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Synthesis, characterization and reactivity of palladium(II) compounds containing terdentate $[\text{Csp}^2, \text{N}, \text{S}]^-$ or $[\text{Csp}^3, \text{N}, \text{S}]^-$ ligands

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Abstract

The study of the reactivity of $\text{R}-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{SMe})$ with $\text{R} = \text{C}_6\text{H}_5$ or $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ with palladium(II) salts is reported. These studies have allowed us to prepare and characterize the coordination complexes: *cis*- $[\text{Pd}\{\text{R}-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{SMe})\}\text{Cl}_2]$ ($\text{R} = \text{C}_6\text{H}_5$ or $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$) and the cyclopalladated compounds $[\text{Pd}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{SMe})\}\text{Cl}]$ and $[\text{Pd}\{(2\text{-CH}_2\text{-}4,6\text{-Me}_2\text{-C}_6\text{H}_2)-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{SMe})\}\text{Cl}]$. The X-ray crystal structures of the latter complexes reveal that the thioimines act as a $[\text{Csp}^2, \text{phenyl}, \text{N}, \text{S}]^-$ and as a $[\text{Csp}^3, \text{N}, \text{S}]^-$ terdentate group, respectively. The study of the reactions of the cyclopalladated compounds with PPh_3 is also reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Cyclopalladated; Terdentate ligands

1. Introduction

The study of cyclopalladated compounds has attracted great interest in last decade due to their applications in different areas [1]. A wide variety of palladacycles containing a $\sigma(\text{Pd}-\text{Csp}^2)$ or a $\sigma(\text{Pd}-\text{Csp}^3)$ bond and a bidentate $[\text{C}, \text{X}]^-$ $\{\text{X} = \text{N}, \text{P}, \text{O}\}$ ligand or a terdentate $[\text{C}, \text{X}, \text{Y}]^-$ or $[\text{X}, \text{C}, \text{Y}]^-$ $\{\text{X}, \text{Y} = \text{N}, \text{P}, \text{O}\}$ groups have been described so far [2,3]. However, few articles focus on cyclopalladated compounds with terdentate $[\text{C}, \text{N}, \text{S}]^-$ ligands [4,6], and in most of these cases, the palladacycles arise from the activation of $\sigma(\text{Csp}^2, \text{phenyl-H})$ bonds of benzylthio- or benzosulfinyl substituted azobenzenes exclusively (Fig. 1, 1 and 2) [4,5]. Besides that, cyclopalladated compounds containing a $[\text{Csp}^3, \text{N}, \text{S}]^-$ chelating ligand are even less common [6]. To our knowledge only one compound of this kind has been reported (Fig. 1, 3) [6].

As a part of a project directed towards the syntheses and characterization of pallada- and platinacycles, some of us have recently reported the activation of the $\sigma(\text{Csp}^2, \text{aryl-H})$ bond of the thioimine: $\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{SEt}$, which has lead to syntheses and characterization of the mononuclear compounds: $[\text{M}\{\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{CH}_2-\text{CH}_2-\text{SEt}\}\text{Cl}]$ $\{\text{M} = \text{Pd}$ (**4a**) or Pt (**4b**) $\}$ (Fig. 1) [7]. In the view of these facts we decided to study whether: (a) the replacement of the $-\text{CH}_2-\text{CH}_2-$ moiety by a less flexible backbone between the two heteroatoms (N and S) or (b) the incorporation of alkyl groups in the *ortho* sites of the aryl ring of the thioimine could be important in determining the nature of the final product and/or the ease with which the activation of the $\sigma(\text{C}-\text{H})$ bond takes place. On this basis, we were prompted to prepare the ligands: $\text{R}-\text{CH}=\text{N}-(\text{C}_6\text{H}_4-2-\text{SMe})$ with $\text{R} = \text{C}_6\text{H}_5$ (**5a**) or $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ (**5b**) (Fig. 1) and to study their reactivity versus palladium(II) salts. In this paper we present a general procedure to easily achieve the activation of the $\sigma(\text{Csp}^2-\text{H})$ bond (in **5a**) or the $\sigma(\text{Csp}^3-\text{H})$ bond (in **5b**) of the thioimines using palladium(II) salts, which has allowed us to isolate and characterize the first example

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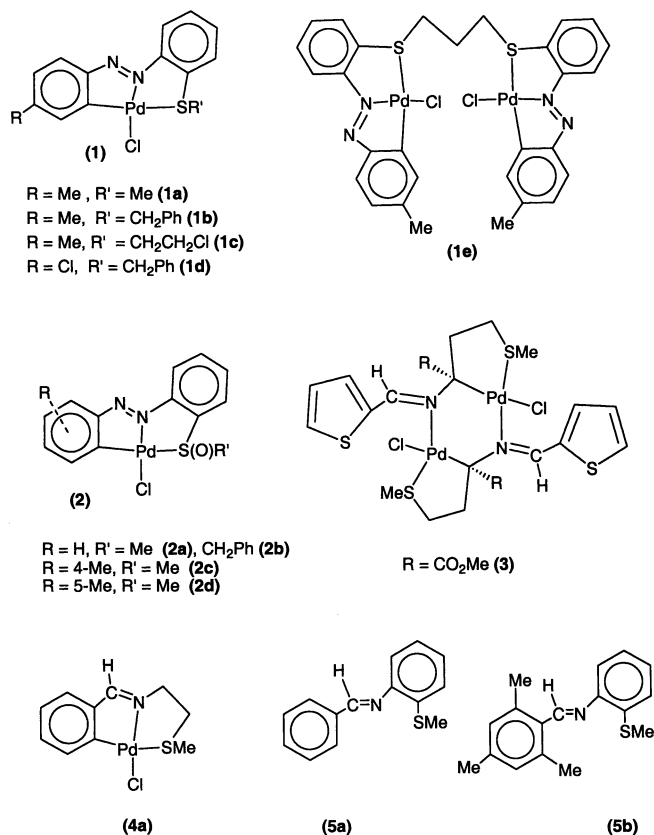


Fig. 1. Schematic view of the cyclopalladated compounds containing terdentate (C,N,S)[−] ligands described so far together with that of the thioimines under study of general formula: R-CH=N-(C₆H₄-2-SMe) with R = C₆H₅ (5a) or 2,4,6-Me₃-C₆H₂ (5b).

of a mononuclear cyclopalladated complex containing a [Csp³,N,S][−] terdentate ligand. Besides that, the comparison of the reactivity of 4a and those of the cyclopalladated complexes obtained from ligands 5a and 5b, has allowed us to establish the factors affecting the lability of the Pd–S and Pd–N bond in palladacycles with [C,N,S][−] terdentate ligands.

2. Results and discussion

2.1. The ligands and the palladium(II) compounds

Compounds: R-CH=N-(C₆H₄-2-SMe) with R = C₆H₅ (5a) or 2,4,6-Me₃-C₆H₂ (5b), were prepared by condensation between equimolar amounts of 2-mercaptoaniline and the corresponding aldehyde in refluxing ethanol, and they were characterized by IR, and NMR spectroscopy (see Section 3). According to NMR data, only one isomer (*anti*-form) of compounds 5 was present in solution.

When the thioimines 5a or 5b were treated with the stoichiometric amount of Na₂[PdCl₄] in methanol at room temperature a pale yellow (for 5a) or an orange

(for 5b) solid formed {Scheme 1, steps (a)}. Their characterization data based on elemental analyses, IR and NMR spectroscopy (see Section 3) were consistent with those expected for *cis*-[Pd{R-CH=N-(C₆H₄-2-SMe)}Cl₂] {R = C₆H₅ (6a) or 2,4,6-Me₃-C₆H₂ (6b)}, in which the ligand acts as a neutral [N,S] bidentate group.

In the ¹H-NMR spectra of 6 the signal due to the imine proton appeared at lower fields than for the free ligands. This finding suggests, according to the literature [8], a *syn*-conformation of the ligands in compounds 6. Complex 6b has also been characterized structurally. A perspective view of its molecular structure together with the atom numbering scheme is shown in Fig. 2.

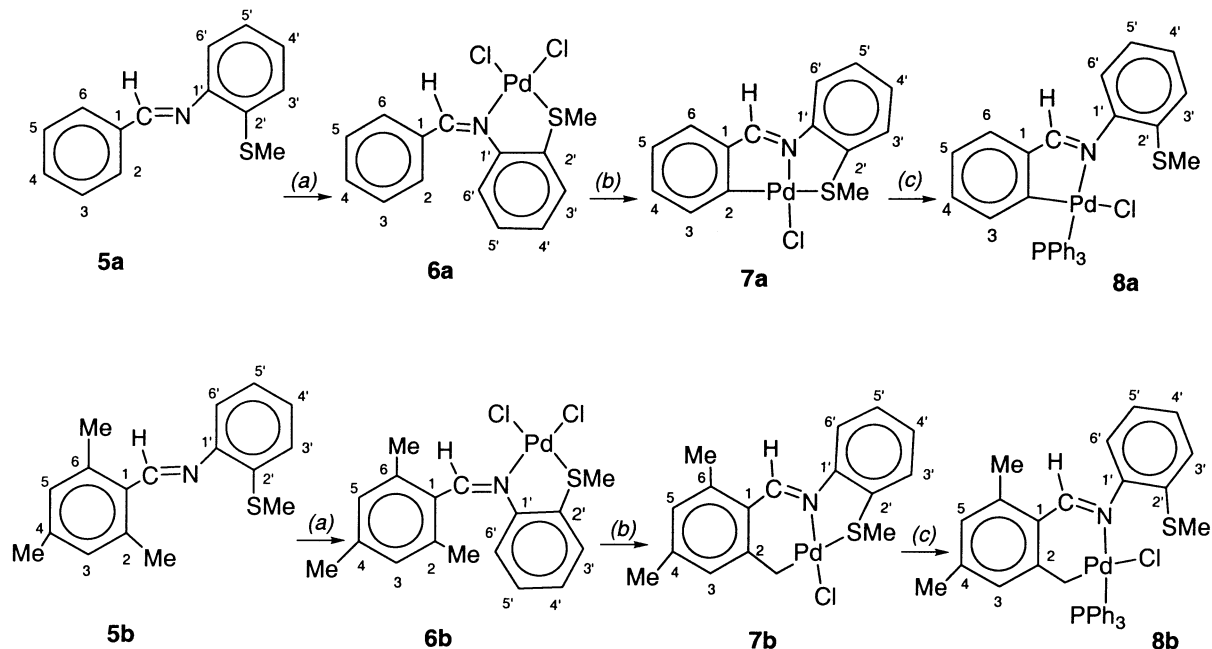
The structure consists of discrete molecules of [Pd{(2,4,6-Me₃-C₆H₂)-CH=N-(C₆H₄-2-SMe)}Cl₂] (6b) separated by van der Waals distances. In each molecule the palladium is in a slightly distorted square-planar environment [9], bound to two chlorines in a *cis*-arrangement and to the two heteroatoms (N and S) of the thioimine forming a five-membered chelate ring with an envelope-like conformation in which the palladium(II) deviates from the plane defined by the remaining atoms [10] by ca. 0.622 Å towards the C(17) atom. The >C=N- bond length is similar to those reported in the literature for related Schiff bases and their palladium(II) compounds [11]. In 6b, the ligand adopts the *syn*-conformation {the torsion angle: C(9)–C(8)–N–C(7) is 4.08°}.

The two aryl rings are planar, and none of them is coplanar with the functional group since they form angles of 59.56 and 36.35° with the imine moiety.

In compound 6b, the distance between the Cl(2) and the imine hydrogen, H(8), is [2.7411 Å] smaller than the sum of the van der Waals radii of these two atoms (Cl: 1.75 Å and H: 1.20 Å) [12], thus suggesting a weak Cl⋯H interaction. A similar type of interaction has also been found in related palladium(II) compounds [7,13].

The crystal contains a (1:1) mixture of the two enantiomers. This result is consistent with the absence of any additional factor of chiral induction during the synthesis of this material.

In order to explore whether the procedure described previously for the cyclometallation of C₆H₅-CH=N-CH₂-CH₂-SEt could be also extended to compounds 6, they were treated with sodium acetate in refluxing methanol for 12 h. This produced the dissolution of the starting materials giving a deep orange (for 6a) or brown (for 6b) solution. For 6a, concentration to dryness on a rotary evaporator followed by the work up of an SiO₂ column chromatography produced the release of a yellow band, which was collected. Slow evaporation of the solution at ca. 20 °C produced golden monocystals. Their characterization data (see below) agreed with those expected for the cyclopalladated compound: [Pd{C₆H₄-CH=N-(C₆H₄-2-SMe)}Cl] (7a) with a σ(Pd–Csp², phenyl) bond.



Scheme 1. (a) $\text{Na}_2[\text{PdCl}_4]$ in methanol at room temperature. (b) $\text{Na}(\text{CH}_3\text{COO})$ in refluxing methanol (see text), followed by SiO_2 -column chromatography. (c) PPh_3 in CH_2Cl_2 at room temperature.

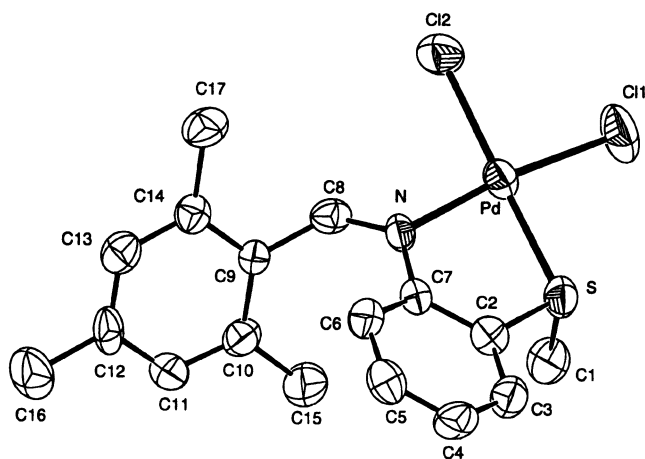


Fig. 2. Molecular structure and atom numbering scheme for compound $\text{cis-}[\text{Pd}\{(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}_2]$ (**6b**). Selected bond lengths (in Å): Pd–N, 2.043(2); Pd–S, 2.2477(8); Pd–Cl(1), 2.2808(8); Pd–Cl(2), 2.2971(8); S–C(1), 1.807(3); S–C(2), 1.767(3); N–C(7), 1.423(3) and N–C(8), 1.267(3). Selected bond angles ($^\circ$): N–Pd–S, 85.50(7); S–Pd–Cl(1), 87.66(3); N–Pd–Cl(2), 93.66(7); Cl(1)–Pd–Cl(2), 93.19(3); Pd–S–C(1), 109.31(11); Pd–S–C(2), 97.39(10); N–C(8)–C(9), 130.5(3); N–C(7)–C(2), 117.1(2) and C(7)–N–C(8), 122.4(2).

When **6b** was used as starting material, the work up of the column yielded unreacted **6b** (ca. 40%) and a new compound **7b**. Its analytical data, mono- and two-dimensional (HSQC and HMBC) NMR data were consistent with those expected for $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7b**) {Scheme 1, steps (b)}. The yield of **7b** improved considerably increasing the reaction period from 12 h (yield = 27%) to

18 h (yield = 62%). Compound **7b** is a monomeric complex with a six-membered palladacycle in which the thioimine behaves as a $[\text{Csp}^3\text{,N,S}]^-$ terdentate group; this type of compounds are really rare in the literature [6].

Compounds **7** have been also characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy (see Section 3) and the assignment of the signals has been carried out unambiguously with the aid of two-dimensional NMR experiments (HSQC and HMBC) which provided conclusive evidence for (a) the binding of the two heteroatoms to the palladium and (b) the formation of the $\sigma(\text{Pd-C})$ bonds. The X-ray crystal structures of **7a** and **7b** (described below) also confirmed this finding. The comparison of $^{13}\text{C}\{^1\text{H}\}$ -NMR data revealed that the resonance due to the metalated carbon of **7a** has low intensity and it is low-field shifted when compared with the free thioimine **5a** and complex **6a**. A similar trend is also found for the resonance of carbon of the metalated $-\text{CH}_2-$ unit in **7b**, when compared with that of the methyl group in the *ortho* sites of **5b** or **6b**. These observations are consistent with previous NMR-studies of related palladacycles [14].

2.2. Description of the crystal structures of $[\text{Pd}\{(\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7a**) and $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7b**)

The molecular structures of **7a** and **7b** and their atom labeling schemes are depicted in Figs. 3 and 4. A selection of bond lengths and bond angles for the two structures are presented in Tables 1 and 2, respectively.

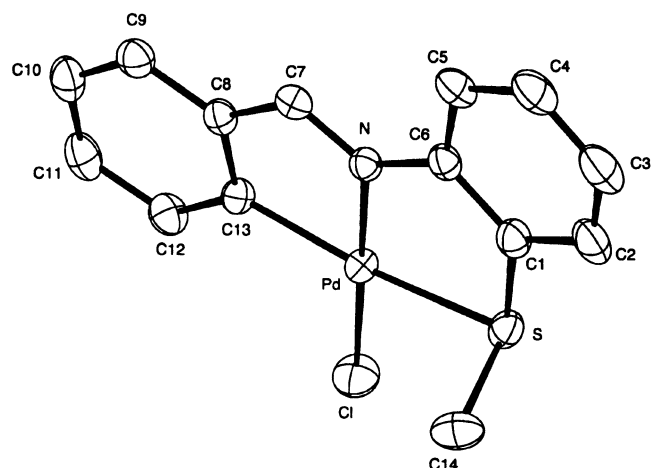


Fig. 3. Molecular structure and atom labeling scheme for $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7a**).

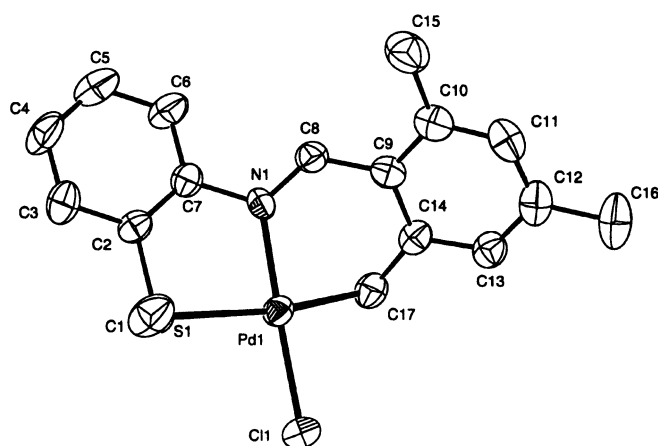


Fig. 4. Molecular structure and atom labeling scheme for $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7b**).

The structures consist of discrete molecules of $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (in **7a**) or of $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (in **7b**) separated by van der Waals contacts.

Each molecule contains a tetracyclic system formed by an aryl ring which shares a -C-C- bond {the $\text{C}(1)\text{-C}(6)$ bond in **7a** or the $\text{C}(2)\text{-C}(7)$ bond in **7b**} with the chelate ring, formed by the coordination of the two heteroatoms (N and S) to the palladium, a five- (in **7a**) or a six- (in **7b**) membered palladacycle and the other phenyl ring.

In the two structures the palladium atom is in a slightly distorted square-planar environment bound to the chlorine, the sulfur, the imine nitrogen and the $\text{C}(13)$ atom of the phenyl ring in **7a** or the $\text{C}(17)$ atom in **7b** [15]. This confirmed the mode of binding of the thioimines to the palladium (II).

The Pd-C and Pd-N bond distances are consistent with those reported for a wide variety of palladacycles holding $[\text{C},\text{N}]^-$, $[\text{C},\text{N},\text{N}']^-$ or $[\text{N},\text{C},\text{N}]^-$ ligands [11].

Table 1

Bond lengths (Å) and selected bond angles (°) for $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7a**)

Bond lengths			
Pd-C(13)	1.987(3)	Pd-N	2.008(3)
Pd-Cl	2.3006(17)	Pd-S	2.3863(13)
S-C(1)	1.779(4)	S-C(14)	1.804(5)
N-C(7)	1.293(4)	N-C(6)	1.425(4)
C(1)-C(6)	1.398(5)	C(1)-C(2)	1.402(5)
C(2)-C(3)	1.371(7)	C(3)-C(4)	1.375(7)
C(4)-C(5)	1.389(6)	C(5)-C(6)	1.385(5)
C(7)-C(8)	1.441(5)	C(8)-C(9)	1.400(5)
C(8)-C(13)	1.401(5)	C(9)-C(10)	1.370(5)
C(10)-C(11)	1.371(6)	C(11)-C(12)	1.392(6)
C(12)-C(13)	1.393(5)		
Selected bond angles			
C(13)-Pd-N	81.94(12)	C(13)-Pd-Cl	96.46(10)
N-Pd-S	84.83(9)	Cl-Pd-S	96.90(5)
C(1)-S-Pd	96.17(12)	C(6)-C(1)-S	121.0(3)
C(2)-C(1)-S	119.5(3)	N-C(7)-C(8)	116.6(3)
C(5)-C(6)-N	123.1(3)	C(1)-C(6)-N	117.1(3)

The labeling of the atoms refers to Fig. 3. S.D. parameters are given in parenthesis.

Table 2

Bond lengths (Å) and selected bond angles (°) for $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7b**)

Bond lengths			
Pd-C(17)	2.041(4)	Pd-N	2.026(4)
Pd-Cl(1)	2.313(3)	Pd-S	2.409(3)
S-C(1)	1.786(4)	S-C(2)	1.764(4)
N-C(8)	1.296(4)	N-C(7)	1.445(4)
C(2)-C(7)	1.370(5)	C(2)-C(3)	1.402(5)
C(3)-C(4)	1.382(5)	C(4)-C(5)	1.382(6)
C(5)-C(6)	1.390(5)	C(6)-C(7)	1.404(5)
C(8)-C(9)	1.460(5)	C(9)-C(10)	1.400(5)
C(9)-C(14)	1.425(5)	C(10)-C(11)	1.394(5)
C(10)-C(15)	1.508(5)	C(11)-C(12)	1.373(5)
C(12)-C(13)	1.381(5)	C(12)-C(16)	1.516(5)
C(13)-C(14)	1.405(5)	C(14)-C(17)	1.468(5)
Selected bond angles			
C(17)-Pd-N(1)	87.47(15)	C(17)-Pd-Cl	92.52(14)
N(1)-Pd-S(1)	84.04(12)	Cl(1)-Pd-S(1)	94.44(10)
C(3)-C(2)-S(1)	120.1(3)	C(7)-C(2)-S(1)	121.0(3)
N(1)-C(8)-C(9)	126.5(3)	C(2)-C(7)-N(1)	118.4(3)

The labeling of the atoms refers Fig. 4. S.D. parameters are given in parenthesis.

The variations observed in the Pd-S bond lengths in **6b** {2.2477(8) Å}, **7a** {2.386(13) Å} and **7b** {2.409(3) Å} can be ascribed to the different nature of the atom [16] in a *trans*-arrangement: the Cl in **6b**, a metallated Csp^2 atom in **7a** or a Csp^3 atom in **7b**.

The angles between adjacent atoms in the coordination sphere lie in the ranges: 81.94(12)–96.90(5)° (for **7a**) and 84.04(12)–94.44(10)° (in **7b**) the smallest angles corresponding to the terdentate ligand.

In **7a**, the metallacycle, which is formed by the atoms: Pd, N, C(7), C(8) and C(13), is nearly planar [17] and it

forms angles of 2.04, 3.65, 5.68 and 2.80° with the attached aryl group, the five-membered chelate ring, the other phenyl ring and with the coordination plane of the palladium, respectively. In **7b**, the palladacycle, formed by the atoms: Pd(1), N(1), C(8), C(9), C(14) and C(17), has a chair-conformation in which the atoms C(9) and Pd deviate by ca. 0.258 and 0.858 Å from the main plane towards the Me group of the SMe substituent [18].

In the two structures, the ligand adopts the *anti*-conformation and the imine group is contained in the metallacycle (*endocyclic*). The >C=N– bond lengths [1.293(4) Å in **7a** and 1.296(4) Å in **7b**] are similar to those found for **6b** as well as for related palladacycles derived from Schiff bases [14].

In compound **7a**, the distance between the Cl and the H(12) atom [2.859 Å] [12], also suggests a weak Cl⋯H⋯C(12) intramolecular interaction.

On the other hand, since these compounds crystallize in the centrosymmetric space group: $P2_1/n$, the crystals contain a (1:1) mixture of the two enantiomers. This result is consistent with the absence of any additional factor of chiral induction during the synthesis of these compounds.

Besides that, it should be noted that, since the ligand has the *syn*-conformation in **6a** and **6b** and adopts the *anti*-form in **7a** and **7b**, we can conclude that, the transformation **6**→**7** requires: (a) the isomerization of the ligand (*syn*-→*anti*-) and (b) the activation of the $\sigma(\text{Csp}^2, \text{phenyl-H})$ bond (in **6a**) or the $\sigma(\text{Csp}^3\text{-H})$ bond (in **6b**).

2.3. Study of the reactivity of compounds **7** with PPh_3

As a first attempt to explore the ease with which the hapticity of the ligand in compounds **7** could be modified we proceeded to study their reactivity versus PPh_3 . When **7a** or **7b** were treated separately with equimolar amounts of PPh_3 in CH_2Cl_2 at room temperature, compounds: $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)\Cl(PPh}_3)\}]$ (**8a**) or $[\text{Pd}\{(2\text{-CH}_2\text{-4,6-Me}_2\text{-C}_6\text{H}_2)\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)\Cl(PPh}_3)\}]$ (**8b**) (Scheme 1) were obtained. These compounds arise from **7** by the cleavage of the Pd–S bond and the incorporation of a PPh_3 in the coordination sphere of the palladium. The characterization data of compounds **8**, presented in the Section 3, agreed with the proposed formula. Their $^{31}\text{P}\{^1\text{H}\}$ -NMR showed a singlet at 38.00 ppm for **8a** and at 34.79 ppm for **8b**. The position and multiplicity of these signals are consistent with the presence of one PPh_3 ligand bound to the palladium in a *trans*-arrangement to the nitrogen [19]. This is the usual result of the reaction between $(\text{C},\text{N})^-$ cyclopalladated compounds and phosphine ligands [20] due to the so-called *transphobia* effect [21].

When compounds **8a** or **8b** were treated separately with larger excesses of PPh_3 {molar ratio PPh_3 : **8** up to 8} no evidences of the cleavage of the Pd–N bond were

detected by NMR spectroscopy. This suggests that in compounds **7–8** the Pd–N bond exhibits low lability. These findings are in sharp contrast with those reported for $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-CH}_2\text{-CH}_2\text{-SMe}\Cl}]$ (**4a**) and $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-CH}_2\text{-CH}_2\text{-SMe}\Cl(\text{PPh}_3)]$ (**9a**), which react with PPh_3 in a (1:2) or (1:1) molar ratio, respectively, producing the cleavage of the Pd–N bond and the formation of $[\text{Pd}\{\text{C}_6\text{H}_4\text{-CH=N-CH}_2\text{-CH}_2\text{-SMe}\Cl(\text{PPh}_3)_2]$ (**10a**) [7a]. The results presented here suggest that compounds **4a** and **9a** are more prone to undergo the cleavage of the Pd–N bond, with the subsequent opening of the palladacycle, than their partners **7a** and **8a**. Despite the formal similarity between the two pairs of compounds (**4a** and **5a**) and (**8a** and **9a**), they exhibit different reactivity versus excesses of PPh_3 . This may be related to the effects induced by the replacement of the ‘–CH₂–CH₂–’ moiety (intercalated between the two heteroatoms N and S) by a more rigid system such as the 1,2-disubstituted C_6H_4 ring.

To sum up, the results presented here provide a neat and useful procedure for the preparation of palladacycles containing terdentate $[\text{Csp}^2, \text{phenyl}, \text{N}, \text{S}]^-$ or $[\text{Csp}^3, \text{N}, \text{S}]^-$ ligands derived from thioimines. As far as we know compounds **7b** and **8b** are the first examples of monomeric and cyclopalladated complexes containing a $[\text{Csp}^3, \text{N}, \text{S}]^-$ terdentate ligand. The comparison of the results obtained in the reactions of compounds **7** and **4a** with PPh_3 reveal that the Pd–N is more prone to cleave in **4a** than in **7a** or **7b**. This can be explained on the basis of the greater flexibility of the five-membered chelate ring formed by the coordination of the two heteroatoms (N and S) in **4a** than in **7**. Besides that, the cyclopalladated complexes reported here have an additional interest since it is well known that the insertion of small molecules (i.e. alkynes, alkenes, isonitriles, oxygen or CO) into the $\sigma(\text{Pd-C})$ of cyclopalladated derivatives may lead to novel organic or organometallic compounds [1a, 1e, 1f, 5]. Further work focused on the reactivity of compounds **7a** and **7b** is currently on the way.

3. Experimental

3.1. Materials and methods

Elemental analyses (C, H, N and S) were carried out at the Serveis Científic-Tècnics (Universitat de Barcelona). Infrared spectra were recorded with a Nicolet Impact 400 instrument using NaCl discs for the ligand and KBr pellets for the remaining compounds. Routine ^1H -NMR and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were obtained with a Gemini-200 MHz and with a Bruker 250 DXR instruments. High resolution ^1H -NMR and the two dimensional NMR experiments {heteronuclear single quantum coherence (HSQC) and heteronuclear multiple

bond coherence (HMBC)} were carried out using a Varian 500 or a Bruker 500 instrument. In all cases, the solvent used for the NMR experiments was CDCl_3 (99.9%) and SiMe_4 was used as internal reference. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **8a** and **8b** were recorded with a Bruker 250 DXR instrument using CDCl_3 as solvent and $\text{P}(\text{OMe})_3$ as reference [$\delta^{31}\text{P}\{\text{P}(\text{OMe})_3\} = 140.17$ ppm]. In all cases the chemical shifts (δ) are given in ppm.

2-Mercaptoaniline was obtained from Aldrich and used as received. The remaining reagents were obtained from commercial sources and used as received. Benzaldehyde and all the solvents used in this work, except methanol, were dried and distilled before use. The methanol used for the preparation of compounds **7** was HPLC grade [22].

3.2. Preparation of the compounds

3.2.1. Preparation of: $R\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}$ with $R = \text{C}_6\text{H}_5$ (**5a**) or $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ (**5b**)

2-Mercaptoaniline (1.000 g, 7.19×10^{-3} mol) was dissolved in 10 cm^3 of ethanol. Then a solution formed by 7.19×10^{-3} mol of the corresponding aldehyde and 5 cm^3 of ethanol was added. The resulting mixture was refluxed for 2 h. The bright yellow solution was concentrated to dryness on a rotary evaporator giving a yellow oil (for **5a**) or a yellow solid (for **5b**), [yields: 1.50 g (91.6%) and 1.82 g (86%), respectively].

3.2.1.1. Characterization data for 5a. Anal. (%) Calc. for: $\text{C}_{14}\text{H}_{13}\text{NS}$ (found): C, 73.90 (73.8); H, 5.76 (5.6); N, 6.16 (6.2) and S, 14.10 (14.0)%. IR: 1637 cm^{-1} . ^1H -NMR data [23]: 2.46 [s, 3H, S-Me], 8.41 [s, 1H, -CH=N-], 7.98 [d, 1H, H^2], 6.95 [m, 1H, H^3], 7.46–7.52 [m, 2H, H^4 and H^5], 7.94 [d, 1H, H^6], 7.16 [d, 1H, H^3], 7.14 [m, 1H, H^4], 7.16 [m, 1H, H^5] and 7.94 [d, 1H, H^6]. $^{13}\text{C}\{^1\text{H}\}$ -NMR data [23]: 14.8 [SMe], 159.0 [-CH=N-], 136.1 [C^1], 129.7 [C^2 and C^6], 131.4 [C^4], 128.9 [C^3 , C^5], 150.0 [C^1], 133.3 [C^2], 117.39 [C^3], 126.3 [C^4], 125.1 [C^5], 126.3 [C^6]. For **5b**: Anal. (%) Calc. for: $\text{C}_{17}\text{H}_{19}\text{NS}$ (found): C, 75.79 (75.8); H, 7.11 (7.1); N, 5.20 (5.2) and S, 11.9 (11.9)%. IR: 1606 and 1616 cm^{-1} . ^1H -NMR data [23]: 2.45 [s, 3H, S-Me], 2.61 [s, 6H, Me], 2.31 [s, 3H, Me], 8.79 [s, 1H, -CH=N-], 6.96 [s, 2H, H^3 and H^5], 7.19 [d, 1H, H^3], 7.14 [m, 1H, H^4], 7.16 [m, 1H, H^5] and 7.32 [d, 2H, H^6]. $^{13}\text{C}\{^1\text{H}\}$ -NMR data [23]: 14.7 [SMe], 21.7 and 21.3 [Me], 160.43 [-CH=N-], 140.1 [C^1], 139.3 [C^2], 129.9 [C^3], 140.1 [C^4], 129.9 [C^5], 139.3 [C^6], 150.2 [C^1], 133.7 [C^2], 117.3 [C^3], 126.0 [C^4], 125.1 [C^5] and 124.0 [C^6].

3.2.2. Preparation of $\text{cis-[Pd}\{R\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}_2\}$ ($R = \text{C}_6\text{H}_5$ (**6a**) or $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$ (**6b**))

A 2.91×10^{-3} mol amount of the corresponding ligand (**5a** or **5b**) was dissolved in 10 cm^3 of methanol,

then a solution formed by $\text{Na}_2[\text{PdCl}_4]$ (0.865 g, 2.93×10^{-3} mol) and methanol (15 cm^3) was added. During the addition an orange precipitate formed. The reaction mixture was stirred at room temperature (r.t.) (ca. $20 \text{ }^\circ\text{C}$) for 2 h. The solid formed was collected by filtration and air-dried [yields: 0.621 g (72.9%) and 0.638 g (68%), for **6a** and **6b**, respectively].

3.2.2.1. Characterization data for 6a. Anal. (%) Calc. for: $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{NSPd}$ (found): C, 41.6 (41.5); H, 3.3 (3.2); N, 3.5 (3.5) and S, 7.91 (7.9)%. IR: 1597 and 1570 cm^{-1} . ^1H -NMR data [23]: 2.81 [s, 3H, -SMe], 8.69 [s, 1H, -CH=N-], 7.83 [d, 1H, H^2], 7.19 [m, 3H, H^3], 7.46–7.50 [m, 2H, H^4 and H^5], 7.60 [d, 1H, H^6], 7.41 [H^3], 7.10 [m, 1H, H^4], 7.14 [m, 1H, H^5] and 7.71 [d, 1H, H^6]. For **6b**: Anal. (%) Calc. for: $\text{C}_{17}\text{H}_{19}\text{Cl}_2\text{NSPd}$ (found) C, 45.75 (45.8); H, 4.29 (4.3); N, 3.14 (3.2) and S, 7.18 (7.0)%. IR: 1590 and 1567 cm^{-1} . ^1H -NMR data [23]: 2.99 [s, 3H, -SMe], 9.68 [s, 1H, -CH=N-], 2.30 [s, 3H, Me], 2.17 [s, 3H, Me], 1.90 [s, 3H, Me], 6.88 [s, 1H, H^3], 6.81 [s, 1H, H^5], 7.04 [t, 1H, H^2], 7.58 [d, 1H, H^3], 7.31 [t, 1H, H^4] and 6.72 [d, 1H, H^6]. $^{13}\text{C}\{^1\text{H}\}$ -NMR data [23]: 27.3 [-SMe], 19.5 and 21.3 [Me], 178.9 [-CH=N-], 145.3 [C^1], 129.3 [C^3 and C^5], 157.9 [C^1], 132.3 [C^2], 120.3 [C^3], 130.2 [C^4], 130.3 [C^5] and 133.3 [C^6].

3.2.3. Preparation of $[\text{Pd}\{R\text{-CH=N-(C}_6\text{H}_4\text{-2-SMe)}\}\text{Cl}]$ (**7a**)

Compound **6a** (0.500 g, 1.23×10^{-3} mol) was suspended in 25 cm^3 of methanol [22], then sodium acetate (0.101 g, 1.23×10^{-3} mol) was added. The resulting reaction mixture was then refluxed for 12 h and allowed to cool to r.t. (ca. $20 \text{ }^\circ\text{C}$). Then the undissolved materials removed by filtration and discarded and the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with CH_2Cl_2 (ca. 20 cm^3), filtered out and passed through a SiO_2 -column chromatography using CH_2Cl_2 as eluant. The band released was collected and slow evaporation of the solution produced yellowish crystals which were collected and air-dried. (Yield: 0.305 g, 67.5%).

3.2.3.1. Characterization data. Anal. (%) Calc. for: $\text{C}_{14}\text{H}_{12}\text{ClNSPd}$ (found): C, 45.63 (45.3); H, 3.25 (3.2); N, 3.80 (3.7) and S, 8.69 (8.5)%. IR: $\nu (>\text{C=N-}) = 1590 \text{ cm}^{-1}$. ^1H -NMR data [23]: 2.80 [s, 3H, -SMe], 8.66 [s, 1H, -CH=N-], 7.80 [d, 1H, H^6], 7.60 [d, 1H, H^2], 7.43 [m, 3H, H^3 , H^4 and H^5], 7.75 [d, 2H, H^4 and H^5], 7.18 [t, 1H, H^6] and 7.02 [t, 1H, H^3]. $^{13}\text{C}\{^1\text{H}\}$ -NMR data [23]: 24.5 [SMe], 167.4 [-CH=N-], 148.2 [C^1], 147.2 [C^2], 129.4 [C^3], 125.2 [C^4], 135.6 [C^5], 149.4 [C^1], 125.2 [C^2], 118.2 [C^3], 131.2 [C^4], 129.4 [C^5] and 134.2 [C^6].

3.2.4. Preparation of $[Pd\{(2-CH_2-4,6-Me_2)-C_6H_2-CH=N-(C_6H_4-2-SMe)\}Cl]$ (**7b**)

This complex was prepared according to the procedure described above for **7a**, but using complex **6b** as starting material and the stoichiometric amount of sodium acetate. In this case the reaction mixture was refluxed for 18 h and allowed to cool to r.t. (ca. 20 °C). Then the solution was filtered out, the undissolved materials were discarded and the filtrate was concentrated to dryness on a rotary evaporator. The residue was treated with CH_2Cl_2 (20 cm³), filtered out and passed through a SiO_2 -column chromatography. Slow evaporation of the solution obtained from the first band produced orange crystals which were collected and air-dried. (Yield: 0.313 g, 62%). The concentration to dryness of the second band yielded small amounts of unreacted complex **6b** (ca. 11%).

3.2.4.1. Characterization data. Anal. (%) Calc. for $C_{17}H_{18}ClN_2SPd$ (found): C, 49.70 (49.6); H, 4.42 (4.4); N, 3.41 (3.5) and S, 7.81 (7.8)%. IR: 1565 and 1568 cm^{-1} . ¹H-NMR data [23]: 2.44 [s, 3H, -SMe], 2.29 [s, 3H, Me], 2.43 [s, 3H, Me], 3.69 [m, 2H, -CH₂-], 6.81 [s, 1H, H³], 7.18 [s, 1H, H⁵], 8.39 [s, 1H, -CH=N-], 7.65 [d, 1H, d, 2H, H³], and 7.40–7.50 [m, 3 H, H⁴, H⁵ and H⁶]. ¹³C{¹H}-NMR data [23]: 23.1 [SMe], 27.3 [C-Pd], 19.6 and 21.7 [Me], 176.4 [-CH=N-], 140.1 [C¹], 128.2 [C²], 148.1 [C⁴], 126.9 [C⁵], 157.8 [C¹], 130.3 [C²], 117.9 [C³], 130.3 [C⁴], 126.9 [C⁵], 133.3 [C⁶].

3.2.5. Preparation of compounds **8**

Triphenylphosphine (50 mg, 1.91×10^{-4} mol) was added to a CH_2Cl_2 solution (50 cm³) containing the equimolar amount (1.91×10^{-4} mol) of the corresponding cyclopalladated complex **7a** or **7b**. The reaction mixture was stirred at r.t. (ca. 20 °C) for ca. 20 min and filtered out. The filtrate was concentrated on a rotary evaporator to ca. 5 ml. The yellow (for **7a**) or orange (for **7b**) solid formed was collected and dried under vacuum for 2 days. Yields: 0.106 g (88.3%) for **8a** and 0.107 g (83.4%) for **8b**.

3.2.5.1. Characterization data for 8a. Anal. (%) Calc. for: $C_{32}H_{27}NCIFeNPPdS$ (found): C, 60.96 (60.8); H, 4.32 (4.3); N, 2.22 (2.2) and S, 5.09 (5.0)%. IR: 1597 cm^{-1} . ¹H-NMR data [23]: 2.80 [s, 3H, -SMe], 8.66 [s, 1H, -CH=N-], 7.80 [d, 1H, H⁶], 7.60 [d, 1H, H²], 7.43 [m, 3H, H³, H⁴ and H⁵], 7.75 [d, 2H, H⁴ and H⁵], 7.18 [t, 1H, H⁶] and 7.02 [t, 1H, H³]. ³¹P{¹H}-NMR data: 38.09. For **8b**: Anal. (%) Calc. for: $C_{35}H_{33}ClNPPdS$ (found): C, 62.51 (62.3); H, 4.95 (5.0); N, 2.00 (2.1) and S, 4.77 (4.7)%. IR: 1580 and 1592 cm^{-1} . ¹H-NMR data [23]: 2.62 [s, 3H, -SMe], 1.96 [s, 3H, Me], 2.19 [s, 3H, Me], 3.33 [m, 2H, -CH₂-], 6.04 [s, 1H, H³], 6.98 [s, 1H, H⁵], 8.02 [d, 1H, H³], 8.55 [s, 1H, -CH=N-] and 7.40–7.50 [m, 18H, H⁴, H⁵, H⁶ and aromatic protons of the

PPh_3 ligand]. ¹³C{¹H}-NMR (selected data) [23]: 24.0 [SMe], 37.2 [C-Pd], 20.4 and 21.9 [Me], 161.1 [-CH=N-], 144.9 [C¹], 143.8 [C²], 129.5 [C³], 147.7 [C⁴], 128.7 [C⁵], 151.9 [C¹], 131.2 [C²], 120.3 [C³], 131.7 [C⁴], 127.3 [C⁶] and four additional doublets centered at ca. 133.9, 131.9 and 131.2 and 129.1. The signals due to the [C⁵] and [C⁶] carbon atoms are partially masked by these doublets. ³¹P{¹H}-NMR data (in ppm): 34.79.

3.3. Crystallography

A prismatic crystal of **6b**, **7a** or **7b** was selected and mounted on a MAR345 diffractometer with image plate detector (for **6b**) or on a ENRAF-CAD4 four-circle diffractometer (for **7a** and **7b**). Unit cell parameters were determined from automatic centring of 25 reflections in the range $12 < \theta < 21^\circ$ and refined by least-squares method. Intensities were collected with a graphite monochromatized Mo-K α radiation, using $\omega-2\theta$ scan-technique. For **6b**, 9934 reflections were measured in the range: $3.08 \leq \theta \leq 28.84^\circ$, of which 3994 were non-equivalent by symmetry $\{R_{int}(\text{on } I) = 0.069\}$, 1987 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **7a**, 4167 reflections were measured in the range $2.47 \leq \theta \leq 29.97^\circ$, of which 3963 were non-equivalent by symmetry $\{R_{int}(\text{on } I) = 0.020\}$. For **7b**, 4738 reflections were measured in the range $2.32 \leq \theta \leq 29.94^\circ$, of which 2226 were assumed as observed. In the three cases, Lorentz polarization corrections were made but absorption corrections were not performed. The structures were solved by direct methods using SHELXS computer program [24] and refined by full-matrix least-squares method with SHELX97 computer program [25], using 3963 reflections for **7a** (very negative intensities were not assumed). The function minimized was $\sum w \{|F_o|^2 - |F_c|^2|^2$, where $w = \{\sigma^2(I) + (0.0163 P)^2\}^{-1}$ for **6b**; $w = \{\sigma^2(I) + (0.0396 P)^2 + (0.2477 P)\}^{-1}$, for **7a** and $w = \{\sigma^2(I) + (0.0094 P)^2\}^{-1}$ for **7b**, and $P = \{|F_o|^2 - 2|F_c|^2\}/3$; f , f' and f'' were taken from the literature [26]. For compound **6b**, nine-hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and the remaining ten hydrogen atoms were computed and refined with an overall isotropic temperature factor equals to 1.2 times the equivalent isotropic temperature factor of the attached atom, using a riding model. For **7a**, all hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. For **7b**, all hydrogen atoms were computed and refined with an overall isotropic temperature factor equals to 1.2 times the equivalent isotropic temperature factor of the attached atom, using a riding model. The final $R(\text{on } F)$ factor were: 0.026 (for **6b**) and 0.035 (for **7a**) and 0.029 (for **7b**), $wR(\text{on } F_o) = 0.040$ (for **6b**) and 0.074 (for **7a**) and 0.045 (for **7b**) and the goodness-of-fit were 0.792 (for **6b**), 1.031 (for **7a**)

Table 3

Crystal data and details of the refinement of the crystal structures of compounds: *cis*-[Pd{(2,4,6-Me₃-C₆H₂)-CH=N-(C₆H₄-2-SMe)}Cl₂] (**6b**), [Pd{(C₆H₄-CH=N-(C₆H₄-2-SMe)}Cl] (**7a**) and [Pd{(2-CH₂-4,6-Me₂-C₆H₂)-CH=N-(C₆H₄-2-SMe)}Cl] (**7b**)

	6b	7a	7b
Empirical formula	C ₁₇ H ₁₉ Cl ₂ NPdS	C ₁₄ H ₁₂ ClNPdS	C ₁₇ H ₁₈ ClNPdS
Formula weight	446.69	368.16	410.23
Temperature (K)	293(2)	293(2)	293(2)
λ (Mo-K α) (Å)	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.432(1)	9.985(9)	10.376(8)
<i>b</i> (Å)	8.112(1)	12.367(5)	11.056(15)
<i>c</i> (Å)	16.660(1)	11.100(3)	14.487(15)
$\alpha = \gamma$ (°)	90.0	90.0	90.0
β (°)	101.956(1)	96.21(4)	91.60(7)
<i>V</i> (Å ³)	1775.9(3)	1362.6(14)	1661(3)
<i>Z</i>	4	4	4
<i>D</i> _{calc.} (mg m ⁻³)	1.671	1.795	1.640
Absorption coefficient (mm ⁻¹)	1.458	1.690	1.396
<i>F</i> (000)	896	728	824
Crystal size (mm ³)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.2
θ Range for data collection (°)	From 3.08 to 28.84	From 1.47 to 29.97	From 2.32 to 29.94
Index ranges	-16 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 10, 0 ≤ <i>l</i> ≤ 22	-14 ≤ <i>h</i> ≤ 12, -6 ≤ <i>k</i> ≤ 17, -1 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 20
Number of reflections collected	9934	4167	4738
Number of unique reflections	3994 [<i>R</i> _{int} = 0.0692]	3963 [<i>R</i> _{int} = 0.0209]	4738 [<i>R</i> _{int} = 0.0000]
Completeness to 2 θ = 29.97°	75.3%	95.7%	93.5%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Number of data	3994	3963	4738
Number of parameters	235	212	199
Goodness-of-fit on <i>F</i> ²	0.792	1.031	0.810
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0264, <i>wR</i> ₂ = 0.0407	<i>R</i> ₁ = 0.0356, <i>wR</i> ₂ = 0.0748	<i>R</i> ₁ = 0.0291, <i>wR</i> ₂ = 0.0454
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1034, <i>wR</i> ₂ = 0.0463	<i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.0855	<i>R</i> ₁ = 0.1256, <i>wR</i> ₂ = 0.0603
Extinction coefficient		0.0040(4)	
Largest difference peak and hole (e Å ⁻³)	0.528 and -0.791	0.756 and 0.474	0.479 and -0.930

and 0.810 (for **7b**) for all the observed reflections. The values of the *R* indices and further details concerning the resolution and refinement of this crystal structure are presented in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC no. 172 570, 172 571 and 172 572. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.ac.uk; or www: <http://www.ccdc.cam.ac.uk>).

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