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Versatility in the mode of coordination [(C)$^-$, (N,S), (C,N)$^-$ or (C,N,S)$^-$] of the Schiff base: C_6H_5–CH=N–CH_2–CH_2–SEt to palladium(II). X-ray crystal structures of *cis*-[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] and [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl]

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Abstract

The reaction of ligand C_6H_5–CH=N–CH_2–CH_2–SEt (**1**) with $Na_2[PdCl_4]$ is studied. It yields, depending on the experimental conditions, two different sorts of palladium(II) complexes: *cis*-[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] (**2b**) and [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl] (**3b**). Compounds **2b** and **3b** differ in the mode of binding of the ligand to the palladium: as a neutral (N,S) group in **2b** or as a monoanionic (C,N,S)$^-$ terdentate ligand in **3b**. The results presented here show that the formation of **3b** is promoted thermally and requires the presence of sodium acetate. The cyclopalladated complex **3b** reacts with PPh_3, in a 1:1 or 1:2 molar ratio, to produce [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl(PPh_3)] (**4b**) or [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl$(PPh_3)_2$] (**5b**), respectively. All the complexes have been characterised by elemental analysis, infrared and NMR spectroscopy. Compounds **2b** and **3b** have also been characterised structurally: **2b** is triclinic, space group $P\bar{1}$, with $a = 8.081(2)$, $b = 8.230(2)$, $c = 10.836(2)$ Å, $\alpha = 109.16(3)$, $\beta = 96.65(3)$ and $\gamma = 92.29(3)°$ and **3b** is triclinic, space group $P\bar{1}$, with $a = 10.201(2)$, $b = 11.927(2)$, $c = 17.568(4)$ Å, $\alpha = 104.35(3)$, $\beta = 94.21(3)$ and $\gamma = 111.56(3)°$. The structural studies confirmed the mode of binding of the ligand to the palladium and revealed that the ligand has the *Z*-form in **2b** and the *E*-form in **3b**. Semiempirical calculations based on the pm3(tm) method have also been used to explain the isomerisation of **2b**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Schiff base; Palladium; Thioimine; Cyclometallation

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1. Introduction

Palladium(II) and platinum(II) complexes containing 'M(L)Cl_2' cores, where L represents a neutral bidentate group or anionic (C,X)$^-$ {X = N, S or P} group have attracted great interest in the last decade [1], mainly due to their applications in a wide variety of areas, i.e.: as precursors in organic and organometallic syntheses, as catalysts, as auxiliary substrates for the separation of racemic mixtures of Lewis bases, as chiral recognitors, etc. [2]. In addition, the antitumor activity of some palladium(II) or platinum(II) compounds containing (C,N)$^-$ bidentate groups have also been published in recent years [3]. Despite the variety of cyclopalladated complexes containing bidentate (C,N)$^-$, (C,P)$^-$, (C,S)$^-$ ligands described so far, those having monoanionic and terdentate groups are not so common [4]. In particular, palladacycles holding (C,N,S)$^-$ ligands are scarce and practically restricted to a few benzylthio- or benzosulphinyl-substituted azobenzenes [5,6].

We have recently reported the syntheses of C_6H_5–CH=N–CH_2–CH_2–SEt (**1**) (Fig. 1) and the study of its

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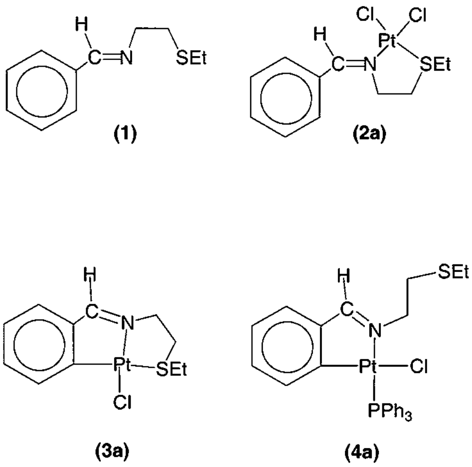


Fig. 1. Schematic view of ligand: C_6H_5–CH=N–CH_2CH_2SEt (**1**) and the platinum(II) derivatives described previously.

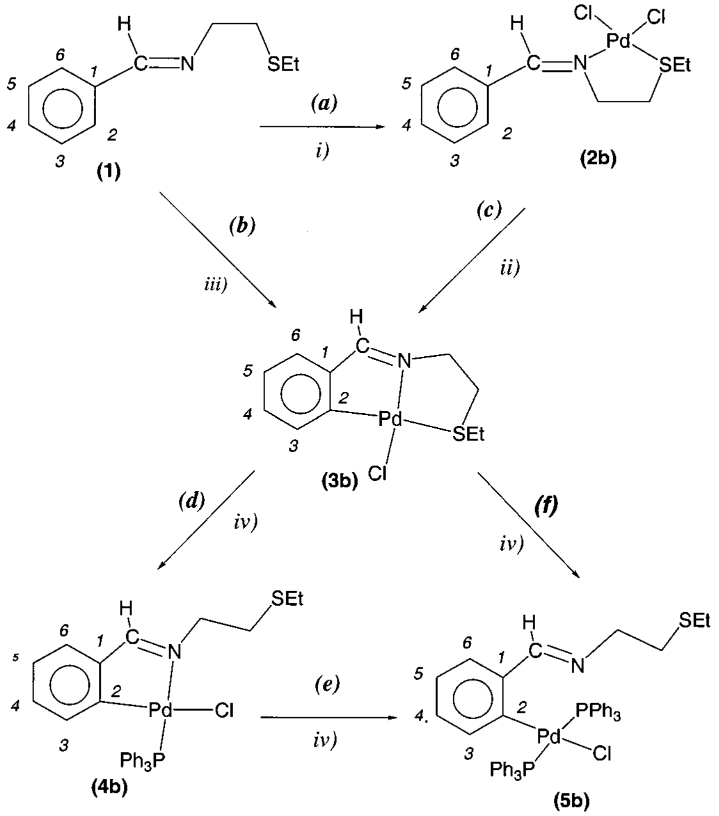
reactivity towards platinum(II) salts [7]. These studies have allowed the isolation and characterisation of different types of platinum(II) complexes (**2a**–**4a** in Fig. 1) which differ in the mode of binding of the ligand **1** to the metal ion. In view of these results, we decided to elucidate whether this versatility of bonding of **1** could also be extended to palladium(II). We herein describe the results obtained in the reaction of ligand **1** with palladium(II) salts.

2. Results and discussion

2.1. Syntheses of the compounds

When the stoichiometric amount of ligand **1** was added to a solution of $Na_2[PdCl_4]$ (in methanol) at room temperature, a pale yellow solid formed immediately (Scheme 1, step (a)). Its characterisation data (see below) were consistent with those expected for *cis*-[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] (**2b**), in which the ligand acts as a neutral (N,S) donor group. According to the NMR studies and the X-ray crystal structure of **2b** (see below), the ligand has the *Z*-form in solution as well as in the solid state.

It has been recently reported that the reaction of **1** with *cis*-[$PtCl_2(dmso)_2$] produced the coordination complex: *cis*-[Pt{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] (**2a**) (Fig. 1), but when the reaction was performed in the presence of sodium acetate the $\sigma(C_{sp^2,\ phenyl}{-}H)$ bond underwent activation giving *cis*-[Pt{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl] (**3a**) (Fig. 1), in which the ligand behaves as a $(C,N,S)^-$ terdentate group [7]. In addition, the coordination complex **2a** could be also transformed into the platinacycle **3a** by treatment with Na(CH_3COO) in refluxing methanol [7]. On this basis, we decided to test whether this sort of reaction could also be extended to the palladium(II) analogue: *cis*-



Scheme 1. (i) $Na_2[PdCl_4]$ in methanol at room temperature. (ii) Na(CH_3COO) in refluxing MeOH (see text). (iii) $Na_2[PdCl_4]$ and Na(CH_3COO) in refluxing MeOH. (iv) PPh_3 in $CDCl_3$ at room temperature.

[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] (**2b**). The reaction of **1** with stoichiometric amounts of $Na_2[PdCl_4]$ and $Na(CH_3COO)$ in refluxing methanol for 2 h, followed by the working up of the solution gave two complexes: the unreacted **2b** and small amounts (ca. 19%) of a new compound **3b**. The charaterisation data of **3b**, based on elemental analyses and {^{1}H and ^{13}C}-NMR data (see below), were consistent with those expected for the cyclopalladated complex: [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl] (**3b**), in which the ligand acts as a monoanionic $(C,N,S)^-$ group.

In addition, the molar ratio **3b**:**2b** increased with time {i.e. 60:40 for a reaction time of 5 h) (Scheme 1, step (b)). Similar results were obtained when **2b** was treated with sodium acetate in refluxing methanol (Scheme 1, step (c)). The formation of **3b** from **2b** requires: (a) the isomerisation of the coordinated ligand from the *Z*-form in **2b** to the *E*-form in **3b**; and (b) the activation of the $\sigma(C_{sp^2,\ phenyl}–H)$ bond.

The formation of the metallacycle **3b** requires the appropiate orientation of the $\sigma(C_{sp^2}–H)$ bond and the abstraction of HCl, and this is only possible if the ligand is in the *E*-form. This finding is similar to that reported for the platinum(II) analogue (**3a**) [7] in which the ligand also behaves as a $(C,N,S)^-$ terdentate group.

On the other hand, since **1** has a prochiral S-donor atom and there is no other source of chiral induction in the reactions described above, compounds **2b** and **3b** are expected to consist of equimolar amounts of the two enantiomers (*S* and *R*).

2.2. Comparison of the reactivity of the Pd–N and Pd–S bonds in compounds 3

The different nature of the four atoms linked to the palladium(II) in complex **3b**, prompted us to study whether the addition of phosphine ligands could induce the cleavage of any of the bonds between the terdentate group and the central atom. This would modify the hapticity and mode of binding of the ligand, and it is well known that these changes are important in catalytic processes. On this basis we studied the reactivity of complex **3b** with PPh_3. When **3b** was treated with the equimolar amount of PPh_3 the monomeric cyclopalladated compound: [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl(PPh_3)] (**4b**) formed (Scheme 1, step (d)). Complex **4b** arises from cleavage of the Pd–S bond and incorporation of a PPh_3 in the coordination sphere of the palladium(II). Further treatment of **4b** with PPh_3 in a 1:1 molar ratio leads to cleavage of the Pd–N bond and the formation of [Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl$(PPh_3)_2$] (**5b**) (Scheme 1, step (e)), in which two PPh_3 ligands in a *trans*-arrangement are bound to the palladium. This reaction involves the opening of the metallacycle. The results obtained here differ from those reported for the cycloplatinated derivative [Pt{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl] (**3a**) [7]. Complex **3a** reacted with PPh_3 (in a 1:1 molar ratio) to produce: [Pt{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl(PPh_3)] (**4a**). However, no evidence for cleavage of the Pt–N bond was detected by ^{31}P-NMR spectroscopy, when compounds **3a** or **4a** were treated with larger excess of PPh_3 [7].

2.3. Characterisation

The compounds prepared in this work are orange or yellow solids which are stable at room temperature and have been characterised by elemental analysis, infrared and NMR (^{1}H, ^{13}C and ^{31}P (for **4b** and **5b**)) spectroscopy. Compounds **2b** and **3b** were also characterised structurally. In all cases, elemental analysis was consistent with the proposed formulae (see Section 3). The most relevant feature observed in the infrared spectra of the compounds is a sharp and intense band in the range: 1550–1650 cm^{-1} which is due to the stretching of the >C=N– group. For **2b**–**4b** this band is shifted to lower wavenumbers when compared with **1** {ν(>C=N–): 1644 cm^{-1} [7]}, thus suggesting that the imine nitrogen binds to the palladium(II). Proton and ^{13}C{^{1}H}-NMR spectroscopic data for **2b**–**5b** are presented in Section 3. In all cases the assignments of the signals were carried out with the aid of 2D-{^{1}H–^{13}C} heteronuclear NMR experiments.

Previous NMR studies on palladium(II) compounds containing Schiff bases have shown that the variations observed in the positions of the imine proton in the free imines and in the palladium(II) derivatives is indicative of the conformation of the ligand (*E*- or *Z*-form) [8–10]. If the ligand is in the *Z*-form, the paramagnetic anisotropy of the metal, which is close to the imine proton, produces a downfield shift of the imine proton signal when compared with the free ligand [8]. In constrast, for complexes containing the ligand in the *E*-form, the resonance of the imine proton is shifted upfield. So, comparison of the ^{1}H-NMR spectra of **2b**–**4b** and that of the free ligand **1** not only reveals the mode of coordination of the ligand but also its conformation (*E*- or *Z*-form). The small lowfield shift of the signal due to the –CH=N– proton in **2b** [$\delta = 8.64$ ppm in dmso-d_6], when compared with **1** {$\delta = 8.36$ ppm [7] in dmso-d_6}, suggested [11–13] a *Z*-form of the imine in this complex and a weak –CH···Cl interaction. The use of molecular models further indicates that in **2b** the relative arrangement of the imine proton and the Cl(2) atom bound to the palladium might likewise be suitable for this type of interaction. The X-ray crystal structure of **2b** (see below) confirms this hypothesis. This sort of interaction is similar to those reported in solution as well as in the solid state for palladium(II) and platinum(II) complexes derived from arylimines (in the *Z*-form) having fluorine or chlorine groups at the *ortho*- sites [11–13].

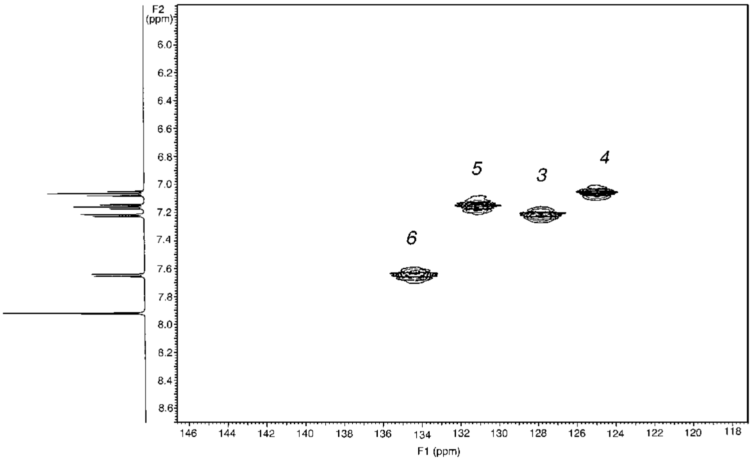


Fig. 2. Section of the 2D-{^{1}H–^{13}C} NMR spectrum {500 MHz} of complex **3b** (in CD_2Cl_2). The numbers refer to the labelling of the atoms shown in Scheme 1.

In contrast to these trends, the signal of the imine proton in **3b** [$\delta = 7.93$ ppm (in CD_2Cl_2)] appeared at higher fields than in **1** [$\delta = 8.32$ ppm (in CD_2Cl_2)], thus suggesting that the imine adopts the *E*-form. As mentioned above the formation of the metallacycle with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2,\ \text{phenyl}})$ bond requires a *trans*-arrangement of the phenyl ring and the alkyl chain bound to the nitrogen (*E*-form). The X-ray crystal structure of **3b** also confirms this finding.

The most relevant features observed in the $^{13}C\{^1H\}$-NMR spectra of the free ligand and its palladium(II) compounds (see Section 3) are the lowfield shifts of imine carbon signals (in compounds **2b**–**4b**) and of the carbon carrying the metal in compounds **3b**–**5b**. This trend, together with the magnitude of the shift, is similar to that reported for related palladium(II) compounds derived from organic Schiff bases [7,14,15].

On the other hand, the 2D-{^{1}H–^{13}C} NMR spectra of **3b** (Fig. 2) showed only four cross-peaks in the aromatic region, thus confirming that palladation took place at the phenyl ring.

Compounds **4b** and **5b** were also characterised by ^{31}P-NMR spectroscopy. In both cases the spectra displayed singlets at 41.26 ppm (**4b**) and at 28.90 ppm (**5b**). The positions of these signals are consistent with the values reported for palladated complexes containing one or two PPh_3 ligands in a *trans*-arrangement at the palladium(II), respectively [9,10,14–16].

2.4. Description of the crystal structure of 2b

A perspective drawing of the molecular structure of **2b**, together with the atom labelling scheme is depicted in Fig. 3, and a selection of bond lengths and angles is presented in Table 1.

The structure of **2b** consists of discrete molecules of *cis*-[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] separated by van der Waals contacts. In each molecule the palladium is tetracoordinated, bound to two chlorines, Cl(1) and Cl(2), the imine nitrogen and the sulphur atom, and is in a slightly distorted square-planar environment [17].

The variations observed in the two Pd–Cl bond lengths [Pd–Cl(1): 2.296(1) Å and Pd–Cl(2): 2.325(1)

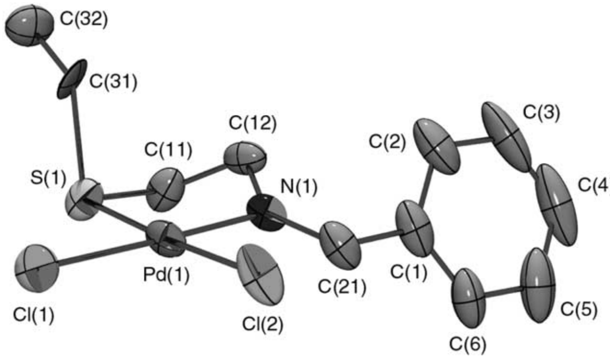


Fig. 3. Molecular structure and atom labelling scheme for **2b**.

Table 1
Selected bond lengths (Å) and bond angles (°) for **2b**

Bond lengths			
Pd(1)–N(1)	2.038(3)	Pd(1)–S(1)	2.255(1)
Pd(1)–Cl(1)	2.296(1)	Pd(1)–Cl(2)	2.325(1)
S(1)–C(11)	1.812(4)	S(1)–C(31)	1.832(7)
N(1)–C(21)	1.267(5)	N(1)–C(12)	1.482(5)
Bond angles			
N(1)–Pd(1)–S(1)	86.80(9)	N(1)–Pd(1)–Cl(1)	176.26(9)
S(1)–Pd(1)–Cl(1)	89.47(4)	N(1)–Pd(1)–Cl(2)	92.84(9)
S(1)–Pd(1)–Cl(2)	176.96(4)	Cl(1)–Pd(1)–Cl(2)	90.90(4)
N(1)–C(12)–C(11)	108.1(3)	N(1)–C(21)–C(1)	129.9(4)
Pd(1)–S(1)–C(11)	98.3(1)	Pd(1)–S(1)–C(31)	92.7(3)
Pd(1)–N(1)–C(21)	123.1(3)	Pd(1)–N(1)–C(12)	114.9(2)

Estimated S.D. values in parenthesis.

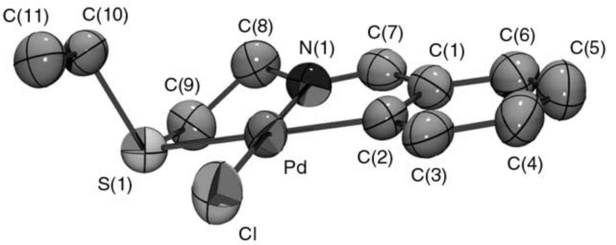


Fig. 4. ORTEP diagram of one of the three independent molecules (C) found in the crystal structure of compound **3b**, together with the atom labelling scheme.

Table 2
Selected bond lengths (Å) and bond angles (°) for the three non-equivalent molecules (**A**, **B** and **C**) found in the crystal structure of **3b**

	Molecule **A**	Molecule **B**	Molecule **C**
Bond lengths			
Pd(1)–N(1)	1.994(4)	1.986(4)	1.992(4)
Pd(1)–S	2.421(1)	2.391(2)	2.416(1)
Pd(1)–Cl	2.311(1)	2.311(1)	2.312(1)
Pd(1)–C(2)	1.987(4)	1.987/5)	2.007(7)
N(1)–C(7)	1.278(6)	1.257(6)	1.265(5)
C(1)–C(2)	1.409(6)	1.412(6)	1.420(6)
C(7)–C(1)	1.449(6)	1.431(7)	1.448(7)
C(8)–C(9)	1.506(7)	1.504(7)	1.501(6)
C(9)–S(1)	1.810(6)	1.829(4)	1.820(4)
S(1)–C(10)	1.817(5)	1.808(5)	1.810(4)
N(1)–C(8)	1.468(5)	1.458(6)	1.471(6)
Bond angles			
N(1)–Pd(1)–C(2)	81.0(2)	80.8(2)	81.3(2)
N(1)–Pd(1)–Cl(1)	174.1(1)	178.7(1)	176.1(1)
N(1)–Pd(1)–S(1)	84.7(1)	84.8(1)	85.1(1)
C(2)–Pd(1)–Cl	95.3(1)	98.0(1)	95.2(1)
C(2)–Pd(1)–S(1)	165.6(1)	165.6(1)	165.6(1)
S(1)–Pd(1)–Cl(1)	97.07(6)	96.5(1)	98.53(5)
N(1)–C(7)–C(1)	116.3(5)	117.3(5)	117.1(4)
C(7)–C(1)–C(2)	113.6(4)	113.4(5)	113.9(5)
C(1)–C(2)–Pd(1)	112.7(3)	112.1(4)	111.3(4)
C(8)–N(1)–C(7)	122.4(5)	124.0(5)	124.4(4)
C(9)–S(1)–C(10)	100.7(3)	102.0(2)	102.0(2)
C(10)–S(1)–Pd	104.6(2)	108.4(2)	105.2(12)
C(7)–N(1)–Pd	116.2(3)	116.2(4)	116.2(4)

Estimated S.D. values are given in parenthesis.

Å] can be related to the different influence of the donor atoms in a *trans*-arrangement [N_{imine} and $S_{thioether}$, respectively].

The metallacycle, formed by the '$-N-CH_2-CH_2-S-$' fragment and the palladium, has an envelope-like conformation [18] in which the C(12) atoms deviate by 0.581(5) Å from the least-square planes through Pd(1), N(1), S(1) and C(11), directed toward C(2).

The $>C{=}N-$ bond length [1.267(5) Å] is similar to the values reported in the literature for related palladium(II) compounds containing imine ligands [19]. The functional $>C{=}N-$ group, which is not included in the metallacycle (*exocyclic*) forms an angle of ca. 26.6° with the coordination plane of the metal and the value of the torsion angle: C(12)–N(1)–C(21)–C(1) = 8.2(6)° indicates that the ligand adopts the *Z*-form.

The phenyl ring is planar [20]. It forms an angle of 63.42(10)° with the coordination plane of the metal and it is nearly orthogonal to the functional $>C{=}N-$ group [the angle between the normals to their main planes is 99.66(5)°].

In **2b**, the distance between the imine hydrogen [H(21)] and the Cl(2) atom is clearly smaller [2.58(4) Å] than the sum of the van der Waals radii of Cl (1.75 Å) and H (1.20 Å) [21,22], thus suggesting a weak $-CH\cdots Cl(2)$ interaction. Similar type interactions have also been described for imines containing chloro or fluoro groups in the *ortho*-sites of the aryl rings, such as in: $4\text{-Me}-C_6H_4-N{=}CH-C_6F_5$ [23], $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_5-CH_2-N{=}CH(2,6\text{-}Cl_2-C_6H_3)\}]$ [13], and other palladium(II) complexes containing *cis*-'$Pd(L)Cl_2$' cores, where L represents a neutral (N,N) group [24].

The intermolecular Pd···Pd distance [3.647(1) Å] is clearly larger than the sum of the van der Waals radii (ca. 3.20 Å) [21,22], which suggests that there is no direct bonding between the two metals.

Finally it should be mentioned that since the space group is centrosymmetric, both enantiomers of **2b** (*R* and *S*) are present in the unit cell. This finding is consistent with the fact that there was no source of chiral induction in the reaction media and consequently the formation of the racemate should be expected, in principle.

*2.5. Description of the crystal structure of **3b***

The molecular structure of **3b** consists of discrete molecules of $[Pd\{C_6H_4-CH{=}N-CH_2-CH_2-SEt\}Cl]$ separated by van der Waals forces. Three non-equivalent molecules [hereinafter referred to as A, B and C] form the asymmetric unit of the structure. The ORTEP diagram of one of the these molecules (C) is depicted in Fig. 4, and a selection of bond lengths and angles is presented in Table 2.

Each molecule contains a [5,5,6] tricyclic system derived from the fusion of a five-membered chelate ring formed by the coordination of the sulphur and nitrogen atoms to the palladium(II), a five-membered palladacycle, and the phenyl ring. In each molecule the palladium atom is in a slightly distorted square-planar environment [25], coordinated to a chlorine, the two heteroatoms (S and N) of the ligand and the *ortho*-carbon of the phenyl ring {C(2)}, thus confirming that metallation at the phenyl ring had taken place and consequently, in **3b** the ligand acts as a $(C,N,S)^-$ terdentate group.

The Pd–N and Pd–Cl bond lengths as well as the N–Pd–S bond angles in the three molecules do not differ significantly from those obtained for the coordination complex **2b** (Table 2), and the Pd–C bond length is in good agreement with the values reported for palladacycles containing a $\sigma(\mathrm{Pd-C_{sp^2,\,aryl}})$ bond [19]. On the other hand, comparison of data shown in Tables 1 and 2 reveals that the Pd–S bond length in the cyclopalladated complex **3b** is clearly greater than in the coordination compound **2b**. This fact can be attributed to the stronger *trans*-influence of the metallated carbon atom as compared to a chlorine ligand [26]. Bond angles around the palladium vary from ca. 80.8(2) to 98.0(1)° and for the three molecules the minimum of these values corresponds to the C(7)–Pd(1)–N(1) angle.

The palladacycles, which are formed by the sets of atoms Pd, N, C(1), C(2) and C(7), are practically planar [27] and contain the functional >C=N– group (*endocyclic*), and their main planes form angles of 2.4(3)° (in A), 3.0(3)° (in B) and 3.0(3)° (in C) with their attached phenyl rings. The >C=N– bond lengths in **3b** agree with the values reported for most of Schiff bases and their palladium(II) derivatives, and the values of the torsion angles: C(1)–C(7)–N(1)–C(8) [177.3(5), 175.8(4) and 174.1(4)° for molecules A–C, respectively] indicate that the ligands have the *E*-form. As mentioned above, the preparation of **3b** can be achieved using **2b** [in which the ligand has the *Z*-form] as starting material. Consequently, the different arrangement of the substituents on the imine group in **2b** and **3b** confirms that the isomerisation of the ligand takes place during the cyclopalladation process.

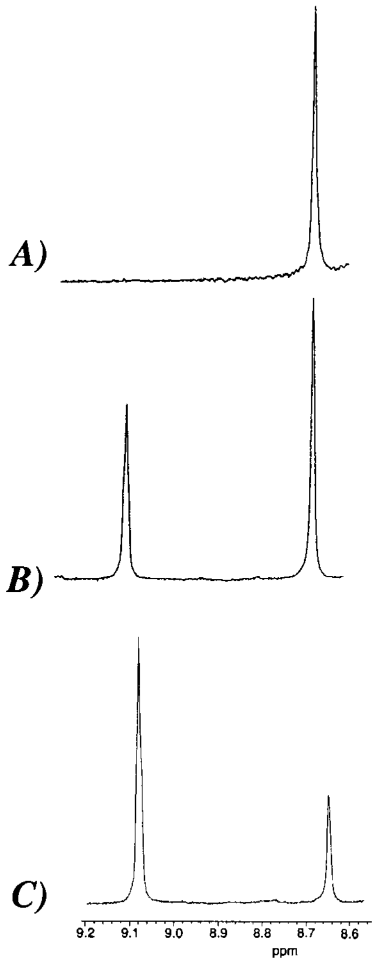


Fig. 5. Section of the proton NMR spectra of **2b** (in dmso-d_6) at different times: $t = 0$ (A), 12 h (B), and 24 h (C), at 20°C.

The phenyl rings are planar [28] and they form angles of 2.4(3), 0.1(2) and 2.4(3)° (in molecules A–C) with the functional group, and of 6.4(3), 4.1(3) and 4.2(3)° (for molecules A–C) with the coordination plane of the palladium.

The five-membered chelate rings, formed by the coordination of the nitrogen and sulphur to the palladium, have an envelope-like conformation in which the C(9) atoms are out of the main plane defined by Pd(1), N(1), C(8) and S(1) [29]. Except for the Pd–S bond distance, the remaining bond lengths and angles in these rings do not differ significantly from those found in **2b** (see above).

In addition, for the three molecules, the Cl···H(3) distance [2.820(2), 2.914(2) and 2.925(2) Å for A, B and C] are somewhat shorter than the sum of the van der Waals radii of Cl (1.75 Å) and H (1.20 Å) [21,22]. This finding could be indicative of a weak –CH···Cl interaction.

The shortest intramolecular Pd···Pd and S···S distances are [3.514(2) and 5.027(3) Å] clearly greater than the sum of their van der Waals radii [21,22], which suggest that there is no direct interaction between these pairs of atoms.

2.6. Solution studies

In order to evaluate whether the cyclopalladation process could also be promoted by coordinating ligands, a solution of **2b** (in dmso-d_6) was prepared and its ^{1}H-NMR spectra was recorded at different times (Fig. 5, A–C). The proton NMR spectrum of the freshly prepared solution showed only one singlet at 8.64 ppm (Fig. 5, A), but after 12 h at room temperature (20°C) the spectrum exhibited higher complexity and an additional singlet appeared at lower fields [$\delta = 9.07$ ppm] (Fig. 5, B). Besides, the relative intensities of the two singlets varied with time (Fig. 5, C). These observations suggested that complex **2b** underwent degradation with time and that new species formed in solution.

The chemical shift of the new signal [$\delta = 9.07$ ppm] and that of the –CHO proton of benzaldehyde [$\delta =$ 10.03 ppm in dmso-d_6] were significantly different. This indicated that the degradation of **2b** could not be related to hydrolysis. Consequently, the changes detected in the ^{1}H-NMR spectra of **2b** with time probably are due to other causes, one of which could involve the replacement of one or the two chlorines in **2b** by the

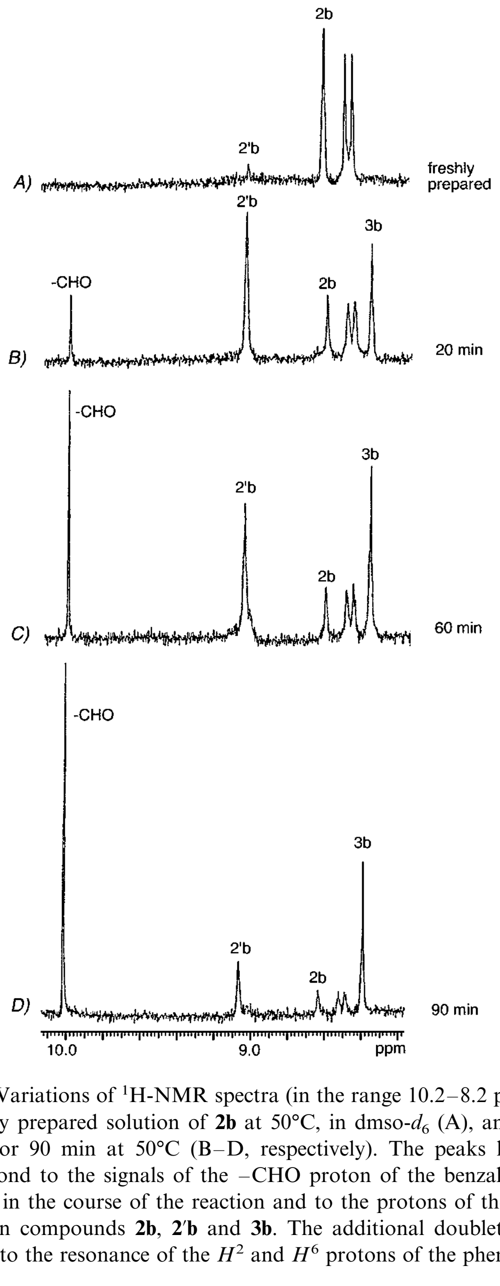
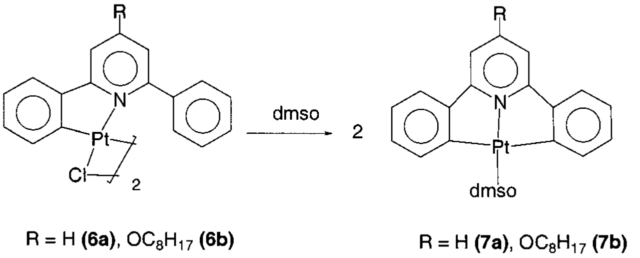


Fig. 6. Variations of ^{1}H-NMR spectra (in the range 10.2–8.2 ppm) of a freshly prepared solution of **2b** at 50°C, in dmso-d_6 (A), and after 20, 60 or 90 min at 50°C (B–D, respectively). The peaks labelled correspond to the signals of the –CHO proton of the benzaldehyde formed in the course of the reaction and to the protons of the imine group in compounds **2b**, **2′b** and **3b**. The additional doublet corresponds to the resonance of the H^2 and H^6 protons of the phenyl ring of **2b**.



Scheme 2.

solvent [dmso-d_6, which has good donor abilities]. According to the X-ray data of **2b** the imine proton is involved in a weak hydrogen interaction with the Cl(2) atom, and the ^{1}H-NMR studies indicated that this is also the case in solution. Consequently, if the replacement of the Cl(2) ligand by the dmso-d_6 takes place, this interaction will vanish and the signal due to the imine proton should shift to lower fields {by ca. 0.60–1.20 ppm} when compared with the free ligand **1**, as observed for the signal at $\delta = 9.07$ ppm. In view of these trends we tentatively assume that complex **2b** undergoes a solvolysis process in the presence of dmso-d_6, to produce **2′b**.

In order to test whether this reaction could be promoted thermally, a freshly prepared solution of **2b** (in dmso-d_6) was heated up to 50°C for varying reaction periods and studied by ^{1}H-NMR spectroscopy (Fig. 6, A–D). After 20 min the ^{1}H-NMR spectrum of the solution in the range 10.2–6.5 ppm became more complex and four singlets at 10.02, 9.07, 8.60 and 8.40 ppm appeared (Fig. 6, B). The position of the signal at lower field [$\delta = 10.02$ ppm] is coincident with that expected for benzaldehyde in dmso-d_6, the two singlets at 8.60 and 9.07 ppm are due to the imine proton of complex **2b** and of the new species (**2′b**) formed in the solvolysis process described above. The remaining singlet at 8.40 ppm can be ascribed to the –CH=N– proton of the metallated complex **3b**. This fact is also supported by the presence of a multiplet centered at ca. 6.7–6.9 ppm which is due to the proton of the aryl ring next to the metallated carbon. It should be noted that the intensities of the four singlets varied with time. For longer reaction periods (60 or 90 min) the relative intensities of these signals changed (Fig. 6, C–D). It is worth noting that the assignments of the signals seen in the proton NMR spectra of these samples were also supported by ^{13}C-NMR data. These observations suggested that an increase in the temperature and the reaction time favoured not only the hydrolysis of the ligand, but also the activation of the $\sigma(C_{sp^2,\ phenyl}{-}H)$ bond. Most of the studies reported so far on cyclopalladation of N-donor ligands involve the use of bases [i.e. Na(CH_3COO) or the ligand itself] to favour the formation of the σ(Pd–C) bond [30]. Besides, when organic Schiff bases are used as ligands, the cyclopalladation reaction is generally carried out under refluxing conditions, suggesting that the formation of the palladacycle is thermally promoted. The results obtained from the studies in solution agree with these general trends, since they reveal that the formation of benzaldehyde takes place upon heating, and consequently, the 2-ethylthioethylamine will be released. These two factors (a basic medium and an increase of the temperature) will favour the activation of the $\sigma(C_{sp^2,\ phenyl}{-}H)$ bond.

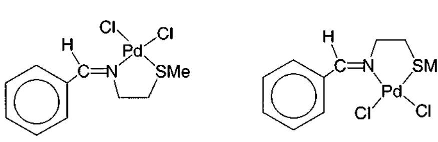
These findings are similar to those recently described for the di-μ-chloro-bridged cycloplatinated complexes: $[Pt\{C_6H_2N{-}[2{-}C_6H_4{-}4{-}R'{-}6{-}C_6H_5]\}(\mu{-}Cl)]_2$ [R = H (**6a**) or $O{-}C_8H_{17}$ (**6b**)] (Scheme 2), which rearranged in dimethylsulphoxide (dmso) to produce the mononuclear bis(cycloplatinated) derivatives [Pt{C_6H_2N–[2-C_6H_4-4-R′-6-C_6H_4]}Cl (dmso)] [R = H (**7a**) or O–C_8H_{17} (**7b**)] (Scheme 2) through the activation of the *ortho* $\sigma(C_{sp^2}$–H) bond of the phenyl ring [31].

2.7. Theoretical approaches to rationalise the isomerisation of **2b**

In an attempt to understand the results obtained in the reactions of ligand **1** with $Na_2[PdCl_4]$ and the isomerisation of the coordinated imine, semiempirical methods based on the pm3(tm) model of the SPARTAN 5.0 program [32] were carried out. The geometries of all the molecules used in this study were fully optimised before calculation of the formation enthalpies ($\Delta H_{form.}$) and the molecular orbitals. In order to test the validity of the program, the geometry of **2b** was optimised and compared with the X-ray data (see above). The structural parameters (bond lengths, bond angles and the relative orientation of the phenyl ring and the coordination plane of the palladium) in the optimised geometry were in excellent agreement with the structural data of **2b** obtained by X-ray diffraction. In addition, some authors have recently reported the high degree of agreement between the optimised geometries obtained with the pm3(tm) for other five-membered palladacycles and their X-ray data [33]. This suggests that for compounds of this kind this semiempirical method gives fairly accurate optimised geometries.

As a first approach to this problem, the two isomers of *cis*-[Pd{C_6H_5–CH=N–CH_2–CH_2–SMe}Cl_2] (Fig. 7) [which differ in the conformation of the ligand: *Z*-form in **2c** and *E*- form in **2d**] were used for the semiempirical calculations.

The formation enthalpy ($\Delta H_{form.}$) for the two isomers **2c** and **2d** was calculated with the aid of the SPARTAN 5.0 program [32] giving $\Delta H_{form.} = -51.24$ kcal mol^{-1} for **2c** and -51.74 kcal mol^{-1} for the isomer **2d** in which the imine adopts the *E*-form. This confirmed that ΔH for the isomerisation reaction is small (-0.50 kcal mol^{-1}). It has been recently reported that the energy required for the isomerisation of the ligand in *cis*-[Pd{(η^5 - C_5H_5)Fe{(η^5 - C_5H_4)–CH=N–CH_2–CH_2–N-$(CH_3)_2$]}Cl_2] (**8**) [34] is -4.32 kcal mol^{-1}, which is greater than the value obtained for complex **2c**. This variation can be ascribed to two factors: A higher bulk of the ferrocenyl group as compared to phenyl [35], which may hinder, at least partially, the isomerisation process and/or the different electron donor ability of the terminal donor atom [$S_{thioether}$ in **2c** or N_{amine} in **8**].



(2c) (2d)

Fig. 7. Schematic view of the two isomers (**2c** and **2d**) of *cis*-[Pd{C_6H_4–CH=N–CH_2CH_2SMe}Cl_2].

2.8. Conclusions

The results presented here provide a useful method to tune the mode of coordination of the imine **1** to palladium-(II) as a neutral (N,S) bidentate ligand (in **2b**), as a monoanionic group acting as monodentate $(C)^-$ (in **5b**), bidentate $(C,N)^-$ (in **4b**) or even as a terdentate $(C,N,S)^-$ group (in **3b**). In addition, comparison of the results summarised here and those reported for the platinum(II) compounds reveal that: (a) the imine binds to the palladium(II) or to the platinum(II) giving the coordination complexes *cis*-[M{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2] [M = Pt (**2a**) or Pd (**2b**)] in which the ligand has a *Z*-conformation; (b) the presence of $Na(CH_3COO)$ favours the isomerisation of the imine and the activation of the $\sigma(C_{sp^2,\ phenyl}$–H) bond to give the cyclometallated complexes: [M{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl] [M = Pt (**3a**) or Pd (**3b**)] in which the imine has the *E* form; this finding suggests that the energy required for the isomerisation of the ligand in **2a** and **2b** should be small, in good agreement with the results obtained from the semiempirical calculations; and (c) the formation of the $\sigma(M–C_{sp^2,\ phenyl})$ bond is promoted thermally. Besides these facts, the results obtained in the reaction of the cyclometallated complexes **3** or **4** with PPh_3 show that the Pd–N bond in **3b** or **4b** is more labile than the Pt–N bonds in their platinum(II) analogues (**3a** or **4a**). Previous studies on cyclopalladated and cycloplatinated complexes containing identical $(C,N)^-$ bidentate groups have shown that in this sort of compounds the Pd–N bond is shorter than the Pt–N bond [36]. In contrast to these results, for compounds **3** the trend is just the opposite: the Pt–N bond lengths are 1.963(7) and 1.948(6) Å for the two non-equivalent molecules of **3a**, while the Pd–N bond lengths in **3b** are 1.994(4), 1.986(4) and 1.992(4) Å for molecules A–C. On this basis, the greater lability of the Pd–N bond in **3b** compared with that of the Pt–N bond in **3a** could be related to these structural differences.

3. Experimental

Elemental analyses (C, H, N and S) were carried out at the Serveis Cientifico-Tècnics (Universitat de Barcelona). Infrared spectra were obtained with a NICOLET-IMPACT 400 spectrophotometer using KBr pellets. Routine and high resolution ^1H-NMR spectra were obtained with Gemini-200 MHz and Varian-500 MHz instruments, respectively. The solvents used for the NMR experiments are specified in the characterisation section of each one of the compounds, where the chemical shifts (δ) are given in ppm, and the coupling constants (J) in Hz. $^{13}C\{^{1}H\}$-NMR spectra were obtained with a Bruker-250DXR instrument using $CDCl_3$ as solvent and $Si(CH_3)_4$ as internal standard, except otherwise when noted. ^{31}P-NMR studies were performed with a Bruker-250DXR instrument using $CDCl_3$ as solvent and $P(OCH_3)_3$ as reference [$\delta^{31}P\{P(OCH_3)_3\} = 140.17$ ppm].

3.1. Materials and synthesis

The ligand C_6H_5–CH=N–CH_2–CH_2–SEt (**1**) was prepared as described previously [7]. Except methanol, which was HPLC grade, the remaining solvents used for the preparation of the complexes were dried and distilled before use.

3.2. *cis-[Pd{C_6H_5–CH=N–CH_2–CH_2–SEt}Cl_2]* (**2b**)

The imine **1** (100 mg, 0.52 mmol) was dissolved in 5 cm^3 of methanol. Then a solution of 153 mg (0.52 mmol) of $Na_2[PdCl_4]$ in 5 cm^3 of methanol was added at room temperature (r.t.) (ca. 20°C). The reaction mixture was stirred for 30 min and the solid formed was collected by filtration, washed with small amounts of methanol (ca. 3 cm^3), air-dried and later dried over silica gel. Yield: 138 mg, 72.1%. Characterisation data: Anal. Calc. for $C_{11}H_{15}Cl_2NPdS$ (found): C, 35.65 (35.7); H, 4.11 (4.1); N, 3.78 (3.8); S, 8.65 (8.4)%. IR: $\nu(>C{=}N-) = 1634$ cm^{-1}. ^{1}H-NMR data (in dmso-d_6) [37]: 1.49 [t, 3H, –CH_3], 2.70–2.90 [br. m, 2H, S–CH_2–], 3.10–3.20 [br. m, H, –CH_2–S], 4.10–4.50 [br. m, 2H, N–CH_2–], 8.51 [d, 2H, H^2 and H^6], 8.64 [s, 1H, –*CH=N*–] and 7.30–7.60 [m, 3H, H^3, H^4 and H^5]. ^{13}C-NMR data (in dmso-d_6) [37]: 14.92 [–CH_3], 32.10 [–SCH_2–], 35.40 [–CH_2S–], 60.16 [–NCH_2–], 173.16 [–*CH=N*–] and 128.49, 129.54, 129.99, 132.06 and 132.57 [$C_{aromatic}$].

3.3. *[Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl]* (**3b**)

This complex was prepared using either ligand 1 or **2b** as starting material.

3.3.1. Method (a)

The Schiff base **1** (133 mg, 0.69 mmol), $Na_2[PdCl_4]$ (203 mg, 0.69 mmol) and $Na(CH_3COO)$ (57 mg, 0.69 mmol) were suspended in 25 cm^3 of methanol. The resulting mixture was refluxed for 12 h and filtered out. The bright yellow filtrate was concentrated on a rotary evaporator to ca. 15 cm^3. The yellow solid formed (**2b**) was removed by filtration and the filtrate was transferred to an erlenmeyer and concentrated to dryness on a rotary evaporator. The deep yellow residue was then dissolved in CH_2Cl_2 (ca. 15 cm^3) and filtered out through Celite. Slow evaporation of the filtrate at ca. 20°C produced bright yellow microcystals of **3b**, which were collected by filtration and air-dried. Yield: 160 mg, 68%.

3.4. Method (b)

Compound **2b** (104 mg, 0.28 mmol) and $Na(CH_3COO)$ (22 mg, 0.28 mmol) were suspended in 25 cm^3 of methanol and refluxed for 12 h. After this period the brownish solution was allowed to evaporate at r.t. to ca. 15 cm^3 and filtered out. The filtrate was then transferred to an open vessel and allowed to evaporate at r.t. The brownish residue was then treated with CH_2Cl_2 and filtered out through Celite to remove the small amounts of metallic palladium formed in the course of the reaction and the inorganic salts. Slow evaporation of the filtrate at ca. 20°C produced bright yellow microcrystals of **3b**. This complex can be recrystallised from CH_2Cl_2. Yield: 73 mg, 75%. Characterisation data: Anal. Calc. for $C_{11}H_{14}ClNPdS \cdot 1/8CH_2Cl_2$ (found): C, 38.77 (38.9); H, 4.24 (4.1); N, 4.06 (4.1); S, 9.29 (9.25)%. IR: $\{\nu(>C{=}N-)\} = 1609$ cm^{-1}. ^{1}H-NMR data (in CD_2Cl_2) [37]: 1.46 [t, 3H, –CH_3, ^{3}J(H–H) = 15], 2.98 [q, 2H, S–CH_2–, ^{3}J(H–H) = 15], 3.04 [t, 2H, –CH_2–S, ^{3}J(H–H) = 12], 3.90 [t, 2H, N–CH_2–, ^{3}J(H–H) = 12], 7.23 [dd, 1H, H^3, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.07 [td, 1H, H^4, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.16 [td, 1H, H^5, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.66 [dd, 1H, H^6, ^{3}J(H–H) = 7.5, ^{4}J(H–H) = 1.5], 7.93 [t, 1H, –*CH=N*–, ^{4}J(H–H) = 2.0]. ^{13}C-NMR data (in CD_2Cl_2) [37]: 13.05 [–CH_3], 29.02 [*S*–CH_2–], 36.32 [–CH_2–*S*], 56.84 [–*N*–CH_2–], 126.21 [C^3], 124.12 [C^4], 130.05 [C^5], 134.29 [C^6] and 174.21 [–*CH=N*–].

3.5. *[Pd{C_6H_4–CH=N–CH_2–CH_2–SEt}Cl(PPh_3)]* (**4b**)

Triphenylphosphine (38 mg, 0.145 mmol) was added to a solution formed by 50 mg (0.149 mmol) of **3b** dissolved in 20 cm^3 of CH_2Cl_2 and stirred at r.t. for 20 min. The resulting yellow solution was then allowed to evaporate at r.t. The solid formed was collected by filtration washed with three portions of ca. 1 cm^3 of *n*-hexane and air-dried. Yield: 71 mg, 82%. Characterisation data: Anal. Calc. for $C_{29}H_{29}ClNPPdS$ (found): C, 58.40 (58.1); H, 4.90 (4.8); N, 2.35 (2.3); S, 5.38 (5.3)%. IR: $\{\nu(>C{=}N-)\} = 1637$ cm^{-1}. ^{1}H-NMR data (in CD_2Cl_2) [37]: 1.17 [t, 3H, –CH_3, ^{3}J(H–H) = 15], 3.12 [t, 2H, CH_2S, ^{3}J(H–H) = 15], 2.52 [q, 2H, SCH_2–, ^{3}J(H–H) = 12], 4.22 [br., 2H, NCH_2–], 6.35 [m, 1H, H^3], 6.55 [t, 1H, H^4], 6.92 [t, 1H, H^5], 8.31 [d, 1H, –*CH=N*–] and 7.45–7.70 [m, 17H, H^6 and protons of

Table 3
Crystal data and details of the structure refinement of **2b** and **3b**

	2b	**3b**
Empirical formula	$C_{11}H_{15}Cl_2NPdS$	$C_{11}H_{14}ClNPdS$
Formula weight	370.60	334.14
T (K)	173(2)	293(2)
λ(Mo–K_α) (Å)	0.71069	0.71069
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.081(2)	10.201(2)
b (Å)	8.230(2)	11.927(2)
c (Å)	10.836(2)	17.568(4)
α (°)	109.16(3)	104.35(3)
β (°)	96.65(3)	94.21(3)
γ (°)	92.29(3)	111.56(3)
V (Å^3)	673.8(3)	1893.5(7)
D_{calc} (Mg m^{-3})	1.827	1.758
μ (mm^{-1})	1.901	1.814
F(000)	368	996
Θ Range (°)	2.56–25.35	2.56–24.71
h, k, l ranges	$0 \leq h \leq 19$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$	$0 \leq h \leq 11$, $-14 \leq k \leq 13$, $-20 \leq l \leq 20$
No. of total reflections	2155	5994
No. of independent reflections	1745	3875
[R_{int} (on F)]	0.040	0.058
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. of data	2155	5994
No. of parameters	207	414
Goodness-of-fit on F^2	1.009	0.886
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$, $wR_2 = 0.0584$	$R_1 = 0.0314$, $wR_2 = 0.0673$
R indices (all data)	$R_1 = 0.0381$, $wR_2 = 0.0950$	$R_1 = 0.0584$, $wR_2 = 0.0713$
Largest difference peak and hole (e Å^3)	0.342 and −0.530	0.417 and −0.526

PPh_3]. ^{13}C-NMR data (in CD_2Cl_2) [37]: 13.87 [$-CH_3$], 26.92 [$S-CH_2-$], 34.11 [$-CH_2-S$], 59.37 [$N-CH_2-$], 138.32 [C^3], 130.73 [C^4], 124.89 [C^5], 177.25 [$-CH{=}N-$] and four additional doublets centered at: 134.41, 131.95, 131.22 and 128.71 due to the ^{13}C nuclei of the PPh_3 ligand. ^{31}P-NMR data: 41.26.

3.6. [$Pd\{C_6H_4-CH{=}N-CH_2-CH_2-SEt\}Cl(PPh_3)_2$] (**5b**)

This reaction was carried out in an NMR tube using the following procedure: triphenylphosphine (15 mg, 0.057 mmol) was added to a solution of **3b** (20 mg, 0.029 mmol) in 0.7 cm^3 of $CDCl_3$. The resulting mixture was shaken vigorously at r.t. for ca. 5 min. The resulting pale yellow solution was studied by NMR spectroscopy. Characterisation data: ^{1}H-NMR data (in $CDCl_3$) [37]: 1.29 [t, 3H, $-CH_3$], 2.56 [q, 2H, SCH_2-], 2.81 [t, 2H, $-CH_2-S$], 3.80 [t, 2H, $-NCH_2-$], 8.20 [s, 1H, $-CH{=}N-$], 6.80–7.80 [m, 34H, aromatic]. ^{13}C-NMR (in $CDCl_3$) selected data [37]: 14.79 [$-CH_3$], 26.20 [SCH_2-], 32.32 [$-CH_2-S$], 61.55 [$-NCH_2-$], 161.19 [$-CH{=}N-$]. ^{31}P-NMR data: 28.90.

3.7. Crystallography

A prismatic orange crystal of **2b** (0.34 × 0.17 × 0.04 mm) or bright yellow crystal of **3b** (0.1 × 0.1 × 0.1 mm) was selected. Intensity data for **2b** and **3b** were collected on a Enraf–Nonius KappaCCD [38] (Mo–K_α = 0.71069 Å, graphite monochromator) with sample-to-detector distances of 29.2 and 30.1 mm, respectively. They covered the whole sphere of reciprocal space by measurements of 36 frames rotating about ω in steps of 1° with scan times of 45 (**2b**) and 30 (**3b**) s per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames, respectively, and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarisation effects using DENZO [39]. The scaling as well as the global refinement of the crystal parameters were performed by SCALEPACK [39]. Reflections, which were partially measured on previous and following frames, are used to scale this frames on each other. Merging of redundant reflections in part eliminates absorption effects and also considers a crystal decay if present. For **2b** a total of 2155 reflections were collected in the range $2.56 \leq \theta \leq 25.35°$ of which 1745 reflections were non-equivalent by symmetry [R_{int} (on I) = 0.040]. For **3b**, 5994 reflections were collected in the range $2.56 \leq \theta \leq 24.71°$ [R_{int} (on I) = 0.058]. The number of reflections assumed as observed [$F_o > 4\sigma(F_o)$] was 1745 for **2b** and 3875 for **3b**. Lorentz polarisation, but no further absorption corrections were made.

The structures were solved by Patterson using SHELXS-86 computer program and refined by full matrix least-squares method with the SHELXL-93 program [40]. f, f' and f'' were taken from the literature [41]. Further details concerning the crystal structures of **2b** and **3b** are presented in Table 3.

3.8. Computational details

The calculations were performed with the SPARTAN 5.0 suite of programs [32] using a Silicon Graphics workstation (INDIGO-2 power XZ). The pm3(tm) method was used with the default parameters provided by the program. Geometrical restrictions were not imposed in any case. The calculations were carried out using the option SFC = converge. The number of cycles required for the optimisation of the geometries was greater than the default value. A minimum of 2000 cycles was necessary for the palladium(II) compounds.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 157800 and 157801 for compounds **2b** and **3b**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[28] The least-squares equation of the plane defined by the atoms: C(1), C(2), C(3), C(4), C(5) and C(6) for molecules A, B and C are, for A: (0.7532)XO + (5867)YO + (0.2976)ZO = 7.1857 (maximum deviations were found for C(4): − 0.008 and C(6): 0.006 Å); for B: (0.4721)XO + (0.7049)YO + (0.5293)ZO = 2.4007 (maximum deviations for C(1): 0.008 and C(2): − 0.007 Å) and for molecule C: (0.7870)XO + (0.4756)YO + (0.3931)ZO = 10.9007 (maximum deviations for C(4): − 0.011 and C(6): + 0.011 Å).

[29] The least-squares equations of the mean planes defined by the atoms Pd, N, C(8) and S(1) in molecules A, B and C are: for A (0.7352)XO + (0.5899)YO + (0.3339)ZO = 7.2030. The C(9) atom deviates by 0.5772 Å towards the opposite direction of the C(10) atom. For B: (0.3986)XO + (0.7424)YO + (0.5385)ZO = 1.808. The C(9) atom deviates by 0.7017 Å towards the direction of the C(10) atom. For C: (0.8154)XO + (0.3298)YO + (0.4558)ZO = 10.6279. The C(9) atom deviates by 0.5162 Å towards the opposite direction of the C(10) atom.

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