Synthesis of New Pd^{II} Complexes Containing a Thioether-Pyrazole Hemilabile Ligand − Structural Analysis by ^1H, ^{13}C NMR Spectroscopy and Crystal Structure of $[PdCl(bdtp)]BF_4$ [bdtp = 1,5-Bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane]

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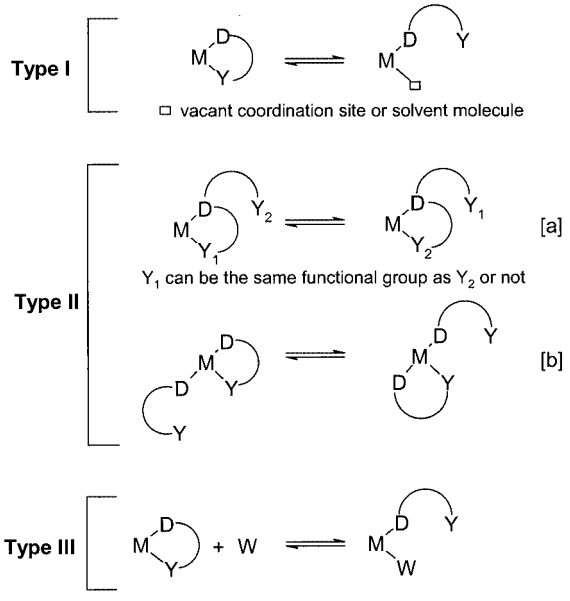
Treatment of the ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) with $[PdCl_2(CH_3CN)_2]$ led to a $[PdCl_2(bdtp)]$ complex. Subsequent treatment of this complex with $AgBF_4$ gave $[PdCl(bdtp)](BF_4)$. These Pd^{II} complexes were characterised by elemental analysis, conductivity measurements, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy. Complex $[PdCl_2(bdtp)]$ was again obtained when the complex $[PdCl(bdtp)](BF_4)$ was heated under reflux in a solution of NEt_4Cl in CH_2Cl_2/MeOH (1:1). Ligand bdtp in complexes **1** and **2** exhibited a hemilabile character. The X-ray structure of the complex $[PdCl(bdtp)](BF_4)$ was determined. The metal atom is tricoordinated by the two azine nitrogen atoms and one thioether sulfur atom of the thioether-pyrazole ligand, its coordination (distorted square planar) being completed with one chloride ion.

Introduction

The chemistry of hemilabile ligands in coordination and organometallic chemistry has been widely studied in recent years due to their potential application in catalysis. In particular, bidentate ligands containing two donor centres of different strengths with respect to substitution (labile Y and inert D) have been reviewed in recent reports and articles.[1] According to the review by P. Braunstein and F. Naud[1a] there are three types of hemilability. In type I hemilability, the labile donor group coordinates and decoordinates from the metal centre spontaneously. In type II, there is intramolecular competition between donor groups of the same ligand (a) or between donor groups of two identical ligands (b). Finally, in type III, the hemilabile character is due to the presence of an external reagent (Scheme 1 shows these types of hemilability for mononuclear complexes).

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,[2] P[3] or O[4] atoms. This paper continues the study of the potential hemilability of ligands containing pyrazolyl and thioether groups.[5]



Scheme 1

The bonding properties of this family of ligands are also well documented,[6] especially the synthesis and structural characterisation of complexes of Co^{II},[7] Zn^{II},[8] Cd^{II},[8] Cu^{I} [7,9] and Ag^{I} [7] with 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-

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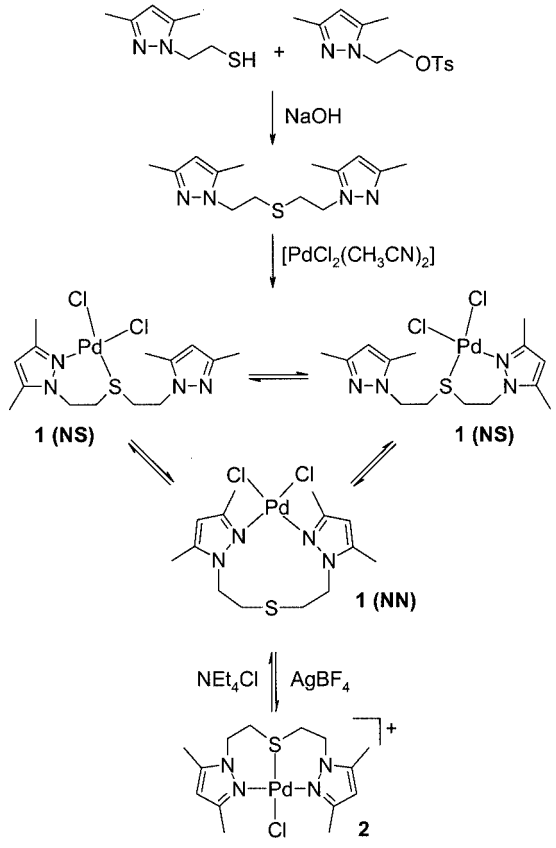
thiapentane (bdtp). The ligand acts in a tridentate manner (NSN) in all these complexes except [$ZnCl_2$(bdtp)], in which it behaves in a bidentate fashion (NN).

In this paper, we report on the study of the coordination of the ligand bdtp[10] with Pd^{II}, and the isolation of the complex [$PdCl_2$(bdtp)] (**1**). Treatment of this complex with $AgBF_4$ gives [PdCl(bdtp)](BF_4) (**2**; Scheme 2). NMR spectroscopic studies and the X-ray crystal structure of **2** are also presented.



Scheme 2

Results and Discussion

Although 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane (bdtp) has previously been reported in the literature,[10] in this paper we describe an alternative synthetic route. Treatment of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole and 1-[2-(*p*-tolylsulfonyloxy)ethyl]-3,5-dimethylpyrazole in the presence of sodium hydroxide in water gave the desired product (Scheme 2). The ligand bdtp was characterised by elemental analysis, mass spectrometry, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy.

[$PdCl_2$(bdtp)] (**1**) was obtained by treatment of the ligand with [$PdCl_2(CH_3CN)_2$] in a 1:1 M/L ratio. Treatment of **1** with one equivalent of $AgBF_4$ gave a compound of formula [PdCl(bdtp)](BF_4) (**2**). Both products are yellow and gave satisfactory C, H, N and S elemental analyses. When complex **2** was heated under reflux in a solution of Et_4NCl in CH_2Cl_2/MeOH (1:1) for 24 hours, complex **1** was again obtained.

Conductivity data in acetonitrile are in agreement with a non-electrolyte nature for compound **1** (37 Ω^{-1} cm^2mol^{-1}) and 1:1 electrolyte for compound **2** (123 Ω^{-1} cm^2mol^{-1}). The reported values for 10^{-3} M solutions of non-electrolyte compounds are lower than 120 $\Omega^{-1}cm^2mol^{-1}$ and between 120−160 Ω^{-1} cm^2mol^{-1} for 1:1 electrolyte compounds in acetonitrile.[11]

According to IR data for compound **1**, the Pd atom is coordinated to nitrogen atoms [ν(Pd−N) 456 cm^{-1}], two chlorine atoms in a *cis* arrangement [two bands are observed, ν(Pd−Cl) 367 and 336 cm^{-1}] and to sulfur atoms [ν(Pd−S) 280 cm^{-1}]. In compound **2** only one band for ν(Pd−Cl) (334 cm^{-1}) was observed as well as ν(Pd−N) (450 cm^{-1}) and ν(Pd−S) (256 cm^{-1}) bands.[12]

NMR Experiments

^1H and ^{13}C NMR spectra of compounds **1** and **2** were recorded in $CDCl_3$ and CD_2Cl_2, respectively, and show the signals of the coordinated ligands. NMR spectroscopic data are reported in the Exp. Sect.

The ^1H NMR spectrum of **1** in solution at 298 K shows sharp resonances for the CH and CH_3 groups of the pyrazolyl cycles, but poorly defined broad bands for the N−CH_2−CH_2−S chain. This suggests a fluxional process occurring in solution, which was studied carrying out a variable temperature ^1H NMR study in $CDCl_3$ (Figure 1). Lowering of the temperature induces a progressive broadening and splitting of the signal corresponding to the CH group of the pyrazolyl rings until 233 K, where three well-defined signals are observed at δ = 5.90, 5.82 and 5.77 ppm. The two signals at lower δ integrate for one H atom each, while the signal at δ = 5.90 ppm integrates for two H atoms. This suggests that at 298 K there is a fluxional process in which the thioether-pyrazole ligand alternates between the *N*,*N* and *N*,*S* bidentate coordinations (in the ratio of approximately 1:1). At 233 K, where both species can be observed, the *N*,*N* coordination shows only one signal for the CH group of the pyrazolyl rings,[5a] whereas in the *N*,*S* coordination mode the pyrazolyl groups are not equivalent

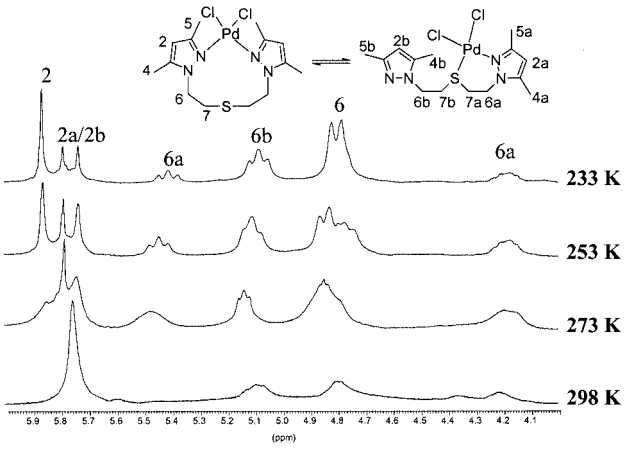


Figure 1. Numbering of complex [$PdCl_2$(bdtp)] and 400 MHz ^1H NMR variable temperature experiments for 2-H and 6-H

(coordinated and free pyrazolyl groups) and there is one signal for each.

Ill defined broad bands corresponding to the methylenic groups of the $N-CH_2-CH_2-S$ chain at 298 K become assignable signals at 233 K. Thus, if we focus on 6-H (7-H is superimposed with other signals) at 233 K, four groups of signals can be attributed to the methylene functionalities directly linked to the pyrazolyl group in the NN and NS isomers. One of them (at $\delta = 4.84$ ppm) can be attributed to the CH_2 of the NN isomer (6-H, Figure 1), as it integrates for four H atoms. The signal at $\delta = 5.12$ ppm can be assigned to the CH_2 of the open arm of the NS isomer (6b-H). It integrates for two H atoms and resembles a triplet. Finally, signals at $\delta = 4.21$ and 5.45 ppm can be assigned to the CH_2 group in the chelating arm of the NS isomer (6a-H), as they integrate for one H atom each. The rigid conformation of this arm in this isomer leads to the two hydrogens of this CH_2 group becoming diastereotopic, and therefore they have different chemical displacements. Although they are not completely defined, these signals resemble those observed for complexes found in the literature with similar $Pd-N-N-C-C-S$ rings.[5]

The ^{13}C NMR spectrum, at room temperature, of complex **1** also shows broad bands. This is consistent with the fluxional process explained for the ^1H NMR spectra.

From the structure of complex **2** it can be seen that the two protons of each CH_2 moiety in the $S-CH_2-CH_2-N$ chains are diastereotopic, thus leading to four groups of signals which can be associated to a single hydrogen atom in each chain. This happens because of the rigid conformation of the ligand when complexed. Thus, each group of signals can be assigned as doublets of doublets of doublets (Figure 2). The HMQC spectrum allowed us to assign the two doublets of doublets of doublets of lower δ to 7-H and the ones at higher δ to 6-H.

Study of the $S-CH_2-CH_2-N$ fragment (in **2**) as an AA′XX′ system gave a set of coupling constants (Table 1). These constants were consistent with the simulated spectra obtained with the aid of the gNMR program.[13]

Table 1. ^1H NMR results: chemical shifts (ppm, CD_2Cl_2) and $^1H,^1H$ coupling constants (Hz) for **2**

δ H (6*S*)	4.92	^2J(6*R*,6*S*)	−15.9
δ H (6*R*)	5.20	^2J(7*R*,7*S*)	−14.8
δ H (7*R*)	2.97	^3J(7*R*,6*S*)	2.5
δ H (7*S*)	3.78	^3J(7*S*,6*S*)	3.2
		^3J(7*R*,6*R*)	12.1
		^3J(7*S*,6*R*)	1.6

In the NOESY spectrum it can be seen that the methyl group at $\delta = 2.40$ ppm shows an NOE interaction with the doublet of doublets of doublets at $\delta = 4.92$ ppm, but not with the one at $\delta = 5.20$ ppm. From the X-ray structure of **2** (Figure 3), it can be observed that the nearest proton to the $CH_3(5)$ moiety is 6S-H and therefore it should be the one with the NOE interaction. This information leads us to assign 6*S*-H to the doublet of doublets of doublets at $\delta = 4.92$ ppm and 6R-H to the signal at $\delta = 5.20$ ppm.

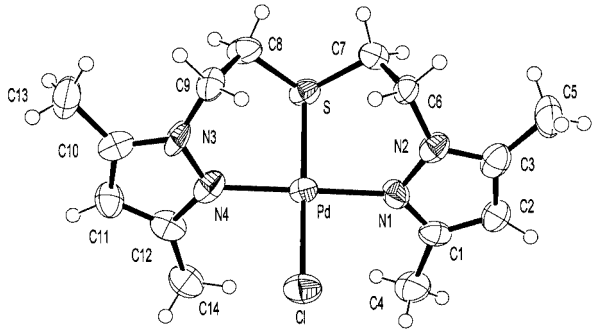


Figure 3. ORTEP drawing of $[PdCl(bdtp)]^+$ cation (293 K determination); 50% probability amplitude displacement ellipsoids are shown

The coupling constants enabled us to differentiate 7*R*-H and 7*S*-H. These coupling constants agree with the conformation of the $S-CH_2-CH_2-N$ chain as seen in Figure 2, which has been corroborated by an X-ray crystal study. Ge-

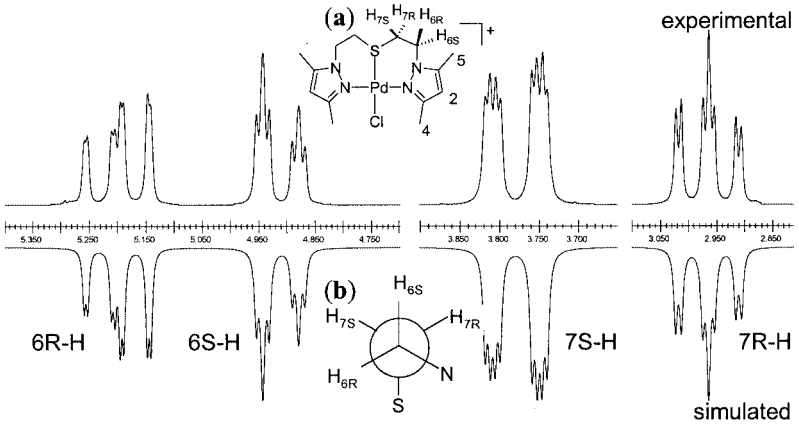


Figure 2. The 250 MHz ^1H NMR and the simulated gNMR spectrum for the NCH_2CH_2S fragment of $[PdCl(bdtp)](BF_4)$ including (a) the numbering and (b) the dihedral angles for the NCH_2CH_2S fragment

minal ^2J and ca. 180° ^3J coupling constants have significantly higher values than ca. 30° and ca. 60° ^3J coupling constants .[14] Thus, 7*R*-H should correspond to the doublet of doublets of doublets at δ = 2.97 ppm and 7*S*-H to the one at δ = 3.78 ppm.

Crystal Structure of [PdCl(bdtp)](BF$_4$) (2)

The molecular structure of compound **2** consists of discrete $[PdCl(bdtp)]^+$ cations and BF_4^- anions (Figure 3), packed according to normal van der Waals forces.

The cation complex is mononuclear. The Pd^{II} ion is coordinated to the bdtp ligand by its three donors atoms via two pyrazole nitrogens and one thioether sulfur, along with one chlorine atom. The PdN_2SCl *core* (S thioether) is found in three complexes in the literature.[15] Some selected bond lengths and bond angles for this complex are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (°) for **2** with estimated standard deviations (e.s.d.s.) in parentheses

Pd−N1	2.004(7)
Pd−N4	2.040(7)
Pd−S	2.308(2)
Pd−Cl	2.291(2)
N1−Pd−S	90.5(2)
N4−Pd−S	88.5(2)
N1−Pd−N4	176.6(3)
N1−Pd−Cl	89.8(2)
N4−Pd−Cl	91.5(2)
S−Pd−Cl	175.18(8)

The Pd−N bond lengths [2.004(7) Å and 2.040(7) Å], the Pd−S bond length [2.308(2) Å] and the Pd−Cl bond length [2.291(2) Å] can be regarded as normal compared with the distances found in the literature.[16] The coordination geometry is square planar with a tetrahedral distortion, as can be deduced from the bond angles and the mean separation [0.0765 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 N1−Pd−Cl and N4−Pd−S is 5.85°. Ligand bdtp acts as a tridentate chelate and forms two Pd−*N*−N−C−C−S six-membered rings with a boat conformation, sharing an edge (Pd−S). The boat distortions in the six-membered rings are $\Delta C_S[(S-C7)] = 12.4(6)°$ and $\Delta C_S[(N1-N2)] = 14.8(10)°$ for Pd−N1−N2−C6−C7−S and $\Delta C_S[(S-C8)] = 4.0(6)°$ and $\Delta C_S[(N3-N4)] = 5.2(9)°$ for Pd−N4−N3−C9−C8−S, respectively [see Equation (1)].

$$\Delta C_S = \sqrt{\frac{\sum_{i=1}^{m}(\phi_i + \phi_i')^2}{m}} \quad (1)$$

m = equivalent torsion angles

$\Phi_i+\Phi_i'$ = torsion angles related to the considered plane [17]

The nitrogen-thioether bite angles of the ligand are 90.5(2)° and 91.5(2)°, respectively, which are similar to the corresponding bite in the $[Co(NO_3)_2(bdtp)]$ and [CuBr(bdtp)] complexes.[7]

Conclusions

The thioether-pyrazole ligand bdtp can coordinate Pd^{II} centres in different ways. In this paper we describe all the possible polydentate coordinations in mononuclear complexes: two bidentate coordinations (NN and NS) and a tridentate coordination (NSN). Furthermore, we have demonstrated the hemilabile properties of this ligand when coordinated to Pd^{II}. In complex **1** the ligand alternates the NN and NS coordination types at room temperature, which would be type II hemilability.[1a]

Complex **2** (where ligand bdtp uses NSN coordination) is obtained from **1** by treatment with $AgBF_4$. When **2** is heated under reflux in a solution of Et_4NCl in CH_2Cl_2/MeOH (1:1), **1** is obtained once again. This could be considered as type III hemilability.

Experimental Section

Generals Remarks: Preparations were performed using usual 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 previously deoxygenated in the vacuum line.

Samples of $[PdCl_2(CH_3CN)_2]$ were prepared as described in the literature.[18]

Analyses (C,N,H,S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in ca. 10^{-3} M acetonitrile solutions employing a Crison, micro CM 2200 conductometer. Infrared spectra were recorded from KBr pellets or polyethylene mulls in the range 4000−100 cm^{-1} under a nitrogen atmosphere. The ^1H NMR, $^{13}C\{^1H\}$ NMR and HMQC spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. Chemical shifts (δ) were determined relative to internal TMS and are given in ppm. A mass spectrum was obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

Synthesis of the Ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp): Although the synthesis of the ligand bdtp has been previously reported in the literature,[10] here, we describe an alternative synthetic route. A solution of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole (2.00 g, 12.8 mmol), 1-[2-(*p*-tolylsulfonyloxy)ethyl]-3,5-dimethylpyrazole (3.77 g, 12.8 mmol) and of sodium hydroxide (0.53 g, 12.9 mmol; 97%) of water (25 mL) was refluxed for five hours. After cooling to room temperature, the reaction mixture was extracted three times with $CHCl_3$ (15 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed under vacuum to give a white solid. Yield: 2.17 g (61%). M.p. 80.3−80.9 °C. $C_{14}H_{22}N_4S$ (278.42): calcd. C 60.39, H 7.96, N 20.12, S 11.52; found C 60.20, H 7.73, N 20.41, S 11.23. IR (KBr, cm^{-1}): $\nu(C\text{-}H)_{al}$ = 2924, ν(C=C), ν(C=N) 1550, $\delta(CH_3)_{as}$ = 1481−1436, $\delta(CH_3)_s$ 1302, $\delta(C-H)_{oop}$ = 800−775. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.22 (s, 6 H, Me), 2.27 (s, 6 H, Me), 2.84

(t, ^3J = 6.9 Hz, 4 H, pz-CH_2−CH_2−S), 4.10 (t, ^3J = 6.9 Hz, 4 H, pz-CH_2−CH_2−S), 5.79 (s, 2 H, pz-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 63 MHz): δ = 11.4 (Me), 13.7 (Me), 32.5 (pz-CH_2−CH_2−S), 48.7 (pz-CH_2−CH_2−S), 105.3 (pz-CH), 139.5 (pz-C), 148.1 (pz-C) ppm. MS (ESI): *m*/*z* (%) = 279 (72) [M + H^+], 301 (100) [M + Na^+].

Synthesis of [$PdCl_2$(bdtp)] (1): A solution of [$PdCl_2(CH_3CN)_2$] (0.097 g, 0.374 mmol) in dichloromethane (15 mL) was added to a solution of bdtp (0.105 g, 0.378 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. Yield: 0.157 g (92%). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, $9.98\cdot10^{-4}$ M in acetonitrile): 37. $C_{14}H_{22}Cl_2N_4PdS$ (455.74): calcd. C 36.90, H 4.87, N 12.29, S 7.04; found C 36.58, H 4.92, N 12.11, S 6.93. IR (KBr, cm^{-1}): ν(C−H)$_{al}$ = 2920, ν(C=C), ν(C=N) 1557, δ$(CH_3)_{as}$ = 1467−1420, δ$(CH_3)_s$ = 1313, δ(C−H)$_{oop}$ = 788. IR (polyethylene, cm^{-1}): ν(Pd−N)$_{as}$ = 456, ν(Pd−Cl) = 336, 367, ν(Pd−S) = 280 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 233 K): (For simplicity we have used the numeration as in Figure 1; peaks from 2.20 ppm to 2.69 ppm are not integrated because they are superimposed with other signals, although these peaks all together integrate the expected 31 H atoms.) δ (isomer **N,N**) = 2.24, 2.55 [s, Me (4/5)], 2.69 [br., pz-CH_2−CH_2−S (7)], 4.84 [br., 4 H, pz-CH_2−CH_2−S (6)], 5.91 [s, pz-CH (2)]. δ (isomer **N,S**) = 2.25, 2.56 [s, Me (4a/b, 5a/b)], 2.20 [br., pz-CH_2−CH_2−S (7b)], 2.85 [br., 1 H, pz-CH_2−CHH−S (7a)], 3.37 [br., 1 H, pz-CH_2−CHH−S (7a)], 4.21 [br., 1 H, pz-CHH−CH_2−S (6a)], 5.12 [br., 2 H, pz-CH_2−CH_2−S (6b)], 5.45 [br., 1 H, pz-CHH−CH_2−S (6a)], 5.77, 5.83 [s, 1H each, pz-CH (2a/2b)]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 63 MHz, 298 K): δ = 12.3 (br., Me), 15.3 (br., Me), 29.9 (br., pz-CH_2−CH_2−S), 49.8 (br., pz-CH_2−CH_2−S), 108.2 (br., pz-CH), 143.6 (br., pz-C), 150.7 (br., pz-C).

Synthesis of [PdCl(bdtp)]BF_4 (2): A solution of $AgBF_4$ (0.063 g, 0.324 mmol) in methanol (2 mL) was added dropwise with vigorous stirring to a solution of **1** (0.149 g, 0.327 mmol) in dichloromethane (5 mL) and methanol (5 mL). The reaction was carried out in the dark to prevent reduction of Ag^I to Ag^0. After five minutes, stirring was stopped, and AgCl was filtered off through a pad of Celite. 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 dried under vacuum. Yield: 0.146 g (89%). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, $9.87\cdot10^{-4}$ M in acetonitrile): 123. $C_{14}H_{22}BClF_4N_4PdS$ (507.09): calcd. C 33.16, H 4.37, N 11.05, S 6.32; found C 33.45, H 4.40, N 10.93, S 6.12. IR (KBr, cm^{-1}): ν(C−H)$_{ar}$ = 3014, ν(C−H)$_{al}$ = 2967−2923, ν(C=C), ν(C=N) 1554, δ$(CH_3)_{as}$ = 1468−1423, δ$(CH_3)_s$ = 1319, ν(B−F) = 1049, δ(C−H)$_{oop}$ = 817. IR (polyethylene, cm^{-1}): ν(Pd−N)$_{as}$ = 450, ν(Pd−Cl) = 334, ν(Pd−S) = 256. ^1H NMR (250 MHz, CD_2Cl_2): δ = 2.40 (s, 6 H, Me), 2.70 (s, 6 H, Me), 2.97 (ddd, 2 H, pz-CH_2−CHH), 3.78 (ddd, 1 H, pz-CH_2−CHH), 4.92 (ddd, 1 H, pz-CHH−CH_2), 5.20 (ddd, 1 H, pz-CHH−CH_2), 6.08 (s, 2 H, pz-CH) ppm. $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2): δ = 12.2 (Me), 15.7 (Me), 39.8 (S−CH_2−CH_2), 51.2 (pz-CH_2−CH_2), 109.3 (pz-CH), 145.1, 154.1 (pz-C).

Synthesis of [$PdCl_2$(bdtp)] (1) from [PdCl(bdtp)](BF_4): A solution of **2** (0.053 g, 0.104 mmol) and NEt_4Cl (0.033 g, 0.199 mmol) in a mixture (1:1) of dichloromethane and methanol (20 mL) was refluxed for 24 hours. After cooling to room temperature, the reaction mixture was extracted three times with 15 mL of $CHCl_3$. The collected organic layers were dried with anhydrous sodium sulfate and removed in vacuo to yield the desired product. Yield: 0.038 g (80%).

X-ray Crystallographic Study: Suitable crystals of compound **2** were obtained by crystallisation from CH_2Cl_2. Data were collected on an Enraf−Nonius CAD4 four-circle diffractometer, using the ω/2θ scan technique. The crystals were collected with graphite-monochromated Mo-K_α radiation. 2977 reflections were measured in the range $2.11° < \theta < 29.98$. 1529 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control and significant intensity decay was not observed. Lorentz-polarisation but no absorption corrections were performed. The structure was solved by direct methods using the SHELXS 97 computer program and refined by the full-matrix least-squares method with a SHELXL 97 computer program.[19] All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final *R* (on *F*) factor and *wR* (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 3.

Table 3. Crystallographic data of **2**

Empirical formula	$C_{14}H_{22}BClF_4N_4PdS$
Molecular mass, g	507.08
Temperature, K	293(2)
Crystal system	monoclinic
Space group	C_C
Unit cell dimensions	
a, Å	5.138(8)
b, Å	30.957(6)
c, Å	12.355(3)
β, deg	92.87(7)
V, Å^3	1963(3)
Z	4
$D_{calcd.}$, g cm^{-3}	1.716
μ, mm^{-1}	1.230
F(000)	1016
Crystal size (mm)	0.1 × 0.1 × 0.2
θ range, deg	2.11 to 29.98
Reflections collected: total, independent, R_{int}	2977, 2977, 0.0134
Data/restraints/parameters	2977, 2, 235
a[a]	0.0095
Final *R*1, *wR*2	0.0337, 0.0492
*R*1 (all data), *wR*2	0.1430, 0.0656
Residual electron density, e·Å^{-3}	+0.774, −0.777

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

CCDC-208981 contains 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, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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