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Reactivity of $[PdCl(\mu\text{-med})]_2$ with monodentate or bidentate ligands. Structure of the dinuclear complexes $[Pd(\mu\text{-med})(PPh_3)]_2(BF_4)_2$ and $[Pd(\mu\text{-med})(bpy)]_2(BF_4)_2$. [Hmed = *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole]

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Abstract

Treatment of the ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole with $[Pd(CH_3COO)_2]_3$ and reaction of $[PdCl(\mu\text{-med})]_2$ with pyridine (py) or triphenylphosphine (PPh_3) in the presence of $AgBF_4$ produced the following complexes: $[Pd(CH_3COO)(\mu\text{-med})]_2$, $[Pd(\mu\text{-med})(py)]_2(BF_4)_2$ and $[Pd(\mu\text{-med})(PPh_3)]_2(BF_4)_2$. Similar reactions carried out with 2,2′-bipyridine (bpy) or 1,3-bis(diphenylphosphino)propane (dppp) produced $[Pd(\mu\text{-med})(bpy)]_x(BF_4)_x$ ($x = 1$ or 2) and $[Pd(\mu\text{-med})(dppp)]_x(BF_4)_x$ ($x = 1$ or 2). Treatment of $[Pd(\mu\text{-med})(bpy)]_x(BF_4)_x$ with $[PdCl_2(CH_3CN)_2]$ produced $[Pd_3Cl_2(\mu\text{-med})_2(bpy)_2](BF_4)_2$. Treatment of $[Pd(\mu\text{-med})(dppp)]_x(BF_4)_x$ with $[PdCl_2(CH_3CN)_2]$ produced a mixture of $[Pd(\mu\text{-Cl})(dppp)]_2(BF_4)_2$ and $[Pd(\mu\text{-med})_2(dppp)]^{2+}$. X-ray crystal structures of $[Pd(\mu\text{-med})(PPh_3)]_2(BF_4)_2 \cdot 2CH_3CN$ and $[Pd(\mu\text{-med})(bpy)]_2(BF_4)_2 \cdot 0.5CH_3OH$ are presented.

Keywords: Palladium; N ligand; S ligand

1. Introduction

The term ''hemilabile ligand'' – first introduced by Jeffrey and Rauchfuss [1] – refers to polydentate ligands that contain at least two different types of chemical functionalities that bind to metal centres. They must contain at least one substitutionally labile donor group while the other group remains firmly bound to the metal centre [2]. Their interest lies in their potential application in catalysis.

Pyrazole-based ligands are suitable models on which to study hemilabile properties since they are relatively easy to obtain and we can modulate their steric and electronic properties [3].

In recent years we have studied and reported the synthesis and characterisation of ligands based on the pyrazolyl group and another group containing N (amine) [4], P (phosphine) [5], O (alcohol or ether) [6] and S (thioether) [7] atoms.

The complexation of these ligands with Ru(II) [5], Rh(I) [4,5], Pd(II) [6,7] and Pt(II) [6,7] was also studied, but only the complexes of Rh(I) with pyrazole–amine [4a,4e] or pyrazole–ether [6d] ligands and the Pd(II) and Pt(II) complexes of the pyrazole–thioether ligands [7] had hemilabile properties.

This paper continues a recent study based on the coordination of the ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) when treated with group 10 metal salts [8]. In the previous paper, the synthesis and characterisation of $[MCl(\mu\text{-med})]_2$ (M = Ni(II), Pd(II) and Pt(II)) is reported. These complexes consist of dimeric units in which two-thiolate groups bridge two

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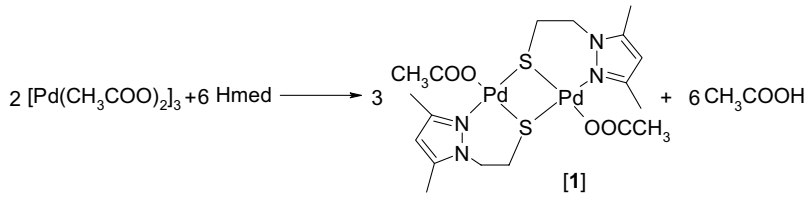
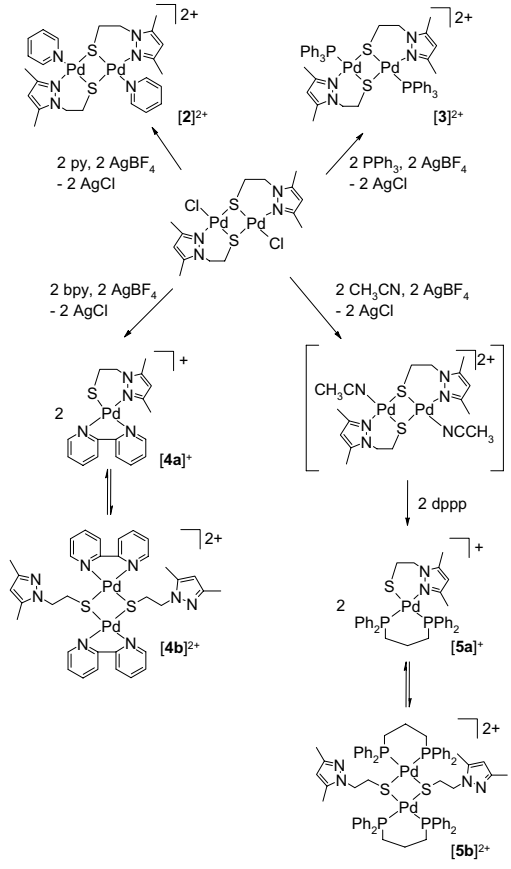


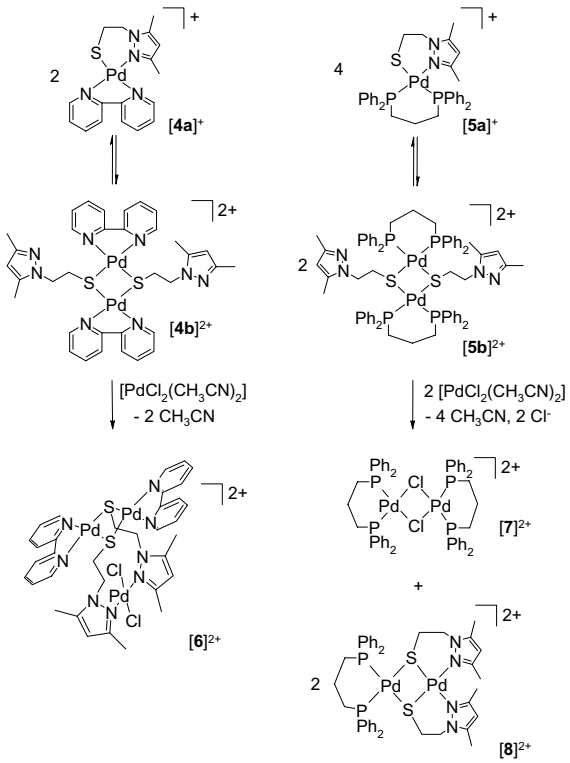
Scheme 1.

metallic centres and each pyrazolyl group coordinates one of these metallic cations.

Here we extend the study of the coordinative properties of the Hmed ligand to Pd(II). Treatment of the ligand with $[Pd(CH_3COO)_2]_3$ and reaction of [PdCl(μ-med)]$_2$ with pyridine (py) or triphenylphosphine (PPh_3) in the presence of $AgBF_4$ produced the following complexes: $[Pd(CH_3COO)(\mu\text{-med})]_2$ [**1**], $[Pd(\mu\text{-med})(py)]_2(BF_4)_2$ [**2**]$(BF_4)_2$ and $[Pd(\mu\text{-med})(PPh_3)]_2(BF_4)_2$ [**3**]$(BF_4)_2$. Similar reactions with 2,2′-bipyridine (bpy) or 1,3-bis(diphenylphosphino)propane (dppp) produced $[Pd(\mu\text{-med})(bpy)]_x(BF_4)_x$ ($x = 1$, [**4a**](BF_4); $x = 2$, [**4b**]$(BF_4)_2$) and $[Pd(\mu\text{-med})(dppp)]_x(BF_4)_x$ ($x = 1$, [**5a**](BF_4); $x = 2$, [**5b**]$(BF_4)_2$). X-ray crystal structures of [**3**]$(BF_4)_2 \cdot 2CH_3CN$ and [**4b**]$(BF_4)_2 \cdot 0.5CH_3OH$ are presented. Treatment of [**4**]$(BF_4)_x$ with $[PdCl_2(CH_3CN)_2]$ produced $[Pd_3Cl_2(\mu\text{-med})_2(bpy)_2](BF_4)_2$ [**6**]$(BF_4)_2$. Treatment of [**5**]$(BF_4)_x$ with $[PdCl_2(CH_3CN)_2]$ produced a mixture of $[Pd(\mu\text{-Cl})(dppp)]_2(BF_4)_2$ [**7**]$(BF_4)_2$ and $[Pd(\mu\text{-med})_2(dppp)]^{2+}$ [**8**]$^{2+}$ (Schemes 1–3).



Scheme 2.



Scheme 3.

2. Results and discussion

The Hmed was synthesised as described by Bouwman et al. [9]. Complexes $[PdCl_2(CH_3CN)_2]$ [10] and [PdCl(μ-med)]$_2$ [8] were synthesised as described elsewhere.

Treatment of the ligand with $[Pd(CH_3COO)_2]_3$ in acetonitrile gave $[Pd(CH_3COO)(\mu\text{-med})]_2$ [**1**]. Treatment of [PdCl(μ-med)]$_2$ with $AgBF_4$ in the presence of pyridine or triphenylphosphine yielded $[Pd(\mu\text{-med})(py)]_2(BF_4)_2$ [**2**]$(BF_4)_2$ and $[Pd(\mu\text{-med})(PPh_3)]_2(BF_4)_2$ [**3**]$(BF_4)_2$. These proposed formulas were corroborated by elemental analyses.

Conductivity in acetonitrile for [**1**] (2 Ω^{-1} cm^2 mol^{-1}) shows that the complex is a nonelectrolyte. Conductivity values in acetonitrile for complexes [**2**]$(BF_4)_2$ and [**3**]$(BF_4)_2$ (278 and 263 Ω^{-1} cm^2 mol^{-1}, respectively) are in agreement with 2:1 electrolytes. The reported values for 10^{-3} M solutions of nonelectrolyte complexes are lower than 120 Ω^{-1} cm^2 mol^{-1} in acetonitrile, while the range of conductivity values for 10^{-3} M solutions of 2:1 electrolyte compounds in acetonitrile is between 220 and 300 Ω^{-1} cm^2 mol^{-1} [11].

IR spectra of complexes [**1**]–[**3**]$(BF_4)_2$ are similar to that of [PdCl(μ-med)]$_2$, the most characteristic bands being those attributable to the pyrazolyl group: ν(C=C)$_{ar}$ and ν(C=N)$_{ar}$ between 1553 and 1551 cm^{-1}. The absence of the ν(S–H) band, found in the free ligand spectrum at 2543 cm^{-1}, shows that the ligand Hmed acts as a thiolate (med) when complexed. The IR spectrum of [**1**] shows the absorption bands assigned to the asymmetric and symmetric ν(OCO) stretching modes. It displays one ν_{as}(OCO) band at 1617 cm^{-1} and one ν_s(OCO) band at 1370 cm^{-1}, separated by $\Delta = \nu_{as}(OCO) - \nu_s(OCO) = 247$ cm^{-1}. This Δ value suggests the presence of unidentate acetate groups in compound [**1**] [12].

IR spectrum of [**2**]$(BF_4)_2$ presents a band attributable to ν(C=C)$_{py}$ and ν(C=N)$_{py}$ at 1606 cm^{-1}. IR spectra of [**2**]$(BF_4)_2$ and [**3**]$(BF_4)_2$ present bands that were assigned to ν(B–F) at 1057 and 1058 cm^{-1}, respectively [13].

The IR spectra of the complexes in 500–100 cm^{-1} region were also studied [14]. In all cases they show bands attributable to ν(Pd–N$_{pz}$)$_{as}$ between 459 and 450 cm^{-1} and ν(Pd–S) between 301 and 280 cm^{-1}. Bands attributable to ν(Pd–O) at 511 cm^{-1} for [**1**] and ν(Pd–P) at 310 cm^{-1} for [**3**]$(BF_4)_2$ were also assigned.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes [**1**]–[**3**]$(BF_4)_2$ show the signals of coordinated ligands [15]. Spectra of [**1**] and [**3**]$(BF_4)_2$ were recorded in $CDCl_3$ and spectra of [**2**]$(BF_4)_2$ were recorded in [D3] acetonitrile.

^{1}H NMR spectra show, for complexes [**1**]–[**3**]$(BF_4)_2$, four groups of doublets of doublets of doublets which can be assigned to a single hydrogen of the N–CH_2–CH_2–S fragment each. This happens because the two protons of each CH_2 are diastereotopic, owing to the rigid conformation of the ligand when it is complexed.

HMQC spectra of [**1**]–[**3**]$(BF_4)_2$ were used to assign 7-H protons to the two doublets of doublets of doublets of lower δ and 6-H protons to those of higher δ (Fig. 1).

We obtained a set of coupling constants for complexes [**1**] and [**2**]$(BF_4)_2$ with the aid of the gNMR program [16]. All these results are reported in Section 4. Fig. 2 shows the experimentally determined and simulated spectra for [**1**]. Coupling constants for complex [**3**]$(BF_4)_2$ could not be obtained due to the broadness of the bands.

These spectra suggest a coordination of the thiolate ligand (med) similar to that found for [PdCl(μ-med)]$_2$ in which two thiolate ligands *N*-(2-mercaptoethyl)-3,5-dimethylpyrazolate (med) bridge two metallic centres and the pyrazolyl groups are bonded to one palladium

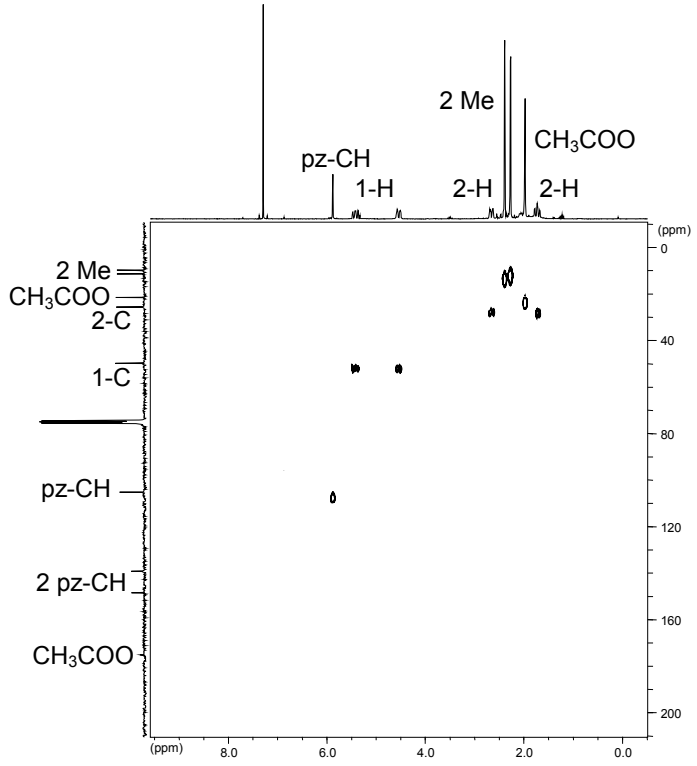


Fig. 1. The 250 MHz 2D HMQC spectrum of [Pd(CH$_3$COO)(μ-med)]$_2$ [**1**] and the numbering for the complexes [**1**]–[**3**]$(BF_4)_2$.

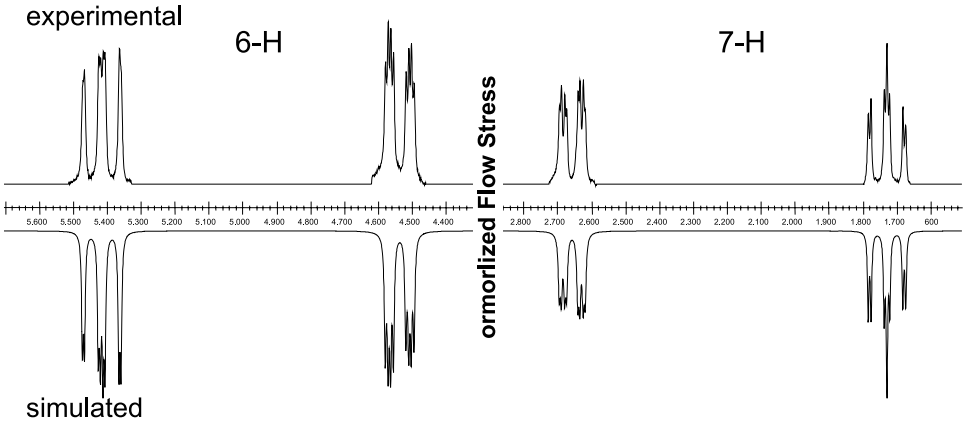


Fig. 2. The 400-MHz ^{1}H NMR and gNMR simulated spectra for the NCH_2CH_2S fragment of $[Pd(CH_3COO)(\mu\text{-med})]_2$ [**1**].

each [8]. The remaining coordination site for each palladium atom (occupied by the chloride ion in $[PdCl(\mu\text{-med})]_2$) is now occupied in [**1**]–[**3**]$(BF_4)_2$ by an unidentate acetate, a pyridine or a triphenylphosphine, respectively.

Further evidence of the N,S:S′ coordination can be seen in the X-ray crystal structure of [**3**]$(BF_4)_2 \cdot 2CH_3CN$.

The structure of [**3**]$(BF_4)_2 \cdot 2CH_3CN$ (Fig. 3) consists of dimeric cationic units of $[Pd(\mu\text{-med})(PPh_3)]_2^{2+}$, BF_4^- anions and solvent molecules (CH_3CN). The structure contains an inversion centre.

Each palladium atom is coordinated by two thiolate-bridging sulfurs (in *anti* conformation), one pyrazole nitrogen and one triphenylphosphine ligand in a distorted square-planar geometry. Table 1 lists selected bond distances and bond angles for the cation $[\mathbf{3}]^{2+}$.

Tetrahedral distortion of the square-planar geometry can be observed in the largest deviations with respect to the mean coordination plane which contains the Pd atom, which are −0.036(1) Å for the sulfur atom and 0.035(3) Å for N(1).

The two planar $PdNPS_2$ units are joined via two bridging thiolate ligands forming a four-membered ring, which is flat, with Pd···Pd and S···S distances of 3.4159(5) and 3.1729(4) Å, respectively. Bridging angle for Pd–S–Pd(a) is 94.23(3)°.

Pd–N distances are slightly shorter than those reported for dinuclear complexes with $PdNS_2X$ cores (N amine, S bridging thiolate and X chloride or nitrogen atom) [17] and Pd–P and Pd–S distances are similar to those reported for dinuclear complexes with $PdPS_2X$ ($P = PPh_3$, S bridging thiolate and X chloride or thiolate) [18] and $PdNS_2X$ (N amine, S bridging thiolate and X chloride or nitrogen) [17] cores, respectively.

The amino–thiolate ligand acts as a bidentate chelate (as well as bridging ligand), forming a Pd–S–C–C–N–N ring. This ring has skew-boat conformation. Bite angle N(1)–Pd–S is 84.12(9)°.

The distortion of the skew-boat in the ring Pd–N(1)–N(2)–C(6)–C(7)–S is $\Delta C_S(N(1)\text{–}N(2)) = 29.8(4)°$ [1].

To examine the influence of the ligands that replace the chloride ion in $[PdCl(\mu\text{-med})]_2$, we exchanged the chloride ion by bidentate chelating ligands 2,2′-bipyridine and 1,3-bis(diphenylphosphino)propane. In contrast, use of the same reaction conditions with the ligand 1,2-bis(diphenylphosphino)ethane (dppe) gave decomposition products.

Treatment of $[PdCl(\mu\text{-med})]_2$ with $AgBF_4$ in the presence of 2,2′-bipyridine produced a complex whose elec-

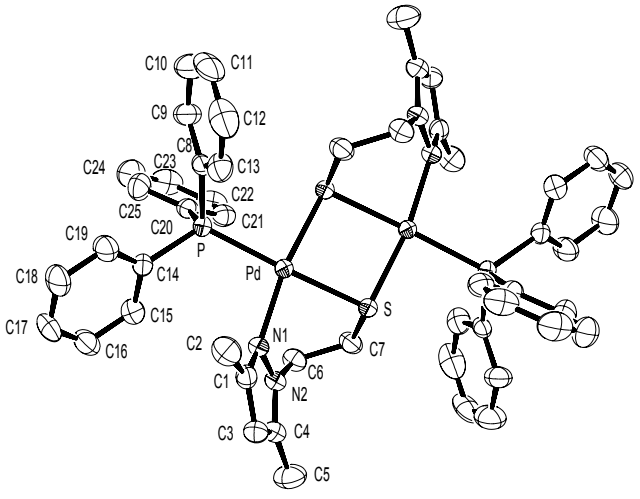


Fig. 3. ORTEP drawing of $[Pd(\mu\text{-med})(PPh_3)]_2^{2+}$ cation ($[\mathbf{3}]^{2+}$) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

[1]

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

where m is the equivalent torsion angles and $\phi_i + \phi_i'$ is the torsion angles related to the considered plane [19].

Table 1
Selected bond lengths (Å) and angles (°) for $[\mathbf{3}]^{2+}$ and $[\mathbf{4b}]^{2+}$ with estimated standard deviations (esds) in parentheses

$[\mathbf{3}]^{2+}$		$[\mathbf{4b}]^{2+}$	
Pd–N(1)	2.060(3)	Pd(1)–N(1)	2.064(4)
Pd–P	2.2936(9)	Pd(1)–N(2)	2.078(3)
Pd–S	2.2972(10)	Pd(1)–S(1)	2.2841(10)
Pd–S(a)	2.3646(9)	Pd(1)–S(2)	2.2906(11)
		Pd(2)–N(3)	2.072(3)
		Pd(2)–N(4)	2.072(4)
		Pd(2)–S(2)	2.2854(10)
		Pd(2)–S(1)	2.2872(11)
		Pd(1)–Pd(2)	3.4159(5)
N(1)–Pd–P	99.24(9)	N(1)–Pd(1)–N(2)	80.13(15)
N(1)–Pd–S	169.02(9)	N(1)–Pd(1)–S(1)	99.21(10)
P–Pd–S	90.17(3)	N(2)–Pd(1)–S(1)	176.75(10)
N(1)–Pd–S(a)	84.12(9)	N(1)–Pd(1)–S(2)	178.60(9)
P–Pd–S(a)	171.21(3)	N(2)–Pd(1)–S(2)	98.66(12)
S–Pd–S(a)	85.77(3)	S(1)–Pd(1)–S(2)	81.97(4)
Pd–S–Pd(a)	94.23(3)	N(3)–Pd(2)–N(4)	80.09(13)
		N(3)–Pd(2)–S(2)	175.18(10)
		N(4)–Pd(2)–S(2)	99.54(10)
		N(3)–Pd(2)–S(1)	98.11(10)
		N(4)–Pd(2)–S(1)	176.56(10)
		S(2)–Pd(2)–S(1)	82.01(4)

trospray mass spectrum is in accordance with the proposed formula [Pd(μ-med)(bpy)](BF_4) [**4a**](BF_4). The ^{1}H NMR spectrum of this complex in $CDCl_3$ is similar to those of [**1**]–[**3**]$(BF_4)_2$. Four groups of broad doublets of doublets of doublets can be assigned to each H from the N–CH_2–CH_2–S chain. This means that the ligand is rigid when complexed to the metallic centre. The ligand (med) is coordinated through the thiolate and pyrazolyl groups, but, in contrast to what happens in [**1**]–[**3**] $(BF_4)_2$, the complex is mononuclear in [**4a**](BF_4) (Scheme 2).

To explore how the pyrazole–thiolate ligand coordinates the metallic centre, [**4a**](BF_4) was recrystallised in a mixture of dichloromethane and methanol (1:1) and, surprisingly, monocrystals of [Pd(μ-med)(bpy)]$_2$ $(BF_4)_2 \cdot 0.5CH_3OH$ [**4b**]$(BF_4)_2 \cdot 0.5CH_3OH$ were obtained. These were structurally characterised by X-ray crystallography. The structure (Fig. 4) consists of cationic units of $[Pd(\mu\text{-med})(bpy)]_2^{2+}$, BF_4^- anions and solvent molecules (methanol).

Each palladium atom is coordinated by two thiolate-bridging sulfurs from two pyrazole ligands (in *syn* conformation) and two nitrogens of 2,2′-bipyridine in a distorted square-planar geometry. The pyrazole groups are not coordinated to the metal centre. Table 1 lists selected bond distances and bond angles for the cation $[\mathbf{4b}]^{2+}$.

Tetrahedral distortion of the square-planar geometry can be observed in the largest deviation with respect to the mean coordination planes, which contain Pd atoms. These deviations are ±0.025(5) Å for the nitrogen atoms and ±0.022(1) Å for the sulfur atoms with respect to Pd(1), and ±0.018(4) Å for the nitrogen atoms and ±0.016(1) Å for the sulfur atoms with respect to Pd(2).

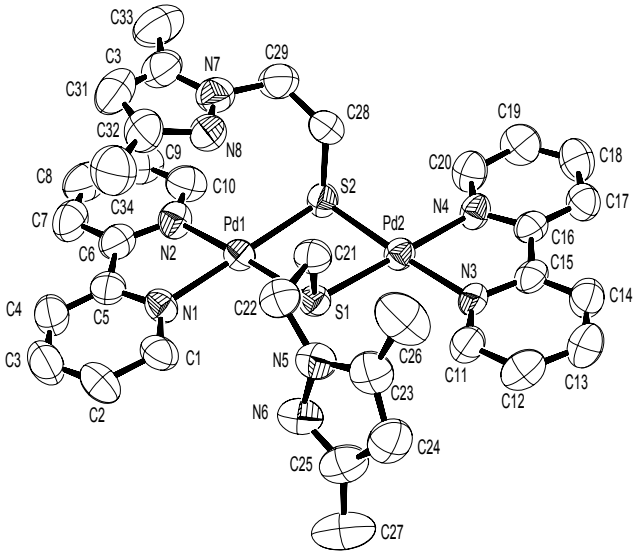


Fig. 4. ORTEP drawing of $[Pd(\mu\text{-med})(bpy)]_2^{2+}$ cation $[\mathbf{4b}]^{2+}$ (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

The two planar PdN_2S_2 units are joined via two bridging thiolate ligands forming a four-membered ring, which is CR form, with Pd···Pd and S···S distances 3.4369(5) Å and 3.0002(17) Å, respectively. The dihedral angle between the planes Pd(1)–S(1)–Pd(2) and Pd(1)–S(2)–Pd(2) is 8.16(5)°. Bridging angles for Pd(1)–S(1)–Pd(2) and Pd(1)–S(2)–Pd(2) are 97.50(4)° and 97.37(4)°, respectively.

2,2′-Bipyridine ligands act as bidentate chelates forming two Pd–N–C–C–N rings. The Pd(1)–N(1)–C(5)–C(6)–N(2) ring is twisted on Pd(1)–N(1) bond whereas the Pd(2)–N(3)–C(15)–C(16)–N(4) ring is flat. Bite angles N(1)–Pd(1)–N(2) and N(3)–Pd(2)–N(4) are 80.13(15)° and 80.09(13)°, respectively. These angles are similar to those reported for complexes with chelating 2,2′-bipiridines [20].

The distortion of the five-membered rings is $\Delta C_S(Pd(1)\text{–}N(1)) = 9.8(5)°$ and $\Delta C_S(Pd(2)\text{–}N(3)) = 5.2(4)°$ for Pd(1)–N(1)–C(5)–C(6)–N(2) and Pd(2)–N(3)–C(15)–C(16)–N(4), respectively.

When the crystals of $[\mathbf{4b}](BF_4)_2 \cdot 0.5CH_3OH$ were redissolved in chloroform or dichloromethane, $[\mathbf{4a}]^+$ was again obtained in solution. Varying the temperature we could not observe the formation of $[\mathbf{4b}]^{2+}$ in solution.

1,3-Bis(diphenylphosphino)propane reacted with $[Pd(\mu\text{-med})(CH_3CN)]_2(BF_4)_2$ (generated in situ from the reaction of $[PdCl(\mu\text{-med})]_2$, acetonitrile and $AgBF_4$ in a mixture of dichloromethane and methanol) to give two complexes in a 1:1 ratio. The $^{31}P\{^1H\}$ NMR spectrum of the mixture shows two doublets centred at 0.2 and 13.5 ppm with the same coupling constant ($^2J = 51.5$ Hz, assigned to $[Pd(\mu\text{-med})(dppp)]^+$ $[\mathbf{5a}]^+$) and a singlet at 10.2 ppm (assigned to $[Pd(\mu\text{-med})(dppp)]_2^{2+}$ $[\mathbf{5b}]^{2+}$). These data are in agreement with $[\mathbf{5a}]^+$ being a

mononuclear species of Pd(II) with dppp and the thiolate ligand (med) chelating the metallic centre as in $[\mathbf{4a}]^+$ and $[\mathbf{5b}]^{2+}$ a dinuclear compound similar to $[\mathbf{4b}]^{2+}$ (Scheme 2).

To confirm the presence of these two species, an electrospray mass spectrum of the mixture was performed (solvent acetonitrile). Sample was measured at 573 K. Surprisingly, only the mononuclear species ($[\mathbf{5a}]^+$) was observed, even though an enhanced resolution technique was applied. This indicated a temperature dependent dynamic equilibrium between the two species. Therefore, we performed variable-temperature NMR studies of the mixture in [D3] acetonitrile. At 343 K, the initial ratio 1:1 ($[\mathbf{5a}]^+$:$[\mathbf{5b}]^{2+}$) turned into a 4:1 ratio. When temperature was returned to 298 K, the initial ratio was restored.

As the equilibrium was displaced towards $[\mathbf{5a}]^+$ when the temperature was raised, we attempted to obtain pure $[\mathbf{5b}]^{2+}$ at low temperatures. When a saturated solution of $[\mathbf{5a}]^+$ and $[\mathbf{5b}]^{2+}$ in a mixture of dichloromethane and methanol was cooled to 243K, we obtained $[\mathbf{5b}](BF_4)_2$ (0.11 g, 83% yield) as dark yellow microcrystals.

The $^{31}P\{^1H\}$ NMR spectrum of pure $[\mathbf{5b}]^{2+}$ in CD_2Cl_2 returned to that of the initial mixture of $[\mathbf{5a}]^+$ and $[\mathbf{5b}]^{2+}$ after approximately 30 min.

Treatment of $[\mathbf{4b}](BF_4)_2$ with $[PdCl_2(CH_3CN)_2]$ produced a complex whose elemental analyses are consistent with the formula $[Pd_3Cl_2(\mu\text{-med})_2(bpy)_2](BF_4)_2$ ($[\mathbf{6}](BF_4)_2$) (Scheme 3). Conductivity value for this complex in acetonitrile (266 Ω^{-1} cm^2 mol^{-1}) corresponds to those of 2:1 electrolytes [11]. The IR spectrum between 500 and 100 cm^{-1} shows bands attributable to $\nu(Pd–N)_{as}$(bpy, pz) at 417 cm^{-1}, ν(Pd–Cl) at 348 cm^{-1} and ν(Pd–S) at 279 cm^{-1} [14]. The ^1H NMR spectrum shows four signals corresponding to the NCH_2CH_2S chain, as expected for the rigid structure of this complex (Scheme 3). Although the four signals resemble the doublets of doublets of doublets found for complexes $[\mathbf{1}]$–$[\mathbf{3}](BF_4)_2$, they could not be further studied due to their broadness. Electrospray mass spectrum of this complex shows the monocationic unit $\{[\mathbf{6}]\cdot BF_4\}^+$. There are four structures reported in the literature on trinuclear Pd(II) complexes with at least one pyrazolyl group coordinated to one of the metal centres [21]. The cores of the metallic centres in the hypothetical structure of $[\mathbf{6}](BF_4)_2$ would be two $[PdN_2S_2]$ and one $[PdCl_2N_2]$. The $[PdN_2S_2]$ core is not found in any of the trinuclear species described in the literature. However, the $[PdCl_2N_2]$ core is found in two of them [21a,21c].

Treatment of a solution of $[\mathbf{5a}](BF_4)$/$[\mathbf{5b}](BF_4)_2$ with $[PdCl_2(CH_3CN)_2]$ produced a mixture of two complexes in a 1:1 ratio, with chemical shifts in the $^{31}P\{^1H\}$ NMR spectrum of 7.5 and 12.6 ppm. Recrystallisation of the mixture with dichloromethane/diethyl ether (1:1) yielded one of the complexes ($\delta = 12.6$ ppm in the $^{31}P\{^1H\}$ NMR spectrum), whose elemental analyses and electrospray mass spectrum are in agreement with the formula $[Pd(\mu\text{-}Cl)(dppp)]_2(BF_4)_2$ ($[\mathbf{7}](BF_4)_2$) (Scheme 3). The cationic part of this complex had previously been reported by Pelzer et al. [22] but with SO_4^{2-} instead of BF_4^-.

The other complex ($\delta = 7.5$ ppm in the $^{31}P\{^1H\}$ NMR spectrum) could not be obtained as a pure product. From the electrospray mass spectrum of a solution in which it is the majority compound, it was possible to assign it to $[Pd_2(\mu\text{-med})_2(dppp)]^{2+}$ $[\mathbf{8}]^{2+}$. The ^1H NMR spectrum of this species shows the four groups of broad doublets of doublets of doublets typical of N,S coordination. The proposed structure is illustrated in Scheme 3.

3. Conclusion

The thiolate ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazolate (med) forms dinuclear Pd(II) units with the general formula $[Pd(\mu\text{-med})X]_2$, X being a monodentate (chloride, acetate, pyridine, triphenylphosphine) or bidentate (2,2′-bipiridine (bpy), 1,3-bis(diphenylphosphino)propane (dppp)) ligand. These dimeric units can be neutral or charged depending on X.

When X is monodentate, the thiolate group in med bridges the two Pd atoms and the pyrazolyl group chelates one of the metallic centres. When X is bidentate, two isomers can be formed, and in one of them (the dinuclear species) the chelate is broken, and the pyrazolyl group is uncoordinated. This shows the different coordinative properties of the thiolate and pyrazolyl groups. Furthermore, when X is bidentate, another isomer is formed. In this isomer (a mononuclear species), med does not act as a bridging ligand, although it does chelate the metallic centre through the thiolate and pyrazolyl groups. When X is dppp, there is a dynamic equilibrium between the dinuclear and the mononuclear species. Therefore, the pyrazolyl group coordinates and de-coordinates the palladium atom in a process that could be considered as hemilabile.

In summary, we have shown that the ligand med, when complexed to Pd(II), can act as a bridge, a chelate or a bridging-chelate, depending on the coordinative environment of the metallic centre.

4. Experimental

4.1. 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.

We recently reported the preparation of [PdCl(μ-med)]$_2$ [8]. *N*-(2-Mercaptoethyl)-3,5-dimethylpyrazole [9] and [$PdCl_2(CH_3CN)_2$] [10] were prepared according to the reported methods.

Analyses (C, N, H, and S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M acetonitrile solutions employing a Crison, micro CM 2200 conductimeter. 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, $^{31}P\{^1H\}$ NMR, HMQC and NOESY spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. $^{31}P\{^1H\}$ NMR chemical shifts are relative to external 85% H_3PO_4 and are given in ppm. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

4.2. Synthesis of the complexes

4.2.1. [Pd(μ-med)(CH_3COO)]$_2$ [1]

A solution of 0.220 g (0.33 mmol) of [$Pd(CH_3COO)_2]_3$ in 10 ml of acetonitrile was added dropwise to a solution of 0.154 g (0.99 mmol) of *N*-mercaptoethyl-3,5-dimethylpyrazole in dry acetonitrile (5 ml).

After 6 h, stirring was stopped, and the solution was filtered to eliminate any solid impurity. Acetonitrile was then evaporated and the solid was recrystallised in a dichloromethane/diethyl ether mixture (1:1) (yellow solid).

Yield: 0.283 g (90%) – $C_{18}H_{28}N_4O_4Pd_2S_2$ (641.41): C, 33.71; H, 4.40; N, 8.73; S, 10.00. Found: C, 33.65; H, 4.31; N, 8.80; S, 10.14%. Conductivity (Ω_{-1} cm^2 mol^{-1}, 9.92×10^{-4} M in acetonitrile): 2 – IR (KBr, cm^{-1}): (ν(C–H)$_{al}$ 2921, $\nu(OCO)_{as}$ 1617, ν(C=C), ν(C=N) 1553, $\delta(CH_3)_{as}$ 1469, $\delta(OCO)_s$ 1370, $\delta(CH_3)_s$ 1312, 1260 δ(C–H)$_{oop}$ 783. IR (polyethylene, cm^{-1}): ν(Pd–O) 511, ν(Pd–N)$_{as}$ 459, ν(Pd–S) 301. ^1H NMR (400 MHz, $CDCl_3$ solution) $\delta = 1.96$ (s, 6H, CH_3COO) 2.25 (s, 6H, *Me*), 2.37 (s, 6H, *Me*), 1.71 (ddd, 2H, pz-CH_2–C*H*H, $^2J = 13.8$ Hz, $^3J = 2.1$ Hz, $^3J = 11.8$ Hz), 2.63 (ddd, 2H, pz-CH_2–C*H*H, $^2J = 13.8$ Hz, $^3J = 3.9$ Hz, $^3J = 1.6$ Hz), 4.52 (ddd, 2H, pz-C*H*H–CH_2, $^2J = 15.2$ Hz, $^3J = 2.1$ Hz, $^3J = 3.9$ Hz), 5.39 (ddd, 2H, pz-C*H*H–CH_2, $^2J = 15.2$ Hz, $^3J = 11.8$ Hz, $^3J = 1.6$ Hz), 5.85 (s, 2H, pz-*CH*). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$ solution) $\delta = 12.1$ (*Me*), 13.6 (*Me*), 23.7 (CH_3COO), 27.8 (S–CH_2–CH_2), 51.9 (pz-CH_2–CH_2), 107.3 (pz-CH), 150.6 (pz-C), 177.2 (CH_3*C*OO).

4.2.2. [Pd(μ-med)(py)]$_2$(BF_4)$_2$ [2](BF_4)$_2$

A solution of 0.078 g (0.13 mmol) of [Pd(μ-med)Cl]$_2$ were dissolved in a mixture of dichloromethane (10 ml) and methanol (10 ml). About 0.025 g (0.32 mmol) of pyridine was then added, followed immediately by a solution of 0.051 g (0.26 mmol) of $AgBF_4$ in methanol (2 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 through Celite pad. Solution had turned from initial orange to bright yellow. When the volume of resultant solution had been reduced to roughly 5 ml, the product precipitated as a yellow solid. This solid was filtered and washed in dichloromethane.

Yield: 0.104 g (93%) – $C_{24}H_{32}B_2F_8N_6Pd_2S_2$ (855.13): C, 33.71; H, 3.77; N, 9.83; S, 7.50. Found: C, 33.46; H, 3.57; N, 9.60; S, 7.22%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.03×10^{-3} M in acetonitrile): 278 – IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3057, ν(C–H)$_{al}$ 2927, ν(C=C)$_{py}$, ν(C=N)$_{py}$ 1606, ν(C=C)$_{pz}$, ν(C=N)$_{pz}$ 1553, $\delta(CH_3)_{as}$ 1454, $\delta(CH_3)_s$ 1382, ν(B–F) 1057, δ(C–H)$_{oop}$ 758. IR (polyethylene, cm^{-1}): ν(Pd–N)$_{as}$(pz, py) 457, ν(Pd–S) 280. ^1H NMR (400 MHz, [D_3]-acetonitrile solution) $\delta = 1.63$ (s, 6H, *Me*), 2.22 (s, 6H, *Me*), 1.55 (ddd, 2H, pz-CH_2–C*H*H, $^2J = 14.6$ Hz, $^3J = 11.9$ Hz, $^3J = 2.1$ Hz), 2.00 (ddd, 2H, pz-CH_2–C*H*H, $^2J = 14.6$ Hz, $^3J = 1.3$ Hz, $^3J = 3.9$ Hz), 4.53 (ddd, 2H, pz-C*H*H–CH_2, $^2J = 15.3$ Hz, $^3J = 11.9$ Hz, $^3J = 1.3$ Hz), 4.98 (ddd, 2H, pz-C*H*H–CH_2, $^2J = 15.3$ Hz, $^3J = 2.1$ Hz, $^3J = 3.9$ Hz), 5.98 (s, 2H, pz-*CH*), 7.67 (m, 4H, py), 8.13 (m, 2H, py), 8.77 (m, 4H, py). $^{13}C\{^1H\}$ NMR (63 MHz, [D_3]-acetonitrile solution) $\delta = 11.9$ (*Me*), 13.6 (*Me*), 29.4 (S–CH_2–CH_2), 52.7 (pz-CH_2–CH_2), 108.8 (pz-CH), 128.5 (py), 141.8 (py), 145.1 (pz-C), 151.8 (pz-C), 153.1 (py).

4.2.3. [Pd(μ-med)(PPh_3)]$_2$(BF_4)$_2$ [3](BF_4)$_2$

A solution of 0.108 g (0.18 mmol) of [Pd(μ-med)Cl]$_2$ and 0.0954 (0.36 mmol) of PPh_3 were dissolved in a mixture of dichloromethane (10 ml) and methanol (10 ml). Then, a solution of 0.0695 g (0.36 mmol) of $AgBF_4$ in methanol (2 ml) was added dropwise with vigorous stirring. The solution turned red. After 5 min, stirring was stopped, and AgCl was filtered off through a Celite pad. 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 in vacuo.

Yield: 0.173 g (78%) – $C_{50}H_{52}B_2F_8N_4P_2Pd_2S_2$ (1221.50): C, 49.16; H, 4.29; N, 4.59; S, 5.25. Found: C, 48.99; H, 4.35; N, 4.46; S, 5.37%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 9.08×10^{-4} M in acetonitrile): 263 – IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3053, ν(C–H)$_{al}$ 2942-2917, ν(C=C), ν(C=N) 1551, $\delta(CH_3)_{as}$ 1480, $\delta(CH_{ar})_{as}$ 1435, $(CH_3)_s$ 1391, ν(B–F) 1058, $\delta(CH_{ar})_{oop}$ 692. IR (polyethylene, cm^{-1}): ν(Pd–N)$_{as}$ 450, ν(Pd–P) 310, ν(Pd–S) 288. ^1H NMR (400 MHz, $CDCl_3$ solution) = 1.62 (s, 6H, *Me*), 2.08 (s, 6H, *Me*), 2.14 (b, 2H, pz-CH_2–C*H*H), 2.84 (b, 2H, pz-CH_2–C*H*H), 4.46 (b, 2H, pz-C*H*H–CH_2), 5.38 (b, 2H, pz-C*H*H–CH_2), 5.78 (s, 2H, pz-*CH*), 7.49 (m,

30H, PPh_3). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$ solution) $\delta = 11.2$ (*Me*), 13.5 (*Me*), 32.4 (S–CH_2–CH_2), 53.6 (pz-CH_2–CH_2), 109.9 (pz-CH), 128.3 (m, PPh_3), 133.9 (m, PPh_3), 145.1 (pz-C), 152.7 (pz-C). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$ solution) $\delta = 21.9$ (s, PPh_3).

4.2.4. *[Pd(μ-med)(bpy)](BF4) [4a](BF4) and [Pd(μ-med)(bpy)]2(BF4)2 [4b](BF4)2*

A solution of 0.034 g (0.22 mmol) of 2,2′-bipyridine in dichloromethane (5 ml) was added to a solution of 0.067 g (0.11 mmol) of [PdCl(μ-med)]$_2$ in a mixture of dichloromethane (10 ml) and methanol (10 ml) and immediately after a solution of 0.043 g (0.22 mmol) of $AgBF_4$ in methanol (2 ml) was also added. After 5 min, stirring was stopped, and AgCl was filtered off through a Celite pad. Solution turned dark orange. When the volume of the resultant solution had been reduced to roughly 5 ml, the product precipitated as an orange solid when it had been filtered and dried in vacuo. As we could not confirm that it was a mixture of [**4a**](BF_4) and [**4b**](BF_4)$_2$, the product was recrystallised in a mixture (1:1) of dichloromethane and methanol, and dark orange monocrystals of [**4b**](BF_4)$_2 \cdot 0.5CH_3OH$ were obtained. [**4a**](BF_4) was again obtained when the crystals of [**4b**](BF_4)$_2$ are redissolved in chloroform or dichloromethane.

[**4a**](BF_4): ^1H NMR (400 MHz, $CDCl_3$ solution) $\delta = 2.45$ (s, 3H, *Me*), 2.48 (s, 3H, *Me*), 2.55 (b, 1H, pz-CH_2–C*H*H), 2.85 (b, 1H, pz-CH_2–C*H*H), 4.62 (b, 1H, pz-C*H*H–CH_2), 4.77 (b, 1H, pz-C*H*H–CH_2), 6.21 (s, 1H, pz-*CH*), 7.66 (m, 2H, bpy), 7.99 (m, 1H, bpy), 8.31 (m, 2H, bpy), 8.62 (m, 2H, bpy), 8.98 (m, 1H, bpy). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$ solution) $\delta = 12.4$ (*Me*), 15.5 (*Me*), 28.4 (S–CH_2–CH_2), 53.4 (pz-CH_2–CH_2), 109.3 (pz-CH), 124.8 (bpy), 128.1 (bpy), 141.1 (pz-C), 141.9 (bpy), 150.0(bpy), 150.5 (pz-C). MS(ESI): *m/z* (%) = 417 (100) [M^+].

[**4b**](BF_4)$_2$:$C_{34}H_{38}B_2F_8N_8Pd_2S_2 \cdot 0.5CH_3OH$ (1025.28): C, 40.41; H, 3.93; N, 10.93; S, 6.25. Found: C, 40.43; H, 3.85; N, 10.69; S, 5.98%. IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3081, ν(C–H)$_{al}$ 2919, ν(C=C)$_{bpy}$, ν(C=N)$_{bpy}$ 1601, ν(C=C)$_{pz}$, ν(C=N)$_{pz}$ 1551, $(CH_3)_{as}$ 1497, $\delta(CH_3)_s$ 1390, ν(B–F) 1059, δ(C–H)$_{oop}$ 769. IR (polyethylene, cm^{-1}): ν(Pd–N_{bpy})$_{as}$ 458, 453, ν(Pd–S) 280.

4.2.5. *[Pd(μ-med)(dppp)](BF4) [5a](BF4)2 and [Pd(μ-med)(dppp)]2(BF4)2 [5b](BF4)2*

A solution of 0.034 g (0.175 mmol) of $AgBF_4$ in methanol (2 ml) was added dropwise under vigorous stirring to a solution of 0.052 g (0.088 mmol) of [PdCl(μ-med)]$_2$ in dichloromethane (10 ml) and acetonitrile (5 ml). After 5 min, stirring was stopped, and AgCl was filtered off through a Celite pad. A solution of 0.072 g (0.175 mmol) of 1,3-bis(diphenylphosphino)propane (dppp) in dichloromethane (2 ml) was then added. The solution turned bright yellow and after 6 h the solvent was evaporated in vacuo. At this point we obtained a mixture (1:1) of [**5a**](BF_4) and [**5b**]$_2$(BF_4)$_2$. When the product was recrystallised in a mixture of dichloromethane and methanol (1:1) at 243 K, [**5b**]$_2$(BF_4)$_2$ was obtained as a pure solid.

[**5a**](BF_4): ^1H NMR (400 MHz, CD_2Cl_2 solution) $\delta = 1.92$ (s, 3H, *Me*), 1.95 (b, 2H, CH_2–C*H*$_2$–CH_2 dppp), 2.58 (s, 3H, *Me*), 2.42 (b, 1H, pz-CH_2–C*H*H), 2.84 (b, 1H, pz-CH_2–C*H*H), 3.09 (b, 4H, C*H*$_2$–CH_2–C*H*$_2$ dppp), 4.33 (b, 1H, pz-C*H*H–CH_2), 4.76 (b, 1H, pz-C*H*H–CH_2), 5.70 (s, 1H, pz-*CH*), 7.42–7.60 (m, 20H, PPh_3). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2 solution) $\delta = 12.1$ (*Me*), 14.9 (*Me*), 18.5 (CH_2-CH_2–CH_2 dppp), 24.3 (b, pz-CH_2–CH_2), 30.8 (b, CH_2–CH_2–CH_2 dppp), 48.6 (b, pz-CH_2–CH_2), 108.2 (pz-CH), 129.4–134.2 (PPh_2 dppp), 139.0, 147.5 (pz-C). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2 solution) $\delta = 0.2$ (d,dppp, $^2J = 51.5$ Hz), 13.5 (d, dppp, $^2J = 51.5$ Hz). MS(ESI): *m/z* (%) = 673 (100) [M^+].

[**5b**]$_2$(BF_4)$_2$: Yield: 0.11 g (83%) – $C_{68}H_{74}B_2F_8N_4P_4Pd_2S_2$ (1521.81): C, 53.67; H, 4.90; N, 3.68; S, 4.21. Found: C, 53.33; H, 4.58; N, 3.43; S, 4.04%. IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3051, ν(C–H)$_{al}$ 2919, ν(C=C), ν(C=N) 1555, $\delta(CH_3)_{as}$ 1483, $\delta(CH_{ar})_{as}$ 1436, $\delta(CH_3)_s$ 1386, ν(B–F) 1059, $\delta(CH_{al})_{oop}$ 745, $\delta(CH_{ar})_{oop}$ 693. IR (polyethylene, cm^{-1}): ν(Pd–P) 302, ν(Pd–S) 280. ^1H NMR (400 MHz, CD_2Cl_2 solution) $\delta = 1.91$ (s, 6H, *Me*), 1.95 (b, 4H, CH_2–C*H*$_2$–CH_2 dppp), 2.15 (s, 6H, *Me*), 2.62, 2.70 (m, 8H, pz-C*H*$_2$C–*H*$_2$), 3.09 (b, 8H, C*H*$_2$–CH_2–C*H*$_2$ dppp), 5.65 (s, 2H, pz-*CH*), 7.42–7.60 (m, 40H, PPh_2). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2 solution) $\delta = 11.3$ (*Me*), 13.6 (*Me*), 18.5 (CH_2–CH_2–CH_2 dppp), 24.3 (b, pz-CH_2–CH_2), 30.8 (b, CH_2–CH_2–CH_2 dppp), 48.6 (b, pz-CH_2–CH_2), 104.9 (pz-CH), 129.4–134.2 (PPh_2 dppp), 139.0, 147.5 (pz-C). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2 solution) $\delta = 10.2$ (s,dppp).

4.2.6. *[Pd3Cl2(μ-med)2(bpy)2](BF4)2 [6](BF4)2*

A solution of 0.0096 g (0.037 mmol) of [$PdCl_2(CH_3CN)_2$] in dichloromethane (2 ml) was added to a solution of 0.037 g (0.037 mmol) of [**4b**](BF_4)$_2$ in dichloromethane (8 ml). The orange solution turned yellow and when the volume of the resulting solution had been reduced to roughly 5 ml the product precipitated as yellow solid. This solid was filtered and dried in *vacuo*.

Yield: 0.034 g (79%) – $C_{34}H_{38}B_2Cl_2F_8N_8Pd_3S_2$ (1186.62): C, 34.41; H, 3.23; N, 9.44; S, 5.40. Found: C, 34.61; H, 3.10; N, 9.24; S, 5.22%. Conductivity (Ω^{-1} cm^2 mol^{-1}, 1.03×10^{-3} M in acetonitrile): 266 – IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3105–3023, ν(C–H)$_{al}$ 2920, ν(C=C)$_{bpy}$, ν(C=N)$_{bpy}$ 1600, (C=C)$_{pz}$, ν(C=N)$_{pz}$ 1550, $\delta(CH_3)_{as}$ 1470, $\delta(CH_3)_s$ 1391, ν(B–F) 1062, (C–H)$_{oop}$ 766. IR (polyethylene, cm^{-1}): ν(Pd–N)$_{as}$(bpy, pz) 417, ν(Pd – Cl) 348, ν(Pd–S) 279. ^1H NMR (400 MHz, CD_2Cl_2 solution) $\delta = 1.88$ (s, 6H, *Me*), 2.42 (s, 6H, *Me*), 2.49 (b, 2H,

pz-CH_2–C*H*H), 3.62 (b, 2H, pz-CH_2–C*H*H), 4.79 (b, 2H, pz-C*H*H–CH_2), 5.44 (b, 2H, pz-C*H*H–CH_2), 6.06 (s, 2H, pz-*CH*), 7.45 (m, 4H, bpy), 7.95 (m, 4H, py), 8.21 (m, 4H, bpy), 8.69 (m, 2H, bpy), 9.34 (m, 2H, bpy). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2 solution) $\delta = 11.9$ (*Me*), 13.5 (*Me*), 36.4 (S–CH_2–CH_2), 51.3 (pz-CH_2–CH_2), 108.9 (pz-CH), 124.6 (bpy), 128.5 (bpy), 142.6 (bpy), 144.9 (pz-C), 149.4 (bpy), 151.3 (pz-C). MS(ESI): *m/z* (%) = 1099 (5) [$M \cdot BF_4^+$].

4.2.7. [Pd(μ-Cl)(dppp)]$_2$(BF$_4$)$_2$ [7](BF$_4$)$_2$ and [Pd$_2$(μ-med)$_2$(dppp)]$^{2+}$ [8]$^{2+}$

A solution of 0.0041 g (0.016 mmol) of $[PdCl_2(CH_3CN)_2]$ in dichloromethane (2 ml) was added to a solution of 0.024 g (0.016 mmol) of [**5b**]$(BF_4)_2$ in dichloromethane (8 ml).The solution was stirred for 4 h and a mixture of $[Pd(\mu\text{-}Cl)(dppp)]_2^{2+}$ [**7**]$^{2+}$ and $[Pd_2(\mu\text{-}med)_2(dppp)]^{2+}$ [**8**]$^{2+}$ was formed. When the mixture was recrystallised with dichloromethane/diethyl ether (1:1), $[Pd(\mu\text{-}Cl)(dppp)]_2(BF_4)_2$ [**7**]$(BF_4)_2$ was obtained as a pure solid. [**8**]$^{2+}$ was always obtained in the presence of $[Pd(\mu\text{-}Cl)(dppp)]_2^{2+}$.

[**7**]$(BF_4)_2$: Yield: 0.006 g (59%) –$C_{54}H_{52}B_2Cl_2F_8P_4Pd_2$ (1282.24): C 50.58, H 4.09. Found: C 50.86, H 4.26%. IR (KBr, cm^{-1}): ν(C–H)$_{ar}$ 3055, (C–H)$_{al}$ 2919, $\delta(CH_3)_{as}$ 1484, $\delta(CH_{ar})_{as}$ 1435, ν(B–F) 1067, $\delta(CH_{al})_{oop}$ 743, $\delta(CH_{ar})_{oop}$ 692. IR (polyethylene, cm^{-1}): ν(Pd–P) 289, $\nu(Pd–Cl)_B$ 313. ^1H NMR (400 MHz, CD_2Cl_2 solution) $\delta = 2.06$ (b, 4H, CH_2–CH_2–CH_2 dppp), 2.45 (b, 8H, CH_2–CH_2–CH_2 dppp), 7.49–7.81 (m, 40H, PPh_2). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2 solution) $\delta = 18.9$ (CH_2–CH_2–CH_2 dppp), 26.2 (b, CH_2–CH_2–CH_2 dppp), 128.9–134.1 (PPh_2 dppp). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2 solution) $\delta = 12.6$ (s, dppp). MS(ESI): *m/z* (%) = 1145 (5) [$M \cdot Cl^+$].

[**8**]$^{2+}$: ^1H NMR (400 MHz, CD_2Cl_2 solution) $\delta = 1.89$ (s, 6H, *Me*), 2.06 (b, 4H, CH_2–CH_2–CH_2 dppp), 2.31 (s, 6H, *Me*), 2.40, 3.79 (b, pz-CH_2–C*H*H), 2.95 (b, 4H, CH_2–CH_2–CH_2 dppp), 4.80, 5.72 (b, pz-*CH*H–CH_2), 5.94 (s, 2H, pz-*CH*), 7.44–7.84 (b, 20H, PPh_2). $^{13}C\{^1H\}$ NMR (63 MHz, CD_2Cl_2 solution) $\delta = 12.0$ (*Me*), 13.7 (*Me*), 18.6 (CH_2–CH_2–CH_2 dppp), 23.5 (b, CH_2–CH_2–CH_2 dppp), 27.7 (b, pz-CH_2–CH_2), 52.0 (b, pz-CH_2–CH_2), 108.0 (pz-CH), 129.1–134.1 (PPh_2 dppp), 143.5, 150.6 (pz-C). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2 solution) $\delta = 7.5$ (s, dppp). MS(ESI): *m/z* (%) = 468 (26) [M^{2+}]; 961 (9) [$M \cdot Cl^+$].

4.3. X-ray crystallographic study

Suitable crystals for X-ray diffraction experiments of compounds [**3**]$(BF_4)_2 \cdot 2CH_3CN$ and [**4b**]$(BF_4)_2 \cdot 0.5CH_3OH$ were obtained by crystallisation from acetonitrile and methanol, respectively. Data were collected on a MAR345 diffractometer with Image Plate detector, using φ-scan technique. Both crystals were collected with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods using the

Table 2
Crystallographic data for the two crystal structures

Compound	[**3**]$(BF_4)_2 \cdot 2CH_3CN$	[**4b**]$(BF_4)_2 \cdot 0.5CH_3OH$
Empirical formula	$C_{54}H_{58}B_2F_8N_6P_2Pd_2S_2$	$C_{34.5}H_{40}B_2F_8N_8O_{0.5}Pd_2S_2$
Molecular mass (g)	1303.54	1025.28
Temperature (K)	293	293
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.7500(10)	11.8760(10)
b (Å)	10.8610(10)	12.9140(10)
c (Å)	13.0670(10)	15.5750(10)
α (°)	104.45	104.32
β (°)	100.75	100.07
γ (°)	100.15	110.95
Volume (Å^3)	1411.1(2)	2068.0(3)
Z	1	2
$D_{calc.}$ (g cm^{-3})	1.534	1.647
μ (mm^{-1})	8.36	10.45
F(000)	636	1026
Crystal size (mm)	0.2 × 0.1 × 0.2	0.1 × 0.1 × 0.3
θ Range (°)	1.99–28.84	2.63–28.90
Reflexions collected:total, independent, R_{int}	6223, 4954, 0.0212	12131, 7442, 0.0224
Data/restraints/parameters	4954/20/385	7442/20/489
a/*b*∗	0.0496, 3.3649	0.0878, 0.8021
Final R_1, wR_2	0.0439, 0.1053	0.0430, 0.1301
R_1 (all data), wR_2	0.0555, 0.1113	0.0595, 0.1411
Residual electron density (e Å^{-3})	0.661, −0.867	0.826, −0.786

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

SHELXS 97-computer program and refined by full-matrix least-squares method with a SHELXS 97-computer program [23].

All hydrogen atoms were computed and refined using 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 2.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 212888 ([**3**]$(BF_4)_2 \cdot 2CH_3CN$) and CCDC 212889 ([**4b**]$(BF_4)_2 \cdot 0.5CH_3OH$). 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; email: deposit@ccdc.cam.ac.uk].

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