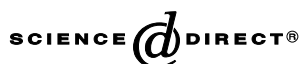




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Reactivity of $[\text{PdCl}(\mu\text{-med})]_2$ with monodentate or bidentate ligands. Structure of the dinuclear complexes $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2$ and $[\text{Pd}(\mu\text{-med})(\text{bpy})]_2(\text{BF}_4)_2$. $[\text{Hmed} = N\text{-}(2\text{-mercaptoethyl})\text{-}3,5\text{-dimethylpyrazole}]$

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Abstract

Treatment of the ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole with $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ and reaction of $[\text{PdCl}(\mu\text{-med})]_2$ with pyridine (py) or triphenylphosphine (PPh_3) in the presence of AgBF_4 produced the following complexes: $[\text{Pd}(\text{CH}_3\text{COO})(\mu\text{-med})]_2$, $[\text{Pd}(\mu\text{-med})(\text{py})]_2(\text{BF}_4)_2$ and $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2$. Similar reactions carried out with 2,2'-bipyridine (bpy) or 1,3-bis(diphenylphosphino)propane (dppp) produced $[\text{Pd}(\mu\text{-med})(\text{bpy})]_x(\text{BF}_4)_x$ ($x = 1$ or 2) and $[\text{Pd}(\mu\text{-med})(\text{dppp})]_x(\text{BF}_4)_x$ ($x = 1$ or 2). Treatment of $[\text{Pd}(\mu\text{-med})(\text{bpy})]_x(\text{BF}_4)_x$ with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ produced $[\text{Pd}_3\text{Cl}_2(\mu\text{-med})_2(\text{bpy})_2](\text{BF}_4)_2$. Treatment of $[\text{Pd}(\mu\text{-med})(\text{dppp})]_x(\text{BF}_4)_x$ with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ produced a mixture of $[\text{Pd}(\mu\text{-Cl})(\text{dppp})]_2(\text{BF}_4)_2$ and $[\text{Pd}(\mu\text{-med})_2(\text{dppp})]^{2+}$. X-ray crystal structures of $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2 \cdot 2\text{CH}_3\text{CN}$ and $[\text{Pd}(\mu\text{-med})(\text{bpy})]_2(\text{BF}_4)_2 \cdot 0.5\text{CH}_3\text{OH}$ are presented.

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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].

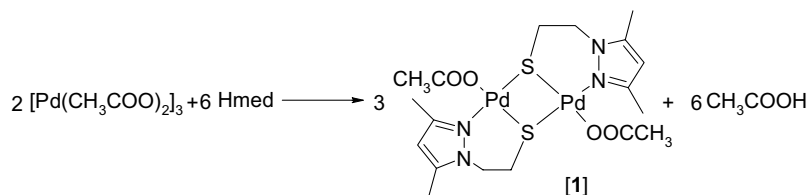
In recent years we have studied and reported the synthesis and characterisation of ligands based on the pyrazolyl group and another group containing N (amine) [4], P (phosphine) [5], O (alcohol or ether) [6] and S (thioether) [7] atoms.

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 $[\text{MCl}(\mu\text{-med})]_2$ ($\text{M} = \text{Ni(II)}$, 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.

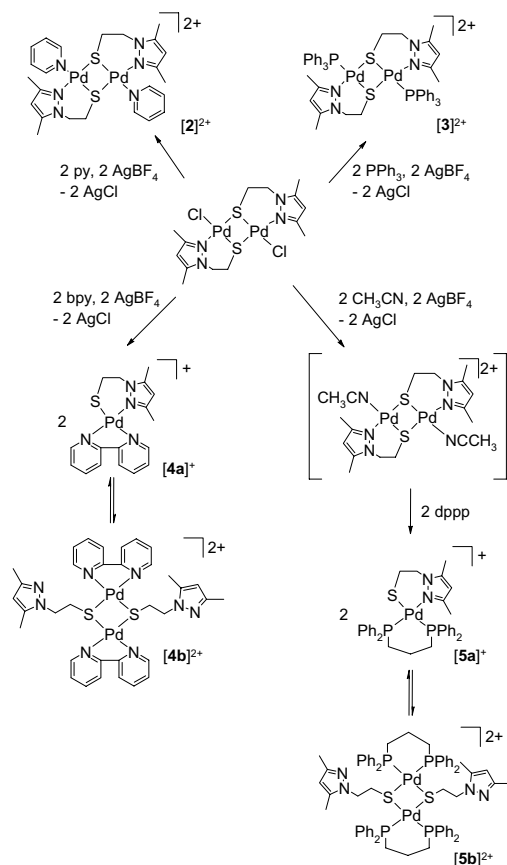
Here we extend the study of the coordinative properties of the Hmed ligand to Pd(II). Treatment of the ligand with $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ and reaction of $[\text{PdCl}(\mu\text{-med})]_2$ with pyridine (py) or triphenylphosphine (PPh_3) in the presence of AgBF_4 produced the following complexes: $[\text{Pd}(\text{CH}_3\text{COO})(\mu\text{-med})_2]$ [1], $[\text{Pd}(\mu\text{-med})(\text{py})]_2(\text{BF}_4)_2$ [2](BF_4)₂ and $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2$ [3](BF_4)₂. Similar reactions with 2,2'-bipyridine (bpy) or 1,3-bis(diphenylphosphino)propane (dppp) produced $[\text{Pd}(\mu\text{-med})(\text{bpy})]_x(\text{BF}_4)_x$ ($x = 1$, [4a](BF_4); $x = 2$, [4b](BF_4)₂) and $[\text{Pd}(\mu\text{-med})(\text{dppp})]_x(\text{BF}_4)_x$ ($x = 1$, [5a](BF_4); $x = 2$, [5b](BF_4)₂). X-ray crystal structures of [3](BF_4)₂ · 2 CH_3CN and [4b](BF_4)₂ · 0.5 CH_3OH are presented. Treatment of [4](BF_4)_x with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ produced $[\text{Pd}_3\text{Cl}_2(\mu\text{-med})_2(\text{bpy})_2]_2(\text{BF}_4)_2$ [6](BF_4)₂. Treatment of [5](BF_4)_x with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ produced a mixture of $[\text{Pd}(\mu\text{-Cl})(\text{dppp})]_2(\text{BF}_4)_2$ [7](BF_4)₂ and $[\text{Pd}(\mu\text{-med})_2(\text{dppp})]^{2+}$ [8]²⁺ (Schemes 1–3).

($\text{CH}_3\text{CN})_2$ produced $[\text{Pd}_3\text{Cl}_2(\mu\text{-med})_2(\text{bpy})_2]_2(\text{BF}_4)_2$ [6](BF_4)₂. Treatment of [5](BF_4)_x with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ produced a mixture of $[\text{Pd}(\mu\text{-Cl})(\text{dppp})]_2(\text{BF}_4)_2$ [7](BF_4)₂ and $[\text{Pd}(\mu\text{-med})_2(\text{dppp})]^{2+}$ [8]²⁺ (Schemes 1–3).

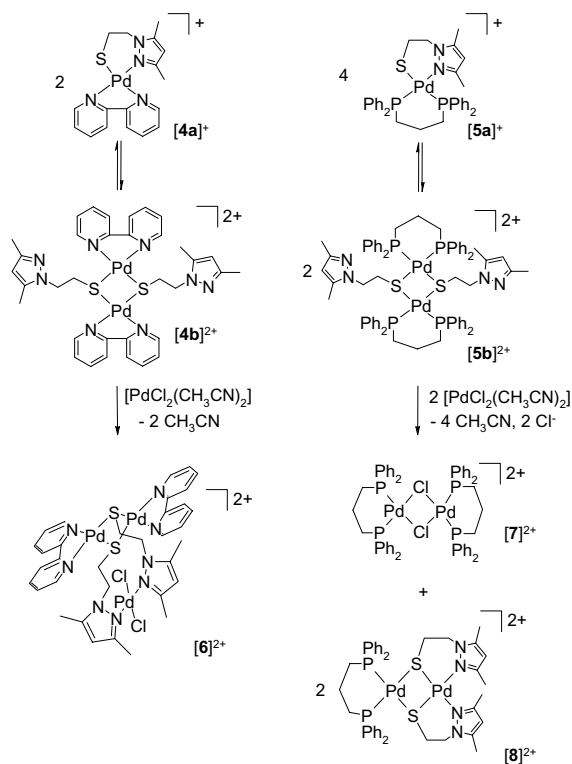
2. Results and discussion

The Hmed was synthesised as described by Bouwman et al. [9]. Complexes $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ [10] and $[\text{PdCl}(\mu\text{-med})]_2$ [8] were synthesised as described elsewhere.

Treatment of the ligand with $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ in acetonitrile gave $[\text{Pd}(\text{CH}_3\text{COO})(\mu\text{-med})_2]$ [1]. Treatment of $[\text{PdCl}(\mu\text{-med})]_2$ with AgBF_4 in the presence of pyridine or triphenylphosphine yielded $[\text{Pd}(\mu\text{-med})(\text{py})]_2(\text{BF}_4)_2$ [2](BF_4)₂ and $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2$ [3](BF_4)₂. These proposed formulas were corroborated by elemental analyses.



Scheme 2.



Scheme 3.

Conductivity in acetonitrile for [1] ($2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) shows that the complex is a nonelectrolyte. Conductivity values in acetonitrile for complexes [2](BF₄)₂ and [3](BF₄)₂ (278 and 263 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively) are in agreement with 2:1 electrolytes. The reported values for 10^{-3} M solutions of nonelectrolyte complexes are lower than $120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in acetonitrile, while the range of conductivity values for 10^{-3} M solutions of 2:1 electrolyte compounds in acetonitrile is between 220 and $300 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ [11].

IR spectra of complexes [1]–[3](BF₄)₂ are similar to that of [PdCl(μ-med)]₂, the most characteristic bands being those attributable to the pyrazolyl group: $\nu(\text{C}=\text{C})_{\text{ar}}$ and $\nu(\text{C}=\text{N})_{\text{ar}}$ between 1553 and 1551 cm^{-1} . The absence of the $\nu(\text{S}-\text{H})$ 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 $\nu(\text{OCO})$ stretching modes. It displays one $\nu_{\text{as}}(\text{OCO})$ band at 1617 cm^{-1} and one $\nu_{\text{s}}(\text{OCO})$ band at 1370 cm^{-1} , separated by $\Delta = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO}) = 247 \text{ cm}^{-1}$. This Δ value suggests the presence of unidentate acetate groups in compound [1] [12].

IR spectrum of [2](BF₄)₂ presents a band attributable to $\nu(\text{C}=\text{C})_{\text{py}}$ and $\nu(\text{C}=\text{N})_{\text{py}}$ at 1606 cm^{-1} . IR spectra of [2](BF₄)₂ and [3](BF₄)₂ present bands that were assigned to $\nu(\text{B}-\text{F})$ at 1057 and 1058 cm^{-1} , respectively [13].

The IR spectra of the complexes in $500\text{--}100 \text{ cm}^{-1}$ region were also studied [14]. In all cases they show

bands attributable to $\nu(\text{Pd}-\text{N}_{\text{pz}})_{\text{as}}$ between 459 and 450 cm^{-1} and $\nu(\text{Pd}-\text{S})$ between 301 and 280 cm^{-1} . Bands attributable to $\nu(\text{Pd}-\text{O})$ at 511 cm^{-1} for [1] and $\nu(\text{Pd}-\text{P})$ at 310 cm^{-1} for [3](BF₄)₂ were also assigned.

The ¹H and ¹³C{¹H} NMR spectra of complexes [1]–[3](BF₄)₂ show the signals of coordinated ligands [15]. Spectra of [1] and [3](BF₄)₂ were recorded in CDCl₃ and spectra of [2](BF₄)₂ were recorded in [D₃] acetonitrile.

¹H NMR spectra show, for complexes [1]–[3](BF₄)₂, four groups of doublets of doublets of doublets which can be assigned to a single hydrogen of the N–CH₂–CH₂–S fragment each. This happens because the two protons of each CH₂ are diastereotopic, owing to the rigid conformation of the ligand when it is complexed.

HMQC spectra of [1]–[3](BF₄)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](BF₄)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](BF₄)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

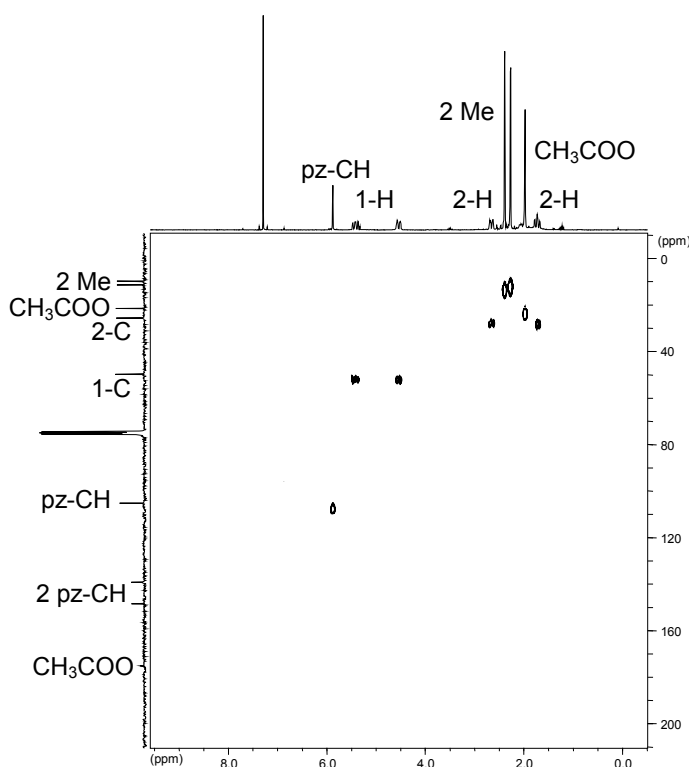


Fig. 1. The 250 MHz 2D HMQC spectrum of [Pd(CH₃COO)(μ-med)]₂ [1] and the numbering for the complexes [1]–[3](BF₄)₂.

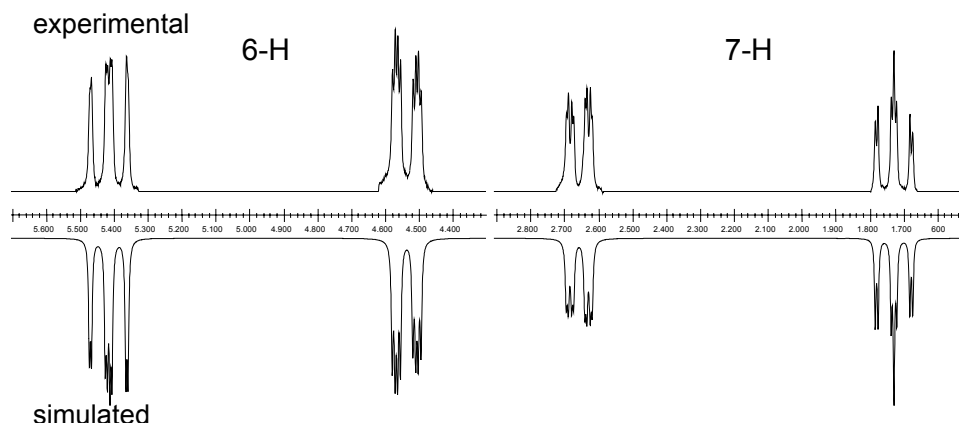


Fig. 2. The 400-MHz ^1H NMR and gNMR simulated spectra for the $\text{NCH}_2\text{CH}_2\text{S}$ fragment of $[\text{Pd}(\text{CH}_3\text{COO})(\mu\text{-med})]_2$ [1].

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

Further evidence of the $\text{N},\text{S}:\text{S}'$ coordination can be seen in the X-ray crystal structure of [3](BF_4) $_2 \cdot 2\text{CH}_3\text{CN}$.

The structure of [3](BF_4) $_2 \cdot 2\text{CH}_3\text{CN}$ (Fig. 3) consists of dimeric cationic units of $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2^{2+}$, 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 [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 PdNS_2 units are joined via two bridging thiolate ligands forming a four-membered ring, which is flat, with $\text{Pd}\cdots\text{Pd}$ and $\text{S}\cdots\text{S}$ distances of $3.4159(5)$ and $3.1729(4)$ Å, respectively. Bridging angle for Pd-S-Pd(a) is $94.23(3)^\circ$.

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 $\text{N}(1)\text{-Pd-S}$ is $84.12(9)^\circ$.

The distortion of the skew-boat in the ring $\text{Pd-N}(1)\text{-N}(2)\text{-C}(6)\text{-C}(7)\text{-S}$ is $\Delta\text{C}_5(\text{N}(1)\text{-N}(2)) = 29.8(4)^\circ$ ¹.

To examine the influence of the ligands that replace the chloride ion in $[\text{PdCl}(\mu\text{-med})]_2$, 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 $[\text{PdCl}(\mu\text{-med})]_2$ with AgBF_4 in the presence of 2,2'-bipyridine produced a complex whose elec-

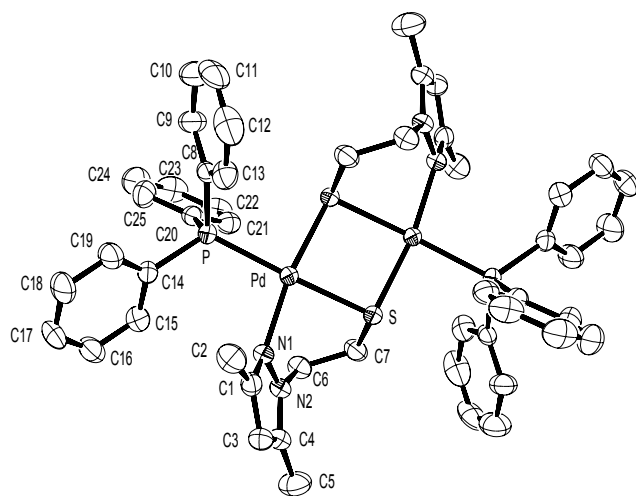


Fig. 3. ORTEP drawing of $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2^{2+}$ cation ([3] $^{2+}$) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

$$\Delta\text{C}_s = \sqrt{\frac{\sum_{i=1}^m (\phi_i + \phi'_i)^2}{m}}$$

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 $[3]^{2+}$ and $[4b]^{2+}$ with estimated standard deviations (esds) in parentheses

$[3]^{2+}$		$[4b]^{2+}$	
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)

troscopy mass spectrum is in accordance with the proposed formula $[Pd(\mu\text{-med})(bpy)](BF_4)[4a](BF_4)$. The 1H 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 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 $[Pd(\mu\text{-med})(bpy)]_2(BF_4)_2 \cdot 0.5CH_3OH$ $[4b](BF_4)_2 \cdot 0.5CH_3OH$ 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 $[4b]^{2+}$.

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 $\pm 0.025(5)$ Å for the nitrogen atoms and $\pm 0.022(1)$ Å for the sulfur atoms with respect to Pd(1), and $\pm 0.018(4)$ Å for the nitrogen atoms and $\pm 0.016(1)$ Å for the sulfur atoms with respect to Pd(2).

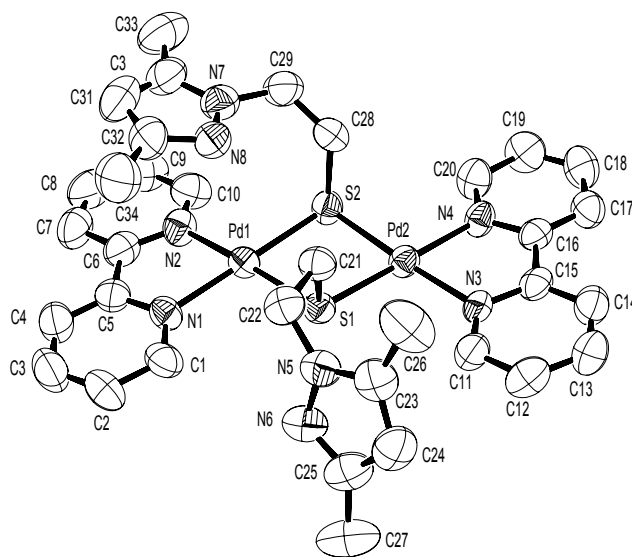


Fig. 4. ORTEP drawing of $[Pd(\mu\text{-med})(bpy)]_2^{2+}$ cation $[4b]^{2+}$ (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

The two planar PdN_2S_2 units are joined via two bridging thiolate ligands forming a four-membered ring, which is CR form, with $Pd \cdots Pd$ and $S \cdots S$ 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'-bipyridines [20].

The distortion of the five-membered rings is $\Delta C_S(Pd(1)–N(1)) = 9.8(5)^\circ$ and $\Delta C_S(Pd(2)–N(3)) = 5.2(4)^\circ$ 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 $[4b](BF_4)_2 \cdot 0.5CH_3OH$ were redissolved in chloroform or dichloromethane, $[4a]^+$ was again obtained in solution. Varying the temperature we could not observe the formation of $[4b]^{2+}$ 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 $[Pd(\mu\text{-med})(dppp)]^+$ $[5a]^+$) and a singlet at 10.2 ppm (assigned to $[Pd(\mu\text{-med})(dppp)]_2^{2+}$ $[5b]^{2+}$). These data are in agreement with $[5a]^+$ being a mono-

nuclear species of Pd(II) with dppp and the thiolate ligand (med) chelating the metallic centre as in **[4a]**⁺ and **[5b]**²⁺ a dinuclear compound similar to **[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 (**[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 (**[5a]**⁺:**[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 **[5a]**⁺ when the temperature was raised, we attempted to obtain pure **[5b]**²⁺ at low temperatures. When a saturated solution of **[5a]**⁺ and **[5b]**²⁺ in a mixture of dichloromethane and methanol was cooled to 243K, we obtained **[5b](BF₄)₂** (0.11 g, 83% yield) as dark yellow microcrystals.

The ³¹P{¹H} NMR spectrum of pure **[5b]**²⁺ in CD₂Cl₂ returned to that of the initial mixture of **[5a]**⁺ and **[5b]**²⁺ after approximately 30 min.

Treatment of **[4b](BF₄)₂** with [PdCl₂(CH₃CN)₂] produced a complex whose elemental analyses are consistent with the formula [Pd₃Cl₂(μ-med)₂(bpy)₂](BF₄)₂ (**[6](BF₄)₂**) (Scheme 3). Conductivity value for this complex in acetonitrile (266 Ω⁻¹ cm² mol⁻¹) corresponds to those of 2:1 electrolytes [11]. The IR spectrum between 500 and 100 cm⁻¹ shows bands attributable to ν(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 NCH₂CH₂S 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 **[1]–[3](BF₄)₂**, they could not be further studied due to their broadness. Electrospray mass spectrum of this complex shows the monocationic unit {[**6**·BF₄]}⁺. 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 **[6](BF₄)₂** would be two [PdN₂S₂] and one [PdCl₂N₂]. The [PdN₂S₂] core is not found in any of the trinuclear species described in the literature. However, the [PdCl₂N₂] core is found in two of them [21a,21c].

Treatment of a solution of **[5a](BF₄)**/**[5b](BF₄)₂** with [PdCl₂(CH₃CN)₂] produced a mixture of two complexes in a 1:1 ratio, with chemical shifts in the ³¹P{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 (δ = 12.6 ppm in the ³¹P{¹H} NMR spectrum), whose elemental analyses and electrospray

mass spectrum are in agreement with the formula [Pd(μ-Cl)(dppp)]₂(BF₄)₂ (**[7](BF₄)₂**) (Scheme 3). The cationic part of this complex had previously been reported by Pelzer et al. [22] but with SO₄²⁻ instead of BF₄⁻.

The other complex (δ = 7.5 ppm in the ³¹P{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 [Pd₂(μ-med)₂(dppp)]²⁺ **[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(μ-med)X]₂, X being a monodentate (chloride, acetate, pyridine, triphenylphosphine) or bidentate (2,2'-bipyridine (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. General 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 $[\text{PdCl}(\mu\text{-med})]_2$ [8]. *N*-(2-Mercaptoethyl)-3,5-dimethylpyrazole [9] and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ [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 $4000\text{--}100\text{ cm}^{-1}$ under a nitrogen atmosphere. The ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, HMQC and NOESY spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. $^{31}\text{P}\{^1\text{H}\}$ 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. $[\text{Pd}(\mu\text{-med})(\text{CH}_3\text{COO})]_2$ [1]

A solution of 0.220 g (0.33 mmol) of $[\text{Pd}(\text{CH}_3\text{COO})_2]_3$ 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%) – $\text{C}_{18}\text{H}_{28}\text{N}_4\text{O}_4\text{Pd}_2\text{S}_2$ (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 ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, 9.92×10^{-4} M in acetonitrile): 2 – IR (KBr, cm^{-1}): $\nu(\text{C-H})_{\text{al}}$ 2921, $\nu(\text{OCO})_{\text{as}}$ 1617, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ 1553, $\delta(\text{CH}_3)_{\text{as}}$ 1469, $\delta(\text{OCO})_{\text{s}}$ 1370, $\delta(\text{CH}_3)_{\text{s}}$ 1312, 1260 $\delta(\text{C-H})_{\text{oop}}$ 783. IR (polyethylene, cm^{-1}): $\nu(\text{Pd-O})$ 511, $\nu(\text{Pd-N})_{\text{as}}$ 459, $\nu(\text{Pd-S})$ 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, $\text{pz-CH}_2\text{-CHH}$, $^2J = 13.8$ Hz, $^3J = 2.1$ Hz, $^3J = 11.8$ Hz), 2.63 (ddd, 2H, $\text{pz-CH}_2\text{-CHH}$, $^2J = 13.8$ Hz, $^3J = 3.9$ Hz, $^3J = 1.6$ Hz), 4.52 (ddd, 2H, pz-CHH-CH_2 , $^2J = 15.2$ Hz, $^3J = 2.1$ Hz, $^3J = 3.9$ Hz), 5.39 (ddd, 2H, pz-CHH-CH_2 , $^2J = 15.2$ Hz, $^3J = 11.8$ Hz, $^3J = 1.6$ Hz), 5.85 (s, 2H, *pz-CH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, CDCl_3 solution) $\delta = 12.1$ (*Me*), 13.6 (*Me*), 23.7 (CH_3COO), 27.8 ($\text{S-CH}_2\text{-CH}_2$), 51.9 ($\text{pz-CH}_2\text{-CH}_2$), 107.3 (*pz-CH*), 150.6 (*pz-C*), 177.2 (CH_3COO).

4.2.2. $[\text{Pd}(\mu\text{-med})(\text{py})]_2(\text{BF}_4)_2$ [2]/ $(\text{BF}_4)_2$

A solution of 0.078 g (0.13 mmol) of $[\text{Pd}(\mu\text{-med})\text{Cl}]_2$ 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%) – $\text{C}_{24}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_6\text{Pd}_2\text{S}_2$ (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 ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, 1.03×10^{-3} M in acetonitrile): 278 – IR (KBr, cm^{-1}): $\nu(\text{C-H})_{\text{ar}}$ 3057, $\nu(\text{C-H})_{\text{al}}$ 2927, $\nu(\text{C}=\text{C})_{\text{py}}$, $\nu(\text{C}=\text{N})_{\text{py}}$ 1606, $\nu(\text{C}=\text{C})_{\text{pz}}$, $\nu(\text{C}=\text{N})_{\text{pz}}$ 1553, $\delta(\text{CH}_3)_{\text{as}}$ 1454, $\delta(\text{CH}_3)_{\text{s}}$ 1382, $\nu(\text{B-F})$ 1057, $\delta(\text{C-H})_{\text{oop}}$ 758. IR (polyethylene, cm^{-1}): $\nu(\text{Pd-N})_{\text{as}}(\text{pz}, \text{py})$ 457, $\nu(\text{Pd-S})$ 280. ^1H NMR (400 MHz, $[\text{D}_3]$ -acetonitrile solution) $\delta = 1.63$ (s, 6H, *Me*), 2.22 (s, 6H, *Me*), 1.55 (ddd, 2H, $\text{pz-CH}_2\text{-CHH}$, $^2J = 14.6$ Hz, $^3J = 11.9$ Hz, $^3J = 2.1$ Hz), 2.00 (ddd, 2H, $\text{pz-CH}_2\text{-CHH}$, $^2J = 14.6$ Hz, $^3J = 1.3$ Hz, $^3J = 3.9$ Hz), 4.53 (ddd, 2H, pz-CHH-CH_2 , $^2J = 15.3$ Hz, $^3J = 11.9$ Hz, $^3J = 1.3$ Hz), 4.98 (ddd, 2H, pz-CHH-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*). $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, $[\text{D}_3]$ -acetonitrile solution) $\delta = 11.9$ (*Me*), 13.6 (*Me*), 29.4 ($\text{S-CH}_2\text{-CH}_2$), 52.7 ($\text{pz-CH}_2\text{-CH}_2$), 108.8 (*pz-CH*), 128.5 (*py*), 141.8 (*py*), 145.1 (*pz-C*), 151.8 (*pz-C*), 153.1 (*py*).

4.2.3. $[\text{Pd}(\mu\text{-med})(\text{PPh}_3)]_2(\text{BF}_4)_2$ [3]/ $(\text{BF}_4)_2$

A solution of 0.108 g (0.18 mmol) of $[\text{Pd}(\mu\text{-med})\text{Cl}]_2$ and 0.0954 g (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%) – $\text{C}_{50}\text{H}_{52}\text{B}_2\text{F}_8\text{N}_4\text{P}_2\text{Pd}_2\text{S}_2$ (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 ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, 9.08×10^{-4} M in acetonitrile): 263 – IR (KBr, cm^{-1}): $\nu(\text{C-H})_{\text{ar}}$ 3053, $\nu(\text{C-H})_{\text{al}}$ 2942–2917, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$ 1551, $\delta(\text{CH}_3)_{\text{as}}$ 1480, $\delta(\text{CH}_{\text{ar}})_{\text{as}}$ 1435, $(\text{CH}_3)_{\text{s}}$ 1391, $\nu(\text{B-F})$ 1058, $\delta(\text{CH}_{\text{ar}})_{\text{oop}}$ 692. IR (polyethylene, cm^{-1}): $\nu(\text{Pd-N})_{\text{as}}$ 450, $\nu(\text{Pd-P})$ 310, $\nu(\text{Pd-S})$ 288. ^1H NMR (400 MHz, CDCl_3 solution) = 1.62 (s, 6H, *Me*), 2.08 (s, 6H, *Me*), 2.14 (b, 2H, $\text{pz-CH}_2\text{-CHH}$), 2.84 (b, 2H, $\text{pz-CH}_2\text{-CHH}$), 4.46 (b, 2H, pz-CHH-CH_2), 5.38 (b, 2H, pz-CHH-CH_2), 5.78 (s, 2H, *pz-CH*), 7.49 (m,

30H, PPh₃). ¹³C{¹H} NMR (63 MHz, CDCl₃ solution) δ = 11.2 (*Me*), 13.5 (*Me*), 32.4 (S–CH₂–CH₂), 53.6 (pz–CH₂–CH₂), 109.9 (pz–CH), 128.3 (m, PPh₃), 133.9 (m, PPh₃), 145.1 (pz–C), 152.7 (pz–C). ³¹P{¹H} NMR (101 MHz, CDCl₃ solution) δ = 21.9 (s, PPh₃).

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 AgBF₄ 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](BF₄) and [4b](BF₄)₂, the product was recrystallised in a mixture (1:1) of dichloromethane and methanol, and dark orange monocystals of [4b](BF₄)₂ · 0.5CH₃OH were obtained. [4a](BF₄) was again obtained when the crystals of [4b](BF₄)₂ are redissolved in chloroform or dichloromethane.

[4a](BF₄): ¹H NMR (400 MHz, CDCl₃ solution) δ = 2.45 (s, 3H, *Me*), 2.48 (s, 3H, *Me*), 2.55 (b, 1H, pz–CH₂–CHH), 2.85 (b, 1H, pz–CH₂–CHH), 4.62 (b, 1H, pz–CHH–CH₂), 4.77 (b, 1H, pz–CHH–CH₂), 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). ¹³C{¹H} NMR (63 MHz, CDCl₃ solution) δ = 12.4 (*Me*), 15.5 (*Me*), 28.4 (S–CH₂–CH₂), 53.4 (pz–CH₂–CH₂), 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](BF₄)₂: C₃₄H₃₈B₂F₈N₈Pd₂S₂ · 0.5CH₃OH (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, (CH₃)_{as} 1497, δ (CH₃)_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 AgBF₄ 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](BF₄) and [5b]₂(BF₄)₂. When the product was recrystallised in a mixture of dichloromethane and methanol (1:1) at 243 K, [5b]₂(BF₄)₂ was obtained as a pure solid.

[5a](BF₄): ¹H NMR (400 MHz, CD₂Cl₂ solution) δ = 1.92 (s, 3H, *Me*), 1.95 (b, 2H, CH₂–CH₂–CH₂ dppp), 2.58 (s, 3H, *Me*), 2.42 (b, 1H, pz–CH₂–CHH), 2.84 (b, 1H, pz–CH₂–CHH), 3.09 (b, 4H, CH₂–CH₂–CH₂ dppp), 4.33 (b, 1H, pz–CHH–CH₂), 4.76 (b, 1H, pz–CHH–CH₂), 5.70 (s, 1H, pz–CH), 7.42–7.60 (m, 20H, PPh₃). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂ solution) δ = 12.1 (*Me*), 14.9 (*Me*), 18.5 (CH₂–CH₂–CH₂ dppp), 24.3 (b, pz–CH₂–CH₂), 30.8 (b, CH₂–CH₂–CH₂ dppp), 48.6 (b, pz–CH₂–CH₂), 108.2 (pz–CH), 129.4–134.2 (PPh₂ dppp), 139.0, 147.5 (pz–C). ³¹P{¹H} NMR (101 MHz, CD₂Cl₂ solution) δ = 0.2 (d, dppp, ²*J* = 51.5 Hz), 13.5 (d, dppp, ²*J* = 51.5 Hz). MS(ESI): *m/z* (%) = 673 (100) [M⁺].

[5b]₂(BF₄)₂: Yield: 0.11 g (83%) – C₆₈H₇₄B₂F₈N₄P₄Pd₂S₂ (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, δ (CH₃)_{as} 1483, δ (CH_{ar})_{as} 1436, δ (CH₃)_s 1386, ν (B–F) 1059, δ (CH_{al})_{oop} 745, δ (CH_{ar})_{oop} 693. IR (polyethylene, cm⁻¹): ν (Pd–P) 302, ν (Pd–S) 280. ¹H NMR (400 MHz, CD₂Cl₂ solution) δ = 1.91 (s, 6H, *Me*), 1.95 (b, 4H, CH₂–CH₂–CH₂ dppp), 2.15 (s, 6H, *Me*), 2.62, 2.70 (m, 8H, pz–CH₂–CH₂), 3.09 (b, 8H, CH₂–CH₂–CH₂ dppp), 5.65 (s, 2H, pz–CH), 7.42–7.60 (m, 40H, PPh₂). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂ solution) δ = 11.3 (*Me*), 13.6 (*Me*), 18.5 (CH₂–CH₂–CH₂ dppp), 24.3 (b, pz–CH₂–CH₂), 30.8 (b, CH₂–CH₂–CH₂ dppp), 48.6 (b, pz–CH₂–CH₂), 104.9 (pz–CH), 129.4–134.2 (PPh₂ dppp), 139.0, 147.5 (pz–C). ³¹P{¹H} NMR (101 MHz, CD₂Cl₂ solution) δ = 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 [PdCl₂(CH₃CN)₂] in dichloromethane (2 ml) was added to a solution of 0.037 g (0.037 mmol) of [4b](BF₄)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%) – C₃₄H₃₈B₂Cl₂F₈N₈Pd₃S₂ (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} cm² 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, δ (CH₃)_{as} 1470, δ (CH₃)_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, CD₂Cl₂ solution) δ = 1.88 (s, 6H, *Me*), 2.42 (s, 6H, *Me*), 2.49 (b, 2H,

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pz-CH₂-CHH), 3.62 (b, 2H, pz-CH₂-CHH), 4.79 (b, 2H, pz-CHH-CH₂), 5.44 (b, 2H, pz-CHH-CH₂), 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). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂ solution) δ = 11.9 (Me), 13.5 (Me), 36.4 (S-CH₂-CH₂), 51.3 (pz-CH₂-CH₂), 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·BF₄⁺].

4.2.7. [Pd(μ-Cl)(dppp)]₂(BF₄)₂ [7](BF₄)₂ and [Pd₂(μ-med)₂(dppp)]²⁺ [8]²⁺

A solution of 0.0041 g (0.016 mmol) of [PdCl₂(CH₃CN)₂] in dichloromethane (2 ml) was added to a solution of 0.024 g (0.016 mmol) of [5b](BF₄)₂ in dichloromethane (8 ml). The solution was stirred for 4 h and a mixture of [Pd(μ-Cl)(dppp)]₂²⁺ [7]²⁺ and [Pd₂(μ-med)₂(dppp)]²⁺ [8]²⁺ was formed. When the mixture was recrystallised with dichloromethane/diethyl ether (1:1), [Pd(μ-Cl)(dppp)]₂(BF₄)₂ [7](BF₄)₂ was obtained as a pure solid. [8]²⁺ was always obtained in the presence of [Pd(μ-Cl)(dppp)]₂²⁺.

[7](BF₄)₂: Yield: 0.006 g (59%) -C₅₄H₅₂B₂Cl₂F₈P₄Pd₂ (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, δ(CH₃)_{as} 1484, δ(CH_{ar})_{as} 1435, ν(B-F) 1067, δ(CH_{al})_{oop} 743, δ(CH_{ar})_{oop} 692. IR (polyethylene, cm⁻¹): ν(Pd-P) 289, ν(Pd-Cl)_B 313. ¹H NMR (400 MHz, CD₂Cl₂ solution) δ = 2.06 (b, 4H, CH₂-CH₂-CH₂ dppp), 2.45 (b, 8H,

CH₂-CH₂-CH₂ dppp), 7.49–7.81 (m, 40H, PPh₂). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂ solution) δ = 18.9 (CH₂-CH₂-CH₂ dppp), 26.2 (b, CH₂-CH₂-CH₂ dppp), 128.9–134.1 (PPh₂ dppp). ³¹P{¹H} NMR (101 MHz, CD₂Cl₂ solution) δ = 12.6 (s, dppp). MS(ESI): *m/z* (%) = 1145 (5) [M·Cl⁺].

[8]²⁺: ¹H NMR (400 MHz, CD₂Cl₂ solution) δ = 1.89 (s, 6H, Me), 2.06 (b, 4H, CH₂-CH₂-CH₂ dppp), 2.31 (s, 6H, Me), 2.40, 3.79 (b, pz-CH₂-CHH), 2.95 (b, 4H, CH₂-CH₂-CH₂ dppp), 4.80, 5.72 (b, pz-CHH-CH₂), 5.94 (s, 2H, pz-CH), 7.44–7.84 (b, 20H, PPh₂). ¹³C{¹H} NMR (63 MHz, CD₂Cl₂ solution) δ = 12.0 (Me), 13.7 (Me), 18.6 (CH₂-CH₂-CH₂ dppp), 23.5 (b, CH₂-CH₂-CH₂ dppp), 27.7 (b, pz-CH₂-CH₂), 52.0 (b, pz-CH₂-CH₂), 108.0 (pz-CH), 129.1–134.1 (PPh₂ dppp), 143.5, 150.6 (pz-C). ³¹P{¹H} NMR (101 MHz, CD₂Cl₂ solution) δ = 7.5 (s, dppp). MS(ESI): *m/z* (%) = 468 (26) [M²⁺]; 961 (9) [M·Cl⁺].

4.3. X-ray crystallographic study

Suitable crystals for X-ray diffraction experiments of compounds [3](BF₄)₂·2CH₃CN and [4b](BF₄)₂·0.5CH₃OH 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 ·2CH ₃ CN	[4b](BF ₄) ₂ ·0.5CH ₃ OH
Empirical formula	C ₅₄ H ₅₈ B ₂ F ₈ N ₆ P ₂ Pd ₂ S ₂	C _{34.5} H ₄₀ B ₂ F ₈ N ₈ O _{0.5} Pd ₂ S 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		
<i>a</i> (Å)	10.7500(10)	11.8760(10)
<i>b</i> (Å)	10.8610(10)	12.9140(10)
<i>c</i> (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)
<i>Z</i>	1	2
<i>D</i> _{calc} (g cm ⁻³)	1.534	1.647
μ (mm ⁻¹)	8.36	10.45
<i>F</i> (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, <i>R</i> _{int}	6223, 4954, 0.0212	12131, 7442, 0.0224
Data/restraints/parameters	4954/20/385	7442/20/489
<i>a</i> / <i>b</i> *	0.0496, 3.3649	0.0878, 0.8021
Final <i>R</i> ₁ , <i>wR</i> ₂	0.0439, 0.1053	0.0430, 0.1301
<i>R</i> ₁ (all data), <i>wR</i> 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](BF₄)₂ · 2CH₃CN) and CCDC 212889 ([4b](BF₄)₂ · 0.5CH₃OH). 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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Study of the coordination properties toward Rh(I) of N₂S- (1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane) or N₂S₂- (bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane or 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene ligand) donor ligands

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1. Introduction

The chemistry of transition metal complexes of hemilabile ligands has been widely studied in recent years [1]. The term hemilabile ligand, first introduced by J.C. Jeffrey and T.B. Rauchfuss in 1979 [2], refers to polydentate ligands that contain at least two types of donor groups in front of substitution (labile and inert). One of them (or some of them) will anchor the ligand to the metal centre and the other one (or other ones) will be easily displaced from the metal centre (leaving a vacant site) or stabilize transition states. P. Braunstein and F. Naud recently reviewed the different types of hemilability [3].

Pyrazole-based ligands are good candidates in the search of hemilabile properties because they can be relatively easily obtained and we can modulate their steric and electronic properties [4]. In recent years, we have studied and reported the synthesis and characterisation of ligands based on the pyrazolyl group and on some other group containing N (amine) [5], P (phosphine) [6], O (alcohol or ether) [7] and S (thiol or thioether) [8] atoms.

More concretely, we have recently reported the potential hemilabile properties of the ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) when complexed to Pd(II) [8d]. This ligand had previously been used to synthesize and structurally characterize complexes of Co(II) [9], Zn(II) [10], Cd(II) [10], Cu(I) [9,11,12] and Ag(I) [9]. The ligand acts as tridentate (NSN) in all the complexes, excepting in [ZnCl₂(bdtp)], in which it acts as bidentate (NN).

In this paper we will extend this study to Rh(I) complexes of this ligand and will compare the results with those recently obtained for the Rh(I) complexes of ligands bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine (L_N)^[5a] and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether (L_O) (Scheme1) [7c].

We have as well recently reported the hemilabile properties of the potentially tetradentate ligand bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) when complexed to Pd(II) [8a]. This ligand had previously been used to synthesize and structurally characterize complexes of Cu(II)[13,14], Ni(II)[15], Zn(II)[15] and Cd(II)[15]. The ligand acts as bidentate (NN) in the Cu(II) and Zn(II) complexes and as

tetradentate (NSSN) in Ni(II) and Cd(II) complexes. Pd(II) complexes of this ligand adopt both NN and NSSN coordination modes.

We also describe in this paper the synthesis of the new 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene ligand (bddf). The bonding properties toward Rh(I) of the bddo and bddf ligands will be presented.

2. Results and Discussion

2.1 Case of the 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) ligand

The bdtp ligand reacts with $[\text{Rh}(\text{COD})(\text{THF})_2][\text{BF}_4]$ – generated in situ from the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and AgBF_4 in THF – to give a complex whose elemental analyses are in agreement with the proposed formula $[\text{Rh}(\text{bdtp})(\text{COD})][\text{BF}_4]$ (**[1]** $[\text{BF}_4]$). The room temperature ^1H NMR spectrum is not very informative as, except thin resonances for the CH and CH_3 groups of the pyrazolyl cycle, broad resonances are observed specially in the 4-5 ppm area where the methylene resonances of the ligand and the olefinic hydrogen resonances are expected. Lowering the temperature until 183K led to a complex spectrum difficult to analyse except the resonances for the CH and CH_3 groups of the pyrazolyl cycle which are only slightly broaden. These results are consistent with a fluxional phenomenon. In the absence of crystals suitable for an X-ray structure determination it is difficult to give a firmly established explanation for this phenomenon. But, if we consider the related complexes with the ligands L_N or L_O (scheme 1) two situations have been encountered. In the case of complex $[\text{Rh}(\text{L}_\text{N})(\text{COD})][\text{BF}_4]$ there is a thermodynamic equilibrium between two isomers, one (the minor) in which the ligand is κ^3 bonded and the other in which the ligand is κ^2 bonded [5a]. In the case of complex $[\text{Rh}(\text{L}_\text{O})(\text{COD})][\text{BF}_4]$ the room temperature NMR spectrum is consistent with the solid state structure. There is no bond but a weak interaction between the rhodium and the oxygen atoms [7c]. So, in the case of **[1]** $[\text{BF}_4]$ a possible explanation of the fluxional phenomenon observed is a third phenomenon: the presence of a dynamic equilibrium between two isomers in which the ligand bdtp is κ^2 or κ^3 bonded as shown on the Scheme 2.

Bubbling carbon monoxide into a solution of **[1]** $[\text{BF}_4]$ in dichloromethane at room temperature led to a mixture of $[\text{Rh}(\text{bdtp})(\text{CO})_2][\text{BF}_4]$ (**[2]** $[\text{BF}_4]$) and $[\text{Rh}(\text{bdtp})(\text{CO})][\text{BF}_4]$ (**[3]** $[\text{BF}_4]$) as shown by IR spectroscopy by comparison with

previously described cationic rhodium carbonyl complexes containing pyrazolyl ligands [5a,7c]. Indeed, the infrared spectrum in CH₂Cl₂ of the $\nu(\text{CO})$ region of the mixture of [2][BF₄] and [3][BF₄] shows a strong band at 2003 cm⁻¹ which corresponds to the cationic unit [3]⁺ and two weak (2103, 2043 cm⁻¹) and two strong bands (2078, 2003 cm⁻¹; the latter one being partially superimposed to [3]⁺) that correspond to two isomers of [2]⁺. This observation shows that the dicarbonyl complexes are easily decarbonylated and indeed, the complex [3][BF₄] can be quantitatively obtained just evaporating the solvent. The decarbonylation is easily reversible and bubbling CO to a CH₂Cl₂ solution of pure [3]⁺, regenerates the initial mixture of products.

The single peak at 2003 cm⁻¹ in the $\nu(\text{CO})$ stretching region of the infrared spectrum is consistent with a κ^3 bonding mode of the bdtP ligand. As it was not possible to obtain suitable crystals for an X-ray structure determination, we repeated the reaction with AgCF₃SO₃ instead of AgBF₄ and suitable crystals of [3][CF₃SO₃] were obtained.

The structure of [3]⁺ is shown in Figure 1 and a list of selected bond distances and angles is shown in Table 1. The rhodium atom is coordinated to two nitrogen and the sulphur atoms of the bdtP ligand and one carbon monoxide in a slightly distorted square-planar geometry. Rh(I) atom lies 0.05 Å above the plane formed by C1, N2, N12 and S1. Rh-N [2.0432(15) and 2.0454(16) Å] and Rh-C [1.8281(19) Å] bond distances are similar to those found for the [Rh(L_N)(CO)][BPh₄][5a] and [Rh(L_O)(CO)][BF₄][7c] complexes, [2.015(3)-2.042(4) Å] and [1.795(5)-1.809(4) Å] for Rh-N and Rh-C bonds, respectively. No other complex with RhCN₂S core (C carbonyl, S thioether) was found in the literature. Rh-S bond distance [2.3938(5) Å] was compared to those found for complexes with Rh-S(thioether) bonds [Interval 2.262-2.39 Å; mean bond distance = 2.322 Å],[16] and is in the upper limit of these bond distances.

The ¹H NMR spectrum of [3]⁺ in CDCl₃ is in agreement with the solid state structure. The two protons of each CH₂ in the pZ-CH₂-CH₂-S chain are diastereotopic, thus leading to four groups of signals (Figure 2) and each group of signals can be assigned as a doublet of doublet of doublet. This happens because of the rigid conformation of the ligand bdtP (NSN) in [3]⁺. This behaviour had been previously described by several of the present authors for similar pyrazole-thioether or pyrazole-thiolate palladium(II) complexes [8]. HMQC spectrum (Figure 3) was used to assign protons H_{10R} and H_{10S} to the two doublets of doublets of doublets of lower δ and H_{9R} and H_{9S} to those of higher

δ . NOESY spectra (Figure 4) allowed us to differentiate H_{9R} from H_{9S} and $CH_3(6)$ from $CH_3(7)$: the singlet that appears at 2.52 ppm shows NOE interaction only with H_5 and was assigned to $CH_3(6)$. The singlet at 2.32 ppm, besides having NOE interaction with H_5 , shows strong NOE interaction with the doublets of doublets of doublets at 4.79 ppm and was assigned to $CH_3(7)$. From the X-ray (Figure 2) crystals structure of $[5][CF_3SO_3]$, it can be seen that the nearest proton to $CH_3(7)$ is H_{9R} and therefore it is the one that should present NOE interaction. This information leads us to assign it to the doublets of doublets of doublets at 4.79 ppm and H_{9S} to the signal at 5.16 ppm. Coupling constants (obtained from the gNMR [17] generated 1H -NMR simulated spectra, Figure 3) helped us to differentiate H_{10R} and H_{10S} . 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 the X-ray crystal study. Geminal 2J and $\approx 180^\circ$ 3J coupling constants have significantly higher values than $\approx 30^\circ$ and $\approx 60^\circ$ 3J coupling constants [18]. Thus, H_{10R} should correspond to the doublet of doublet of doublet at 2.81 ppm and H_{10S} to the one at 3.86 ppm.

Coming back now to the solution that contains the mixture of $[2]^+$ and $[3]^+$ the infrared spectrum shows except the absorption of $[3]^+$ two weak absorption bands at 2103 and 2043 cm^{-1} (isomer $[2a]^+$) and two strong absorption bands at 2078 and 2003 cm^{-1} (isomer $[2b]^+$). By analogy with the related complexes with L_N and L_O ligands $[2a]^+$ was assigned to a 16 valence-electrons dicarbonyl complex with the ligand $bdtP$ κ^2 bonded to Rh(I) and $[2b]^+$ to the 18 valence-electron isomer with the ligand κ^3 bonded to Rh(I).

1H NMR spectrum shows one broad single peak for each CH_2 at room temperature at 4.16 and 3.26 ppm, proving that the equilibrium between $[2a]^+$ and $[2b]^+$ is faster than NMR technique at this temperature. At the same temperature thin resonances are observed for the methyl and CH group of the pyrazolyl cycles at 2.30, 2.37 and 6.22 ppm respectively. Lowering the temperature until 193K induces a progressive splitting of the 4.16 resonance into two broad resonances at 4.36 ppm and 3.81 ppm. The signal at 3.26 ppm splits into two broad resonances at 243K at 3.17 and 3.36 ppm and then into two unresolved multiplets at 3.19 and 3.60 ppm at 193K. During the same time the methyl resonances at 2.30 and 2.37 ppm evolve to a broad resonance centred at 2.39 ppm but no significant change except a slight broadening is observed for the 6.22 ppm

resonance. From these observations it is clear that the fluxional behaviour of [2] is complex and implies certainly several processes. The IR data suggest that one of the processes concerns a dynamic equilibrium between [2a]⁺ and [2b]⁺ and the evolution of the methyl resonances of the pyrazolyl cycles is certainly related to a low energy conformational equilibrium of the six-membered chelate ring in [2b]⁺. This last phenomenon has been recently put in evidence for rhodium complexes of the closely related L_O ligand. Scheme 3 summarises these observations.

To summarize the bonding properties of the bdt_p ligand and the ligands L_N and L_O toward Rh(I) are very similar as in the three cases κ² and κ³ bonding modes have been put in evidence. Nevertheless in the κ³ bonding mode of the bdt_p ligand the carbonyl groups in the Rh(CO)₂ complexes are more labile than with the two other ligands. This is certainly the result of the softer donor character of the sulphur atom compared to nitrogen and oxygen in amine or ether functions.

2.2 Case of the 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene (bddf) and bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) ligands.

The 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene (bddf) was obtained in good yield by treatment of the lithium thiolate salt of N-(2-mercaptoethyl)-3,5-dimethylpyrazole and α,α'-dibromo-*o*-xylene in refluxing tetrahydrofuran (Scheme 4) and its spectroscopic data are in agreement with its structure (see experimental section). The reaction of [Rh(COD)(THF)₂][BF₄] with 1,2-bis[4-(3,5-dimethyl-1-pyrazolyl)-3-thiapropyl]benzene (bddf) or bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) gives [Rh₂(bddf)(COD)₂][BF₄]₂ ([4][BF₄]₂) and [Rh₂(bddo)(COD)₂][BF₄]₂ ([5][BF₄]₂), respectively whatever the initial metal to ligand ratio (1:1 or 2:1). The room temperature ¹H NMR spectra are uninformative as except the thin resonances of the pyrazolyl cycles only broad resonances are observed for the ligands.

It was possible to structurally characterize [5][BF₄]₂ by an X-ray structure determination. The structure of [5][BF₄]₂ (Figure 5) consists of a dimetallic cationic unit of [Rh₂(bddo)(COD)₂]²⁺ associated to two BF₄⁻ anions. Each bddo ligand is coordinated to two Rh(I) atoms and each metallic centre is coordinated to one pyrazolyl and one thioether group from the ligand. The 1,5-cyclooctadiene ligands complete the coordination sphere of the metal. Table 2 lists selected bond distances and angles for

cation $[5]^{2+}$. The structure contains an inversion centre in the middle of the C12-C12' bond. Rh(I) atom lies 0.057 Å above the plane formed by the centroid of C(21)-C(22) and C(25)-C(26) bonds, and N(2) and S(1) atoms. Rh-N [2.092(3) Å] and Rh-S [2.3656(16) Å] bond distances are of the same order of magnitude as those found in the literature for complexes with Rh-N(pz) [Interval 2.015-2.141 Å; mean bond distance = 2.085 Å] and Rh-S(thioether) [Interval 2.262-2.39 Å; mean bond distance = 2.322 Å], respectively [16].

To have some insight into the behaviour of complexes $[4][BF_4]_2$ and $[5][BF_4]_2$ in solution, variable 1H NMR studies were undertaken but in the 273-183K temperature range the results observed were uninformative due to the complexity and the overlapping of signals. But the fluxional phenomenon observed is certainly the result of conformational changes in solution.

Bubbling carbon monoxide into a solution of $[4][BF_4]_2$ gave $[Rh_2(bddf)(CO)_4][BF_4]_2$ $[6][BF_4]_2$ (Scheme 5). Similar reaction carried out with $[5][BF_4]_2$ lead to insoluble products resulting certainly from a polymerisation reaction.

The $\nu(CO)$ region of the infrared spectrum in CH_2Cl_2 solution of $[6][BF_4]_2$ shows two peaks at 2106 and 2041 cm^{-1} , suggesting the formation of a dicarbonyl Rh(I) complex. It is noteworthy that these absorptions are in similar position than for $[2a]^+$. The NMR spectra are consistent with the proposed structure (see experimental section).

It was possible to obtain single crystals of $[6][BF_4]_2$, which was structurally characterised by an X-ray crystallographic study. The structure consists of cationic unit of $[Rh_2(bddf)(CO)_4]^{2+}$ associated to two BF_4^- anions (Figure 6). The ligand bddf coordinates two Rh(I) atoms through one nitrogen of the pyrazolyl cycle and one sulphur of the thioether group each. The metallic centres complete their slightly distorted square-planar geometry with two carbonyls in *cis* position. Each rhodium has 16 valence electron, consistent with the IR data. Table 2 lists selected bond distances and angles for cation $[6]^{2+}$. The Rh(1) atom lies 0.012 Å above the plane formed by C(29), C(30), N(2) and S(8), and Rh(2) atom lies 0.046 Å above the plane formed by C(31), C(32), N(12) and S(18). Rh-N [2.074(11) and 2.094(13) Å] and Rh-S [2.376(4) and 2.375(3) Å] distances are similar to those found in the literature for complexes containing Rh-N(pz) [Interval 2.015-2.141 Å; mean bond distance = 2.085 Å] and Rh-S(thioether) [Interval 2.262-2.39 Å; mean bond distance = 2.322 Å] bonds.

The Rh-C bond distances [1.856(17) and 1.861(16) Å] of carbonyl groups in *trans* position to the pyrazolyl cycles are similar to those found in the literature for Rh(I) complexes containing pyrazolyl and carbonyl groups in *trans* position [Interval 1.776-1.879 Å; mean bond distance = 1.834 Å] [16]. The carbonyl groups in *trans* position to the thioether groups have Rh-C bond distances [1.91(2) and 1.892(17)] slightly longer than those found for complexes containing carbonyl and thioether groups in *trans* position [1.829-1.862 Å] [19].

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. Diethyl ether, tetrahydrofuran and dichloromethane, used for the synthesis, were dried and distilled by standard methods and previously deoxygenated in the vacuum line.

Analyses (C, N, H, S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Infrared spectra were recorded in a Perkin-Elmer 2000 FT spectrophotometer with KBr pellets or in CH₂Cl₂ solutions with CaF₂ cells. The ¹H NMR, ¹³C{¹H} NMR, HMQC and NOESY spectra were obtained either on a Bruker 200 MHz, Bruker 250 MHz, Bruker 400 MHz or Bruker 500 MHz instrument. Chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bntp) [8d] Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) [15] and [RhCl(COD)]₂ [20] have been prepared according to the published procedures.

Synthesis of the ligand

1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropryl]benzene (bddf)

7.2 mL of butyl lithium 1.6 M (11.5 mmol) were added dropwise to a solution of 1.62 g (10.4 mmol) of N-(2-mercaptoethyl)-3,5-dimethylpyrazole in THF (10 mL) keeping the Schlenk in an ice-water bath. Precipitation of the lithium thiolate was observed and then

1.41 g (5.1 mmol) of α,α' -dibromo-*o*-xylene 96% in THF (5 mL) were then added and the solution was heated under reflux for 5 hours. Heating was stopped and after cooling to room temperature the solvent was evaporated. Dichloromethane (25 mL) was added and precipitation of LiCl was observed. The precipitate was filtered and the solution was extracted 3 times with distilled water (20 mL). The organic layer was dried with anhydrous sodium sulphate and removed in vacuum to give a white solid. Yield: 1.62 g (77 %) – C₂₂H₃₀N₄S₂ (414.63): C 63.73, H 7.29, N 13.51, S 15.47; found: C 63.58, H 7.15, N 13.64, S 15.73. IR (KBr, cm⁻¹): $\nu(\text{C-H})_{\text{al}}$ 2925, $\nu(\text{C=C})$, $\nu(\text{C=N})$ 1552, $\delta(\text{C-H})_{\text{oop}}$ 780-763. ¹H NMR (250 MHz, CDCl₃ solution) δ = 2.22 (s, 12H, 4 *Me*), 2.86 (t, ³*J* = 7 Hz, 4H, S-CH₂-CH₂), 3.64 (s, 4H, S-CH₂-ph), 4.08 (t, ³*J* = 7 Hz, 4H, pz-CH₂-CH₂), 5.78 (s, 2H, pz-CH), 7.19 (b, 4H, C₆H₄). - ¹³C{¹H} NMR (CDCl₃ solution, 63 MHz) δ = 11.3 (*Me*), 13.6 (*Me*), 32.0 and 33.6 (S-CH₂-ph and CH₂-CH₂-S), 48.7 (pz-CH₂-CH₂), 105.2 (pz-CH), 127.6-136.2 (C₆H₄), 139.4 and 147.9 (pz-C).

Synthesis of the Rh(I) complexes

[Rh(bdtp)(COD)][BF₄] (**1**)[BF₄] and [Rh(bdtp)(COD)][CF₃SO₃] (**1**)[CF₃SO₃]

A solution of 0.081 g (0.416 mmol) of AgBF₄ or 0.107 g (0.416 mmol) of AgCF₃SO₃ in methanol (5 mL) was added dropwise and under vigorous stirring to a solution of 0.102 g (0.207 mmol) of [RhCl(COD)]₂ in THF (15 mL). The reaction was carried out in the dark to prevent reduction of Ag(I) to Ag(0). Solution turned from initial orange to yellow and AgCl precipitated. After 30 min the solution was filtered through a Celite pad and 0.116 g (0.417 mmol) of bdtp were added. After stirring for 3 hours solution was carried to dryness and the desired product was crystallised in a dichloromethane / diethyl ether mixture.

1[BF₄]: Yield: 0.219 g (92 %) – C₂₂H₃₄BF₄N₄RhS (576.30) C 45.85, H 5.95, N 9.72, S 5.56; found: C 45.63, H 5.87, N 9.63, S 5.65. IR (KBr, cm⁻¹): $\nu(\text{B-F})$: 1056.

1[CF₃SO₃]: Yield: 0.246 g (93 %). – C₂₃H₃₄F₃N₄O₃RhS₂ (638.57) C 43.26, H 5.37, N 8.77, S 10.04; found: C 43.33, H 5.25, N 8.67, S 9.86. IR (KBr, cm⁻¹): $\nu(\text{R-SO}_3^-)$ 1257, 1168, $\nu(\text{C-F})$: 1030. ¹³C{¹H} NMR (63 MHz, CDCl₃ solution) δ = 121.1 (qd, CF₃SO₃⁻).

1⁺: IR (KBr, cm⁻¹): $\nu(\text{C-H})_{\text{al}}$ 2924, $\nu(\text{C=C})$, $\nu(\text{C=N})$ 1558, $\delta(\text{CH}_3)_{\text{as}}$ 1466. ¹H NMR (250 MHz, CDCl₃ solution) δ = 1.96 (b, 4H, CHH_{endo} COD), 2.21 (s, 6H, *Me*), 2.37 (s, 6H, *Me*), 2.45, 2.58 (b, 8H, CHH_{exo} COD, pz-CH₂-CH₂), 4.36, 4.46 (b, 8H, CH COD, pz-CH₂-CH₂), 5.91 (s, 2H, pz-CH). ¹³C{¹H} NMR (63 MHz, CDCl₃ solution) δ = 11.4

(*Me*), 14.3 (*Me*), 32.3 (b, CH₂ COD), 35.9 (CH₂-CH₂-S), 48.6 (pz-CH₂-CH₂), 85.7 (b, CH COD), 107.5 (pz-CH), 142.6, 152.2 (pz-C).

[Rh(bdtp)(CO)₂][BF₄] ([2][BF₄]) and [Rh(bdtp)(CO)₂][CF₃SO₃] ([2][CF₃SO₃])

Carbon monoxide was bubbled through a solution of 0.075 g (0.130 mmol) of [1][BF₄] or 0.079 g (0.124 mmol) of [1][CF₃SO₃] in CH₂Cl₂ (15 mL) for 1 hour. The solution was then evaporated to dryness in vacuum to eliminate free COD and carbon monoxide was bubbled again after adding CH₂Cl₂ (15 mL). This solution contains a mixture of [2]⁺ and [Rh(bdtp)(CO)]⁺.

[2]⁺: IR (CH₂Cl₂ solution, cm⁻¹): Isomer [2a]⁺ ν(CO) 2103 (w), 2043 (w); Isomer [2b]⁺ ν(CO) 2078 (s), 2003 (s). ¹H NMR (250 MHz, CDCl₃, 293 K) δ = 2.19 (s, 6H, *Me*), 2.30 (s, 6H, *Me*), 3.19 (b, 4H, CH₂-CH₂-S), 3.93 (b, 4H, pz-CH₂-CH₂), 6.00 (s, 2H, pz-CH). ¹³C{¹H} NMR (63 MHz, CDCl₃, 293 K) δ = 11.7 (*Me*), 15.0 (*Me*), 34.9 (CH₂-CH₂-S), 47.9 (pz-CH₂-CH₂), 107.7 (pz-CH), 144.3, 151.2 (pz-C), 185.0 (d, ¹J = 71.4 Hz, CO).

[2][CF₃SO₃]: ¹³C{¹H} NMR (63 MHz, CDCl₃) δ = 121.1 (qd, CF₃SO₃⁻).

[Rh(bdtp)(CO)][BF₄] ([3][BF₄]) and [Rh(bdtp)(CO)][CF₃SO₃] ([3][CF₃SO₃])

The solution obtained in the preparation of [2]⁺ is evaporated to dryness and [3]⁺ is obtained quantitatively.

[3][BF₄]: Yield: 0.064 g (99 %). – C₁₅H₂₂BF₄N₄ORhS (496.13) C 36.31, H 4.47, N 11.29, S 6.46; found: C 36.25, H 4.42, N 11.42, S 6.33. IR (KBr, cm⁻¹): ν(B-F): 1056.

[3][CF₃SO₃]: Yield: 0.068 g (98 %). – C₁₆H₂₂F₃N₄O₄RhS₂ (558.40) C 34.41, H 3.97, N 10.03, S ; found: C 34.58, H 3.83, N 10.07, S 11.21. IR (KBr, cm⁻¹): ν(R-SO₃⁻) 1257, 1168, ν(C-F): 1030. ¹³C{¹H} NMR (63 MHz, CDCl₃) δ = 121.1 (qd, CF₃SO₃⁻).

[3]⁺: IR (KBr, cm⁻¹): ν(C-H)_{ar} 3129-3018, ν(C-H)_{al} 2968-2924, ν(C=C), ν(CO) 1995, ν(C=N) 1551, δ(CH₃)_{as} 1462, δ(C-H)_{oop} 822-793. ¹H NMR (250 MHz, CDCl₃) δ = 2.32 (s, 6H, *Me*), 2.52 (s, 6H, *Me*), 2.81 (ddd, 2H, CH₂-CHH-S, ²J = -14.7 Hz, ³J = 3.3 Hz, ³J = 2.2 Hz), 3.86 (ddd, 2H, CH₂-CHH-S, ²J = -14.7 Hz, ³J = 12.1 Hz, ³J = 1.6 Hz), 4.79 (ddd, 2H, pz-CHH-CH₂, ²J = -15.6 Hz, ³J = 2.2, ³J = 12.1), 5.16 (ddd, 2H, pz-CHH-CH₂, ²J = -15.6 Hz, ³J = 3.3 Hz, ³J = 1.6 Hz), 5.98 (s, 2H, pz-CH). ¹³C{¹H} NMR (63 MHz, CDCl₃) δ = 12.3 (*Me*), 16.1 (*Me*), 38.7 (CH₂-CH₂-S), 51.7 (pz-CH₂-CH₂), 108.0 (pz-CH), 143.3, 152.6 (pz-C), 181.8 (d, ¹J = 81.1 Hz, CO).

Complexes [Rh₂(bddf)(COD)₂][BF₄]₂ ([4][BF₄]₂) and [Rh₂(bddo)(COD)₂][BF₄]₂ ([5][BF₄]₂)

A solution of 0.069 g (0.354 mmol) of AgBF₄ in THF (5 mL) was added dropwise and under vigorous stirring to a solution of 0.088 g (0.179 mmol) of [RhCl(COD)]₂ in THF (15 mL). The reaction was carried out in the dark to prevent reduction of Ag(I) to Ag(0). Solution turned from initial orange to yellow and AgCl precipitated. After 30 min the solution was filtered through a Celite pad and 0.073 g (0.177 mmol) of bddf or 0.060 g (0.177 mmol) of bddo were added. After stirring for 3 hours solution was carried to dryness and the desired product was crystallised in a dichloromethane / diethyl ether mixture.

[4][BF₄]₂: Yield: 0.161 g (90 %) – C₃₈H₅₄B₂F₈N₄Rh₂S₂ (1010.41): C 45.17, H 5.39, N 5.54, S 6.35; found: C 44.90, H 5.25, N 5.39, S 6.02. IR (KBr, cm⁻¹): ν(C-H)_{al} 2947, ν(C=C), ν(C=N) 1554, ν(B-F) 1057. ¹H NMR (200 MHz, CD₂Cl₂ solution) δ = 2.32 (b, 8H, CH₂(COD)), 2.41 (s, 6H, Me), 2.64 (s, 6H, Me), 4.93 (b, 4H, CH(COD)), 6.14 (s, 2H, pz-CH), 7.63 (b, 4H, C₆H₄). ¹³C{¹H} NMR (50 MHz, CD₂Cl₂ solution) δ = 12.3 (Me), 16.0 (Me), 29.2, 33.6 (b, CH₂(COD)) 36.1, 40.3 (CH₂-CH₂-S, S-CH₂-ph), 50.3 (pz-CH₂-CH₂-S), 82.8, 88.5, 96.0 (b, CH(COD)), 109.8 (pz-CH), 130.4, 132.6, 133.8 (C₆H₄), 144.6, 150.7 (pz-C).

[5][BF₄]₂: Yield: 0.152 g (92 %) – C₃₂H₅₀B₂F₈N₄Rh₂S₂ (934.31): C 41.14, H 5.39, N 6.00, S 6.86; found: C 40.88, H 5.51, N 5.81, S 6.68. IR (KBr, cm⁻¹): ν(C-H)_{al} 2920-2836, ν(C=C), ν(C=N) 1556, ν(B-F) 1054. ¹H NMR (200 MHz, CD₂Cl₂ solution) δ = 2.17 (b, 8H, CHH_{endo} COD), 2.35 (s, 6H, Me), 2.44 (s, 6H, Me), 2.50 (b, 12H, CHH_{exo} COD, SCH₂-CH₂S), 3.06 (b, 4H, pz-CH₂-CH₂), 4.60 (b, 4H, CH COD), 5.00 (b, 4H, pz-CH₂-CH₂), 5.99 (s, 2H, pz-CH). ¹³C{¹H} NMR (50 MHz, CD₂Cl₂ solution) δ = 12.1 (Me), 15.3 (Me), 29.2, 33.7 (b, CH₂(COD)) 35.6 (pz-CH₂-CH₂-S, S-CH₂-CH₂-S), 50.6 (pz-CH₂-CH₂-S), 85.3 (b, CH(COD)), 109.4 (pz-CH), 144.8, 151.2 (pz-C).

Complexes [Rh₂(bddf)(CO)₄][BF₄]₂ ([6][BF₄]₂)

Carbon monoxide was bubbled through a solution of 0.075 g (0.074 mmol) of [4][BF₄]₂ in CH₂Cl₂ (15 mL) for 1 hour. The solution was then evaporated to dryness in vacuum to eliminate free COD and carbon monoxide was again bubbled for 1 hour after adding CH₂Cl₂ (15 mL). The desired product was crystallised in a dichloromethane / diethyl ether mixture.

[**6**][BF₄]₂: Yield: 0.048 g (71 %) – C₂₆H₃₀B₂F₈N₄O₄Rh₂S₂ (906.09): C 34.46, H 3.34, N 6.18, S 7.08; found: C 34.42, H 3.25, N 6.14, S 7.25. IR (CH₂Cl₂ solution, cm⁻¹): ν(CO) 2105, 2046. IR (KBr, cm⁻¹): ν(C-H)_{ar} 3140-3010, ν(CO) 2106, 2041, ν(C=C), ν(C=N) 1551, ν(B-F) 1056. ¹H NMR (200 MHz, CD₂Cl₂ solution) δ = 2.41 (s, 6H, *Me*), 2.52 (s, 6H, *Me*), 3.18 (m, 4H, CH₂-CH₂-S), 4.07 (s, 4H, S-CH₂-ph), 4.65 (m, 4H, pz-CH₂-CH₂), 6.20 (s, 2H, pz-CH), 7.41-7.51 (m, 4H, C₆H₄). ¹³C{¹H} NMR (50 MHz, CD₂Cl₂ solution) δ = 11.6 (*Me*), 15.3 (*Me*), 33.4, 40.4 (CH₂-CH₂-S, S-CH₂-ph), 49.2 (pz-CH₂-CH₂-S), 108.8 (pz-CH), 130.4, 132.0, 132.7 (C₆H₄), 145.6, 152.4 (pz-C). 178.6 (bd, ¹J = 71.0 Hz, CO), 182.1 (bd, ¹J = 71.0 Hz, CO).

X-ray Crystallographic Study

Suitable crystals for X-ray diffraction experiments of compounds [**3**][CF₃SO₃], [**5**][BF₄]₂ and [**6**][BF₄]₂ were obtained by crystallisation from a dichloromethane/ether mixture. The final R (on F) factor and ωR (on F²) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure are presented in Tables 3 and 4.

CCDC- xxxx for [**3**][CF₃SO₃], CCDC- xxxx [**5**][BF₄]₂ and CCDC- xxxx [**6**][BF₄]₂ 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, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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Caption of figures

Fig. 1 ORTEP drawing of the cation $[\text{Rh}(\text{bdtp})(\text{CO})]^+$ ($[\mathbf{3}]^+$) showing the numbering scheme. 50% probability amplitude displacement ellipsoids are shown.

Fig. 2 The 400 MHz ^1H -NMR and gNMR simulated spectra for the $\text{NCH}_2\text{CH}_2\text{S}$ fragment of $[\text{Rh}(\text{bdtp})(\text{CO})]^+$ ($[\mathbf{3}]^+$), including (a) the numbering and (b) the dihedral angles for the $\text{NCH}_2\text{CH}_2\text{S}$ fragment.

Fig. 3 The 250 MHz 2D HMQC spectrum of $[\text{Rh}(\text{bdtp})(\text{CO})]^+$ ($[\mathbf{3}]^+$).

Fig. 4 The 250 MHz 2D NOESY spectrum of $[\text{Rh}(\text{bdtp})(\text{CO})]^+$ ($[\mathbf{3}]^+$).

Fig. 5 ORTEP drawing of the cation $[\text{Rh}_2(\text{bddo})(\text{COD})_2]^{2+}$ ($[\mathbf{5}]^{2+}$) showing the numbering scheme. 50% probability amplitude displacement ellipsoids are shown.

Fig. 6 ORTEP drawing of the cation $[\text{Rh}_2(\text{bddf})(\text{CO})_4]^{2+}$ ($[\mathbf{6}]^{2+}$) showing the numbering scheme. 50% probability amplitude displacement ellipsoids are shown.

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Table 1. Selected bond lengths (Å) and angles (°) for [3]⁺ with estimated standard deviations (e.s.d.s.) in parentheses.

[3] ⁺	
Rh(1)-C(1)	1.8281(19)
Rh(1)-N(2)	2.0432(15)
Rh(1)-N(12)	2.0454(16)
Rh(1)-S(1)	2.3938(5)
C(1)-Rh(1)-N(2)	92.34(8)
C(1)-Rh(1)-N(12)	90.99(8)
N(12)-Rh(1)-N(2)	176.14(6)
C(1)-Rh(1)-S(1)	172.21(8)
N(12)-Rh(1)-S(1)	87.64(5)
N(2)-Rh(1)-S(1)	89.32(4)

Table 2. Selected bond lengths (Å) and angles (°) for [5]²⁺ and [6]²⁺ with estimated standard deviations (e.s.d.s.) in parentheses.

[5] ²⁺		[6] ²⁺	
Rh(1)-C(21)	2.158(4)	Rh(1)-C(29)	1.91(2)
Rh(1)-C(22)	2.121(4)	Rh(1)-C(30)	1.856(17)
Rh(1)-C(25)	2.174(5)	Rh(2)-C(31)	1.892(17)
Rh(1)-C(26)	2.154(5)	Rh(2)-C(32)	1.861(16)
Rh(1)-N(2)	2.092(3)	Rh(1)-N(2)	2.094(13)
Rh(1)-S(1)	2.3656(16)	Rh(2)-N(12)	2.074(11)
		Rh(1)-S(8)	2.376(4)
		Rh(2)-S(18)	2.375(3)
N(2)-Rh(1)-C(22)	154.71(14)	C(30)-Rh(1)-C(29)	89.0(8)
N(2)-Rh(1)-C(26)	95.00(15)	C(30)-Rh(1)-N(2)	170.7(6)
N(2)-Rh(1)-C(21)	167.45(14)	C(29)-Rh(1)-N(2)	94.4(7)
N(2)-Rh(1)-C(25)	95.34(15)	C(30)-Rh(1)-S(8)	89.7(5)
N(2)-Rh(1)-S(1)	86.26(8)	C(29)-Rh(1)-S(8)	172.7(6)
C(22)-Rh(1)-S(1)	93.4(12)	N(2)-Rh(1)-S(8)	88.0(3)
C(26)-Rh(1)-S(1)	149.64(15)	C(32)-Rh(2)-C(31)	85.6(7)
C(21)-Rh(1)-S(1)	90.80(12)	C(32)-Rh(2)-N(12)	177.0(5)
C(25)-Rh(1)-S(1)	172.97(15)	C(31)-Rh(2)-N(12)	93.6(6)
C(22)-Rh(1)-C(26)	97.71(17)	C(32)-Rh(2)-S(18)	90.5(5)
C(22)-Rh(1)-C(21)	37.62(16)	C(31)-Rh(2)-S(18)	175.7(5)
C(26)-Rh(1)-C(21)	81.43(17)	N(12)-Rh(2)-S(18)	90.2(3)
C(22)-Rh(1)-C(25)	82.08(17)		
C(26)-Rh(1)-C(25)	37.1(2)		
C(21)-Rh(1)-C(25)	89.06(17)		

Table 3. Crystallographic data for crystal structures **[3][BF₄]₂** and **[6][BF₄]₂**

Compound	[3][BF₄]₂	[6][BF₄]₂
empirical formula	C ₃₂ H ₅₀ B ₂ F ₈ N ₄ Rh ₂ S ₂	C ₂₆ H ₃₀ B ₂ F ₈ N ₄ O ₄ Rh ₂ S ₂
molecular mass, g	934.31	906.09
temperature, K	160(2)	293(2)
crystal system	monoclinic	Monoclinic
space group	P21/c (#14)	Cc
Unit cell dimensions		
<i>a</i> , Å	9.259(5)	25.531(5)
<i>b</i> , Å	14.021(5)	7.873(5)
<i>c</i> , Å	14.590(5)	17.415(5)
β, deg	100.993(5)	96.425(5)
volume, Å ³	1859(1)	3479(3)
<i>Z</i>	4	2
<i>D</i> _{calcd.} , g cm ⁻³	1.669	1.730
μ, mm ⁻¹	1.070	1.149
<i>F</i> (000)	948	1800
crystal size (mm)	0.1 x 0.1 x 0.2	0.1 x 0.1 x 0.2
θ range, deg	2.03 to 26.18	2.70 to 26.09
reflexions collected:		
total, independent, <i>R</i> _{int}	14273, 3634, 0.0654	12919, 6578, 0.1366
data / restraints / parameters	3634, 0, 228	6578, 2, 437
<i>a</i> *	1.009	1.000
Final <i>R</i> 1, <i>wR</i> 2	0.0398, 0.0796	0.0817, 0.2121
<i>R</i> 1 (all data), <i>wR</i> 2	0.0674, 0.0892	0.0989, 0.2343
residual electron density, e Å ⁻³	0.644 and -0.523	1.258 and -1.123

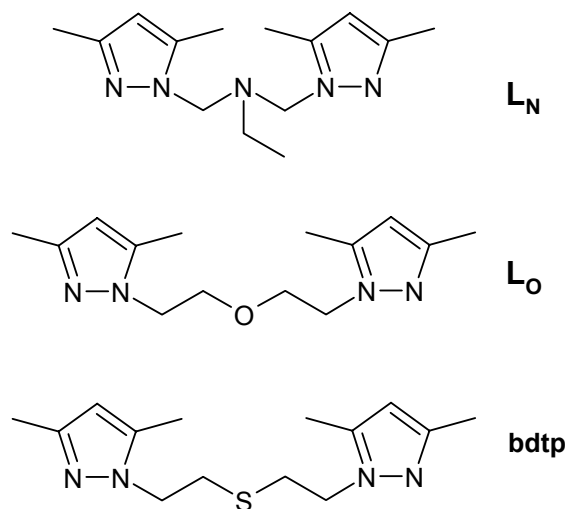
* The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (aP)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$

Table 4. Crystallographic data for crystal structure [5][CF₃SO₃].

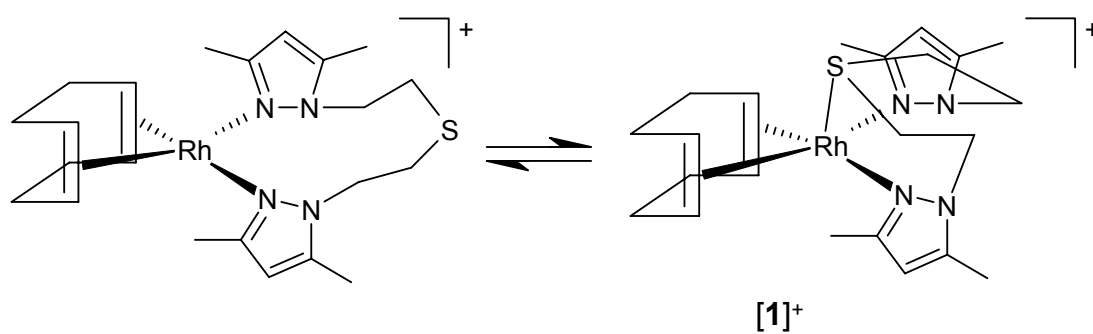
Compound	[5][CF ₃ SO ₃]
empirical formula	C ₁₆ H ₂₂ F ₃ N ₄ O ₄ RhS ₂
molecular mass, g	558.41
temperature, K	293(2)
crystal system	Triclinic
space group	P-1
Unit cell dimensions	
a, Å	8.8473(5)
b, Å	9.0397(5)
c, Å	14.5691(8)
α, deg	103.828(5)
β, deg	101.877(5)
γ, deg	95.474(5)
volume, Å ³	1094.3(1)
Z	2
D _{calcd.} , g cm ⁻³	1.695
μ, mm ⁻¹	1.026
F(000)	564
crystal size (mm)	0.1 x 0.1 x 0.2
θ range, deg	4.22 to 30.22
reflexions collected:	
total, independent, R _{int}	9567, 5802, 0.0259
data / restraints / parameters	5802, 0, 275
a*	0.961
Final R1, wR2	0.0251, 0.0594
R1 (all data), wR2	0.0288, 0.0614
residual electron density, e Å ⁻³	0.456 and -0.613

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

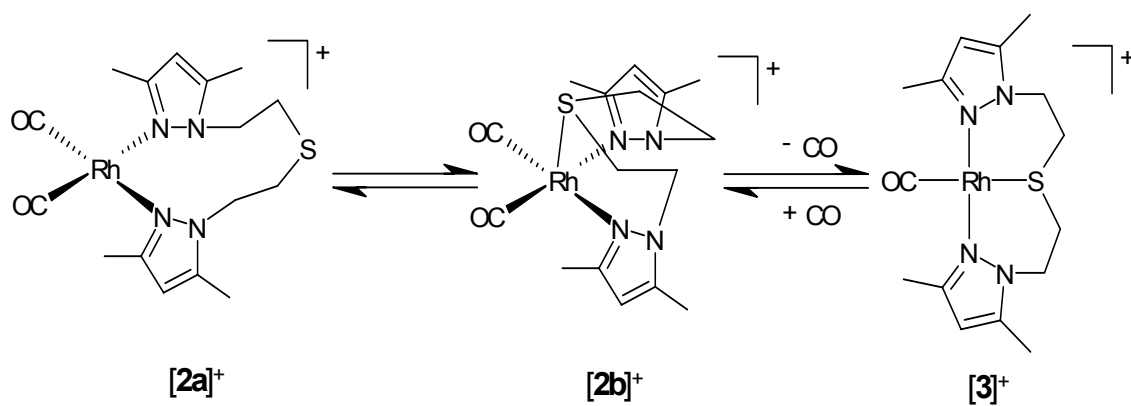
Scheme 1



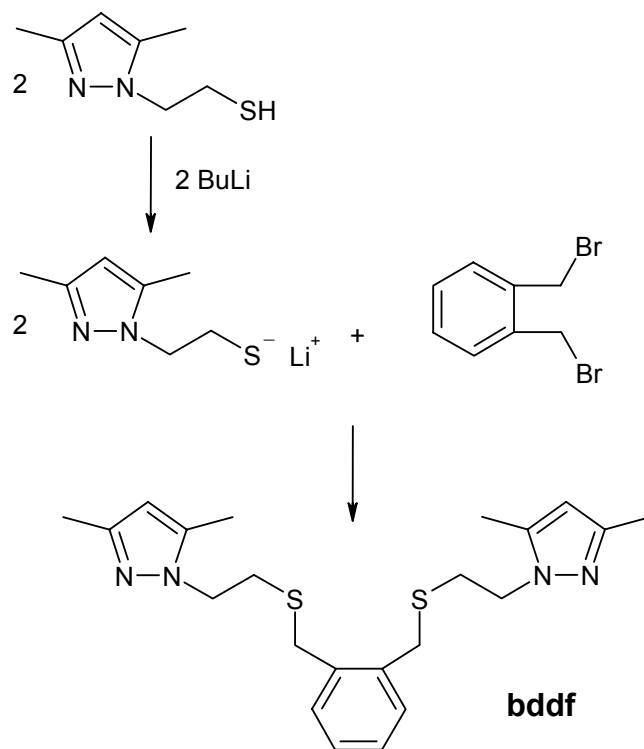
Scheme 2



Scheme 3



Scheme 4



Scheme 5

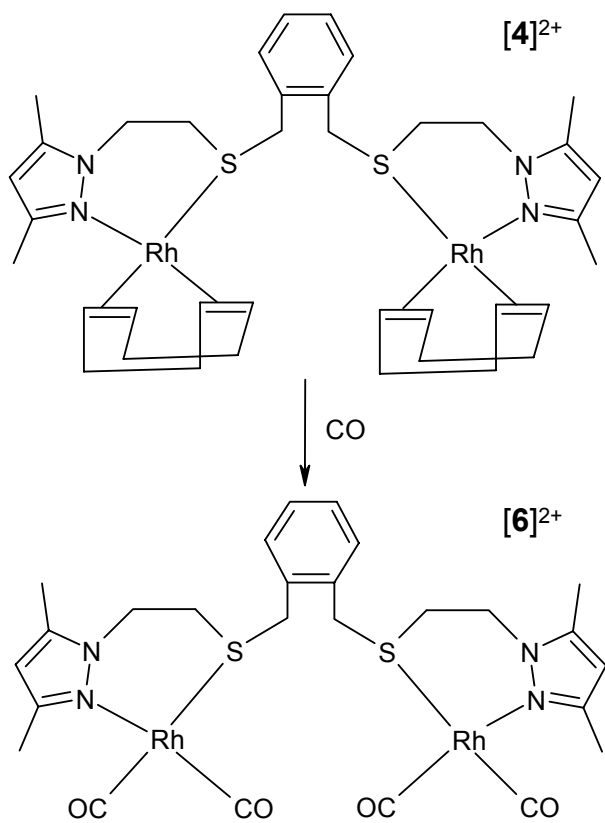


Figure 1

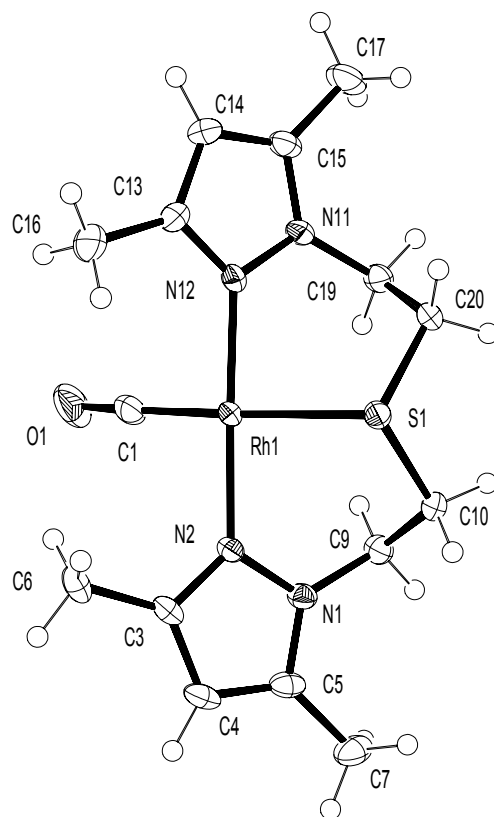


Figure 2

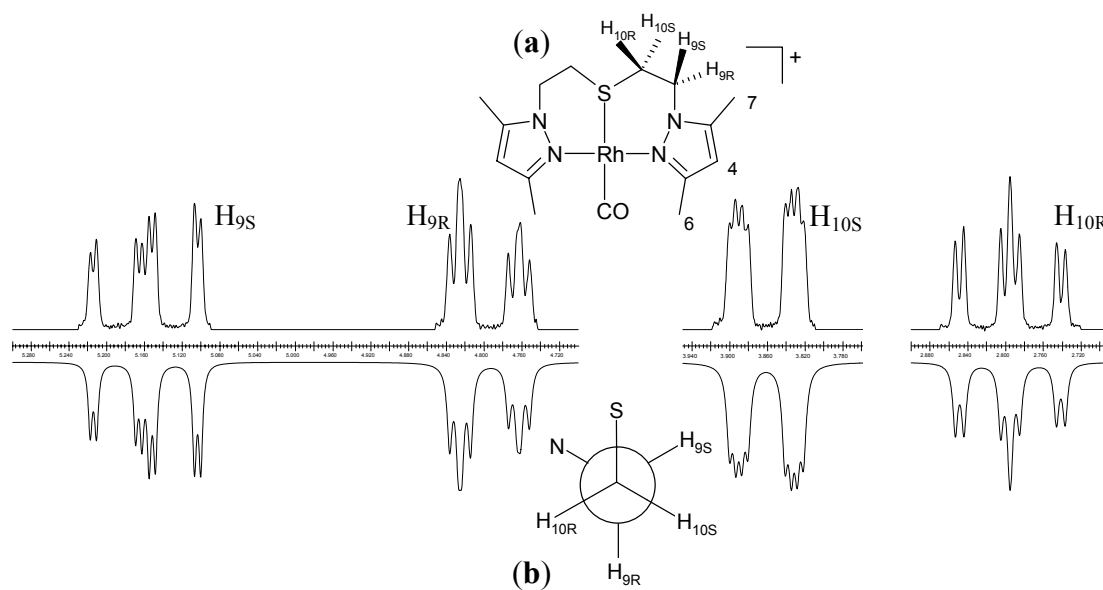


Figure 3

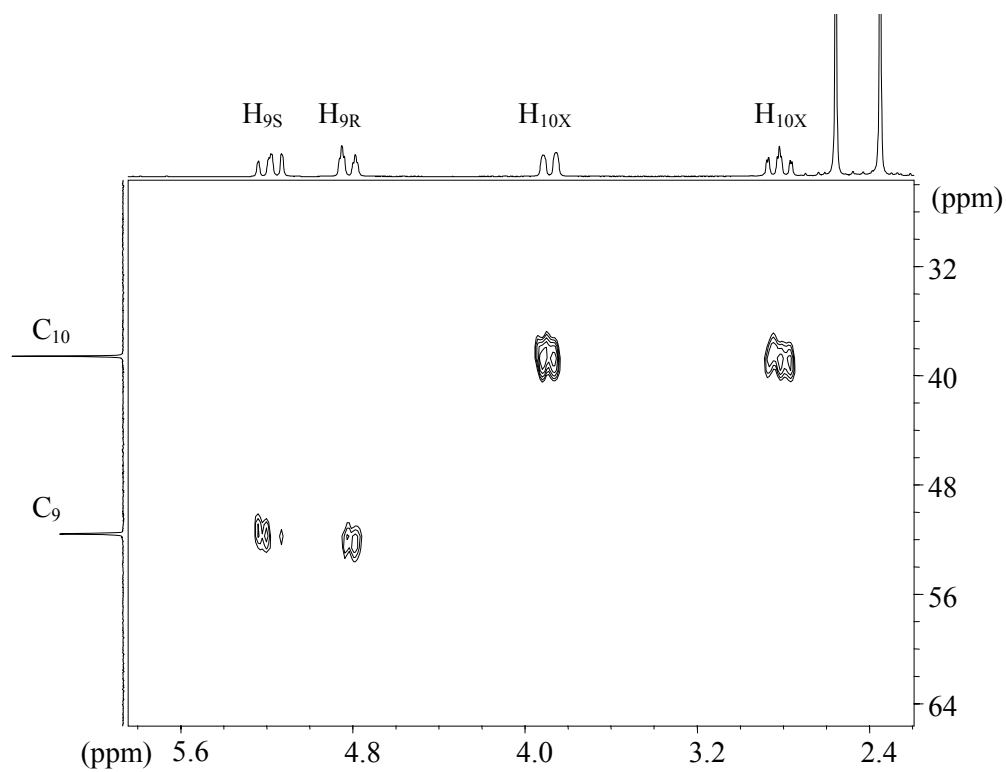
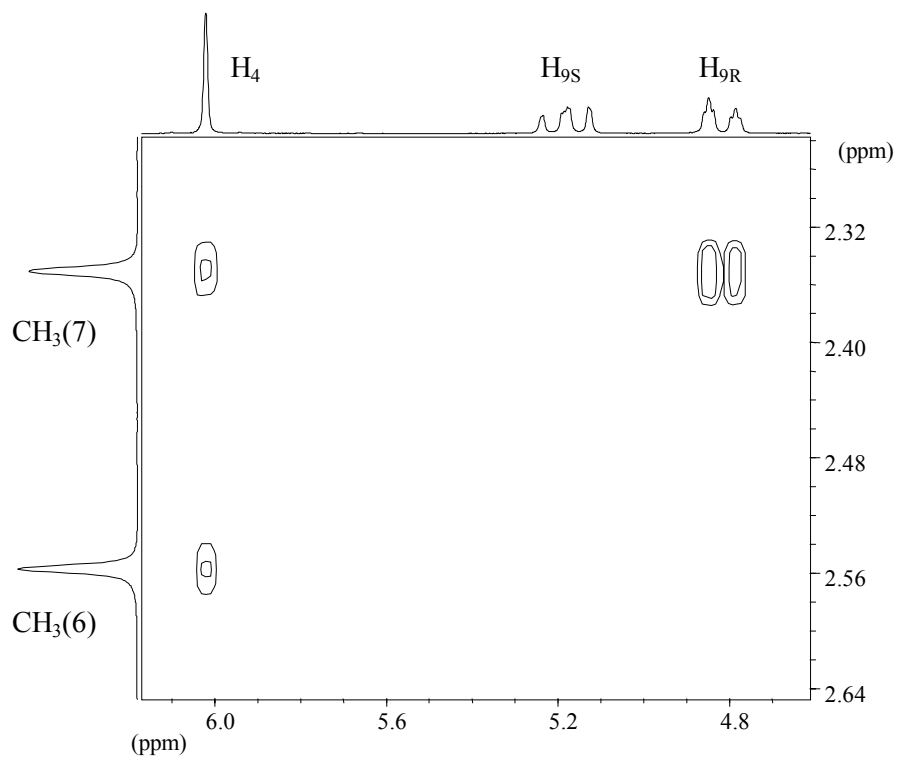


Figure 4



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