CH_2*$-CH_2$), 5.67 (br, 4 H, pz-*CH_2*−S), 5.97 (s, 2 H, pz-CH).

Complex 6: IR (KBr, cm^{-1}): 3120 [ν(C−H)$_{ar}$], 2967 [ν(C−H)$_{al}$, ν(C=C)], 1554 [ν(C=N)], 1467 [$\delta(CH_3)_{as}$], 1395 [$\delta(CH_3)_s$], 797 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): 456 [ν(Pd−N)$_{as}$], 367 [ν(Pd−Cl)], 322 [ν_B(Pd−Cl)]. ^{1}H NMR (400 MHz, [D$_6$]DMSO solution): δ = 2.36 (s, 6 H, *Me*), 2.43 (s, 6 H, *Me*), 2.79 (br, 4 H, CH_2-*CH_2*−S), 4.23 (br, 4 H, S−*CH_2-CH_2*−S), 4.92 (br, 4 H, pz-*CH_2*$-CH_2$), 6.19 (s, 2 H, pz-CH) ppm.

Complex 7: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3126 [ν(C−H)$_{ar}$], 2958 [ν(C−H)$_{al}$], 1560 [ν(C=C), ν(C=N)], 1470 [$\delta(CH_3)_{as}$], 1400 [$\delta(CH_3)_s$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 459 [ν(Pd−N)$_{as}$], 360 [ν(Pd−Cl)], 319 [ν_B(Pd−Cl)]. ^{1}H NMR (400 MHz, [D$_6$]DMSO solution): δ = 2.25 (s, 6 H, *Me*), 2.80 (s, 6 H, *Me*), 2.05 (br, 2 H, CH_2-*CH_2*$-CH_2$), 2.42 (br, 4 H, *CH_2*$-CH_2-$*CH_2*), 4.50 (br, 4 H, CH_2-*CH_2*−S), 4.90 (br, 4 H, pz-*CH_2*$-CH_2$), 6.20 (s, 2 H, pz-CH) ppm.

Complexes [Pd(bddo)]$(BF_4)_2\cdot H_2O$ (8) and [Pd(bddn)]$(BF_4)_2$ (9): A solution of $AgBF_4$ (0.86 mmol) was added dropwise with vigorous stirring to a solution of [$PdCl_2$(L)] (L = bddo or bddn, 0.43 mmol) in dichloromethane (10 mL) and methanol (10 mL). The reaction was carried out in the dark to prevent reduction of Ag^I to Ag^0. After 5 min, stirring was stopped, and AgCl was filtered off. When the volume of the resultant solution had been reduced to roughly 5 mL, the product precipitated as a yellow solid. This solid was filtered and washed with dichloromethane.

Complex 8: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3141 [ν(C−H)$_{ar}$], 2956 [ν(C−H)$_{al}$], 1553 [ν(C=C), ν(C=N)], 1470 [$\delta(CH_3)_{as}$], 1395 [$\delta(CH_3)_s$], 1061 [ν(B−F)], 791 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 461 [ν(Pd−N)$_{as}$], 238 [ν(Pd−S)]. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.99 (s, 6 H, *Me*), 2.52 (s, 6 H, *Me*), 3.72/ 3.78/ 5.19/ 5.50 (pz-*CH_2-CH_2*), 6.26 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 11.9 (*Me*), 13.3 (*Me*), 31.4 (S−*CH_2*$-CH_2$), 48.3 (pz-*CH_2*$-CH_2$−S), 109.0 (pz-CH), 147.0, 152.1 (pz-C) ppm.

Complex 9: IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3129 [ν(C−H)$_{ar}$], 2985−2928 [ν(C−H)$_{al}$], 1549 [ν(C=C), ν(C=N)], 1472 [$\delta(CH_3)_{as}$], 1393 [$\delta(CH_3)_s$], 1061 [ν(B−F)], 810 [δ(C−H)$_{oop}$]. IR (polyethylene, cm^{-1}): $\tilde{\nu}$ = 456 [ν(Pd−N)$_{as}$], 247 [ν(Pd−S)]. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.85 (s, 6 H, *Me*), 2.52 (s, 6 H, *Me*), 3.52/3.92/ 5.23/5.58 (pz-*CH_2*−*CH_2*), 6.24 (s, 2 H, pz-CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 11.3 (*Me*), 12.7 (*Me*), 22.8 (CH_2-*CH_2*$-CH_2$), 31.2 (pz-CH_2-*CH_2*), 36.4 (*CH_2*$-CH_2-$*CH_2*), 49.9 (pz-*CH_2*$-CH_2$), 108.9 (pz-CH), 146.1, 152.1 (pz-C) ppm.

Tables 1 and 2 show coupling constants for complexes **3**, **4**, **8** and **9**; Table 4 shows other analytical and physical data for all complexes.

X-ray Crystallographic Study: Crystals of compounds **3** and **8** suitable for X-ray diffraction experiments were obtained by crystallisation from CH_2Cl_2 and MeOH, respectively. The data for **3** were collected with an Enraf−Nonius CAD$_4$ four-circle diffractometer, by the $\Omega/2\theta$ scan technique. The data for **8** were collected with an MAR345 diffractometer with an image plate detector, by the φ-scan technique. Both crystals were subjected to graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods with the SHELXS 97 computer program[21] and refined by full-matrix, least squares with the SHELXL 97 program.[22] All hydrogen atoms were computed and refined by use of a riding model. The final *R* (on *F*) factor and ωR (on F^2) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 5. CCDC-185048 (**3**) and -185049 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam-

Table 4. Physical and analytical data for complexes **1**−**9**

Compound	Yield (%)	Analysis[a] N	C	H	S	Conductivity (Ω^{-1} cm^2 mol^{-1})
[$PdCl_2$(bddh)] (**1**)	77	(11.49)	(34.47)	(4.55)	(13.15)	80[b]
		11.27	34.35	4.43	13.40	
[$PdCl_2$(bddhp)] (**2**)	74	(11.16)	(35.90	(4.82)	(12.78)	89[b]
		10.88	35.85	4.69	13.07	
[$PdCl_2$(bddo)] (**3**)	96	(10.86)	(37.25	(5.08)	(12.43)	96[b]
		10.98	37.03	5.33	12.57	
[$PdCl_2$(bddn)] (**4**)	98	(10.57)	(38.53	(5.33)	(12.10)	74[b]
		10.32	38.36	5.34	12.47	
[Pd_2Cl_4(bddhp)] (**5**)	80	(8.25)	(26.53)	(3.56)	(9.44)	27[c]
		8.05	26.42	3.33	9.25	
[Pd_2Cl_4(bddo)] (**6**)	87	(8.08)	(27.72)	(3.78)	(9.25)	29[c]
		7.81	27.49	3.88	9.59	
[Pd_2Cl_4(bddn)] (**7**)	83	(7.92)	(28.87)	(3.99)	(9.07)	23[c]
		7.58	28.72	3.95	8.86	
[Pd(bddo)]$(BF_4)_2\cdot H_2O$ (**8**)	89	(8.80)	(30.19)	(4.43)	(10.07)	163[d]
		8.61	30.03	4.36	10.39	
[Pd(bddn)]$(BF_4)_2$ (**9**)	90	(8.86)	(32.28)	(4.46)	(10.14)	175[d]
		8.69	31.89	4.36	10.02	

[a] Calculated analytical values are given in parentheses. [b] 10^{-3} M in acetonitrile. [c] 10^{-3} M in DMSO. [d] 10^{-3} M in MeOH.

Table 5. Crystallographic data for crystal structures **3** and **8**

Compound	**3**	**8**
Empirical formula	$C_{16}H_{26}Cl_2N_4PdS_2$	$C_{16}H_{28}B_2F_8N_4OPdS_2$
Formula mass [g·mol^{-1}]	515.83	636.56
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	Pbca
Unit cell dimensions		
a [Å]	8.821(8)	14.219(1)
b [Å]	28.22(1)	16.493(1)
c [Å]	9.305(2)	20.834(1)
β [°]	112.62(3)	90
Volume [Å^3]	2138(2)	4885.9(5)
Z	4	8
$D_{\text{calcd.}}$ [g cm^{-3}]	1.602	1.736
μ [mm^{-1}]	1.320	1.009
F(000)	1048	2576
Crystal size [mm]	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range [°]	2.48 to 29.99	2.13 to 25.01
Reflections collected: total, independent, R_{int}	6539, 6168, 0.0578	17711, 3987, 0.0438
Data/restraints/parameters	6118/0/263	3987/0/295
$a^{[a]}$	0.0285	0.0829
Final $R1$, $wR2$	0.0313, 0.0631	0.0398, 0.1259
$R1$ (all data), $wR2$	0.0946, 0.0762	0.0657, 0.1343
Residual electron density [e·Å^{-3}]	+0.433, −0.426	+0.694, −0.709

[a] The function minimised was $\Sigma w(|F_o|)^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (aP)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$.

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