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SYNTHESIS AND CHARACTERIZATION OF CYCLOPALLADATED AND NON-CYCLOPALLADATED COMPLEXES OF LIGANDS CONTAINING THE 1,3-BIS(THIOMETHYL)BENZENE UNIT

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Abstract—The reactivity of $[Pd(CH_3CN)_2)Cl_2]$ toward the ligands 1,3-bis(ethylthiomethyl)benzene (HL^1), 1,3-bis(benzylthiomethyl)benzene (HL^2), 1,3-bis(phenylthiomethyl) benzene (HL^3) and dimethyl 2,2′-[1,3-phenylenebis(methylthio)]-dibenzoate (HL^4) has been investigated. In all cases the reaction of the palladium(II) salt with the corresponding ligand in acetonitrile at room temperature afforded the simple non-cyclopalladated complex. Analytical and spectroscopic data of these complexes suggest that the two sulfur atoms of the ligands and two chlorine atoms coordinate simultaneously to the palladium ion defining monomeric species. Cyclopalladated complexes of ligands HL^1–HL^4 have been obtained by refluxing their non-cyclopalladated derivatives in acetonitrile or by direct reaction of the starting materials in the same solvent at refluxing temperature. Different reaction times have been found depending on the ligand. Cyclopalladated complexes of ligands HL^1, HL^2 and HL^4 have been characterized by X-ray diffraction methods. All of them display square-planar coordination around the palladium atom provided by the rigid S_2C chelating moiety of the 1,3-bis(thiomethyl)benzene unit and the chlorine atom which is located in a *trans* position with respect to the Pd—C bond. Copyright © 1996 Elsevier Science Ltd

The intramolecular activation of aromatic C—H bonds by transition metal ions in coordinated ligands is a very well known phenomenon, usually termed as cyclometallation.[1] Cyclometallated complexes, which can be obtained through different synthetic strategies,[2] have been shown to be very important starting materials for organic synthesis,

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especially those containing palladium as metallating agent. For instance, it is well documented that cyclopalladated complexes may be selectively functionalized with different substrates at the metallated carbon atom[3,4] or may undergo intramolecular cyclation yielding heterocyclic compounds.[3] In all cases the nature of the cyclopalladated ligand conditions the final organic product. The interest in developing more selective and efficient synthetic routes has made that area of cyclopalladated systems grow continuously.

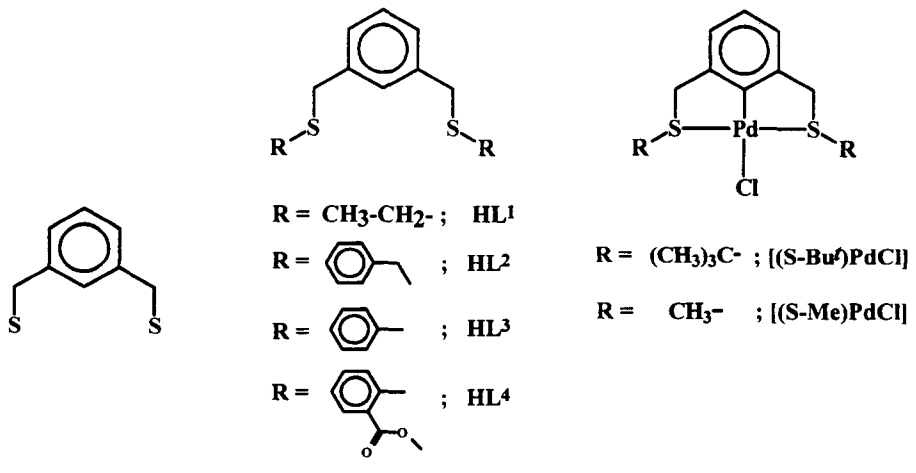
According to the literature, the information on cyclopalladated sulfur-containing metallocycles[5] is relatively limited compared to their group 15 counterparts.[2,6] It is well-known that cyclopalladation of benzylthioethers is a less favoured process with regard to the formation of simple non-palladated complexes, mainly when coordinating anion-containing palladium salts are used.[5a,7] In any case, compounds containing the 1,3-bis(thiomethyl)benzene unit (Scheme 1a) seem to display a better capacity to undergo cyclopalladation reactions,[8,9] in contrast to simple alkyl or aryl benzylthioethers. Recently, Loeb *et al.* have studied the cyclometallation processes in different macrocyclic ligands, all of them containing the 1,3-bis(thiomethyl)benzene unit.[10] This work showed that the cavity size of the macrocyclic ligand is a key factor to promote the cyclometallation reaction.[10b] The same authors have also suggested that some of these cyclopalladated macrocycles could act as selective metalloreceptors toward amino-substituted pyridines.[10c]

It was suggested in earlier works that only 1,3-bis(thiomethyl)benzene-based ligands including bulky groups attached to the sulfur atoms could undergo cyclopalladation reactions;[8] however, exceptions to this initial assumption have been found.[9,10] In earlier works we have studied the effect of the sulfur substitution in closely related systems containing the 1,3-bis(thiomethyl)pyridine unit, proving that the electronic properties of their complexes are appreciably influenced by the nature of the organic group attached to the sulfur atoms.[11] For this reason it seemed to us interesting to learn more on sulfur substitution in cyclopalladation. Thus, studies on the complexing behaviour of sulfur-substituted 1,3-bis(thiomethyl)benzene-based ligands in front of palladium salts were undertaken.

In this paper we describe the reactivity of $[Pd(CH_3CN)_2Cl_2]$ toward ligands HL^1–HL^4 (Scheme 1b), in which aliphatic substituents are attached to the sulfur atoms of the 1,3-bis(thiomethyl)benzene units (S—Alif ligands, HL^1 and HL^2) or where aromatic substituents are in the same position (S—Ar ligands, HL^3 and HL^4). We also report on the synthesis of their non-cyclopalladated and cyclopalladated derivatives. Some of them have been structurally characterized by X-ray diffraction methods.

EXPERIMENTAL

Syntheses were carried out using standard Schlenk techniques under dry N_2. Solvents were dried by conventional methods and distilled under N_2 before use. Methyl 2-mercaptobenzoate and 1,3-bis(chloromethyl)benzene are commercially avail-



(a) (b) (c)

Scheme 1.

able. The 1,3-bis(ethylthiomethyl)benzene (HL^1) and 1,3-bis(phenylthiomethyl)benzene (HL^3) ligands were prepared according to published procedures.[12,13] Elemental analyses were performed in the "Servei d'Anàlisi Química de La Universitat Autònoma de Barcelona" on a Carlo Erba EA-1108 instrument. ^1H and $^{13}C\{^1H\}$ NMR were carried out in the "Servei de RMN de la Universitat Autònoma de Barcelona" on a Bruker 400 MHz AC instrument.

Preparation of ligands

1,3-*Bis*(*benzylthiomethyl*)*benzene* (HL^2). Benzylmercapture (7.09 g, 57 mmol) was added to a stirred solution of 85% KOH (3.76 g, 57.0 mmol) in 1-butanol (200 cm^3). The mixture was refluxed for a further 30 min and added to a solution of 1,3-dichloro-*m*-xylene (5 g, 28.5 mmol) in 1-butanol (100 cm^3) and refluxed for a further hour. The KCl precipitate was filtered off and the remaining solution was evaporated to yield a pale yellow oil. The oil was dissolved in diethyl ether, washed with aqueous Na_2CO_3 and water, and dried over $MgSO_4$. The organic solution was evaporated and the white solid HL^2 obtained was filtered off and recrystallized from methanol. Yield 50% (4.80 g). Found: C, 74.9; H, 6.5; S, 17.9. Calc. for $C_{22}H_{22}S_2$: C, 75.3; H, 6.3; S; 18.3%. ^1H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 4H, S—C$\underline{H}_2$—Ph), 3.67 (s, 4H, S—C$\underline{H}_2$—Ph), 7.19–7.32 (m, 14H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 36.23, 36.32 (S—$\underline{C}H_2$—Ph), 127.71, 128.42, 129.25, 129.35, 129.87, 130.52, 139.44, 139.62 (Ph).

Dimethyl 2,2′-[1,3-*phenylenebis*(*methylthio*)]-*dibenzoate* (HL^4). Methyl 2-mercaptobenzoate (9.35 g, 56.0 mmol) was added to a stirred solution of sodium metal (1.29 g, 56.0 mmol) in methanol (150 cm^3) and the mixture stirred for a further 10 min. The mixture was then added to a solution of 1,3-dichloro-*m*-xylene (4.87 g, 28.0 mmol) in methanol (70 cm^3). After the addition a white precipitate appeared. The mixture was refluxed for 30 min and then cooled to room temperature. The precipitate was filtered off, washed with methanol, vacuum dried and recrystallized from THF to afford HL^4 as a white crystalline product. Yield 97% (11.8 g). Found: C, 65.9; H, 5.1; S, 14.5. Calc. for $C_{24}H_{22}O_4S_2$: C, 65.8; H, 5.0; S; 14.6%. ^1H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 6H, CH_3—OOC—), 4.08 (s, 4H, S—C$\underline{H}_2$—Ph), 7.08–7.92 (m, 12H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 37.03, (S—$\underline{C}H_2$—Ph), 52.11 ($\underline{C}H_3$—OOC—), 124.01, 125.92, 127.35, 128.05, 128.83, 129.72, 131.14, 132.32, 136.40, 141.72 (Ph), 166.8 (—OOC—).

Preparation of non-cyclopalladated complexes $[Pd(HL)Cl_2]$ (HL = HL^1, HL^2, HL^3 *and* HL^4) (**1**–**4**)

In a typical reaction, equimolar solutions of $[Pd(CH_3CN)_2Cl_2]$ and the appropriate ligand (HL^1, HL^2, HL^3 or HL^4), each one dissolved in *ca* 2 cm^3 of acetone, were mixed and stirred. In all cases the solution changed colour immediately from orange to pale yellow and an orange solid precipitated which was filtered off and vacuum dried.

$[Pd(HL^1)Cl_2]$ (**1**). The reactants were $[Pd(CH_3CN)_2Cl_2]$ (0.11 g, 0.44 mmol) and HL^1 (0.10 g, 0.44 mmol). Yield: 62% (0.11 g). Found: C, 35.7; H, 4.7; S, 15.9; Cl, 17.7. Calc. for $C_{12}H_{18}S_2PdCl_2$: C, 35.7; H, 4.5; S; 15.9; Cl, 17.6%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, 6H, S—$CH_2C\underline{H}_3$, $J = 7.1$ Hz), 2.71 (q, 4H, S—$C\underline{H}_2$—CH_3, $J = 7.1$ Hz), 4.12 (s, 4H, S—$C\underline{H}_2$—Ph), 7.35–7.49 (m, 4H, Ph).

$[Pd(HL^2)Cl_2]$ (**2**). The reactants were $[Pd(CH_3CN)_2Cl_2]$ (0.07 g, 0.28 mmol) and HL^2 (0.10 g, 0.28 mmol). Yield: 73% (0.11 g). Found: C, 49.8; H, 4.3; S, 11.9; Cl, 13.4. Calc. for $C_{22}H_{22}S_2PdCl_2$: C, 50.1; H, 4.2; S; 12.1; Cl, 13.4%. ^1H NMR (400 MHz, $CDCl_3$): δ 4.21 (s, br, 4H, S—C$\underline{H}_2$—Ph), 4.50 (s, 4H, S—C$\underline{H}_2$—Ph), 6.88–7.44 (m, 14H, Ph).

$[Pd(HL^3)Cl_2]$ (**3**). The reactants were $[Pd(CH_3CN)_2Cl_2]$ (0.08 g, 0.31 mmol) and HL^3 (0.10 g, 0.31 mmol). Yield: 86% (0.13 g). Found: C, 47.4; H, 3.7; S, 12.5; Cl, 14.6. Calc. for $C_{20}H_{18}S_2PdCl_2$: C, 48.1; H, 3.6; S; 12.8; Cl, 14.2%.

$[Pd(HL^4)Cl_2]$ (**4**). The reactants were $[Pd(CH_3CN)_2Cl_2]$ (0.06 g, 0.31 mmol) and HL^4 (0.10 g, 0.23 mmol). Yield: 78% (0.11 g). Found: C, 47.1; H, 3.8; S, 10.8; Cl, 11.6. Calc. for $C_{24}H_{22}S_2O_4PdCl_2$: C, 46.9; H, 3.6; S; 10.4; Cl, 11.4%.

Preparation of cyclopalladated complexes [Pd(L)Cl] (L = L^1, L^2, L^3 *and* L^4) (**5**–**8**)

Method A. Equimolar solutions of $[Pd(CH_3CN)_2Cl_2]$ and the appropriate ligand (HL^1, HL^2, HL^3 or HL^4), each dissolved in *ca* 75 cm^3 of acetonitrile, were mixed and refluxed for 20–150 h depending on the ligand used. Initially, an orange precipitate appeared that slowly redissolved almost totally to afford a yellow solution. After that the mixture was filtered off, the clean solution was allowed to stand at room temperature until a yellow crystalline precipitate appeared which was filtered off and vacuum dried. For **5**, **6** and **8**, single crystals suitable for X-ray diffraction analysis were obtained directly.

[Pd(L^1)Cl] (**5**). The reactants were [Pd(CH$_3$CN)$_2$Cl$_2$] (0.10 g, 0.39 mmol) and HL^1 (0.09 g, 0.30 mmol). Refluxing time; 20 h. Yield: 47% (0.07 g). Found: C, 38.9; H, 4.8; S, 17.0; Cl, 9.9. Calc. for $C_{12}H_{17}S_2PdCl$: C, 39.2; H, 4.7; S; 17.4; Cl, 9.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, 6H, S—CH$_2$—CH$_3$, J = 7.2 Hz), 3.17 (q, 4H, S—CH$_2$—CH$_3$, J = 7.2 Hz), 4.38 (s, br, 4H, S—CH$_2$—Ph), 6.96–6.98 (m, 3H, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 14.75 (S—CH$_2$—CH$_3$), 33.35 (S—CH$_2$—CH$_3$), 45.88 (S—CH$_2$—Ph), 128.79, 129.56, 144.51, 155.30 (Ph).

[Pd(L^2)Cl] (**6**). The reactants were [Pd(CH$_3$CN)$_2$Cl$_2$] (0.10 g, 0.39 mmol) and HL^2 (0.14 g, 0.39 mmol). Refluxing time: 20 h. Yield: 86% (0.16 g). Found: C, 53.7; H, 4.4; S, 13.0; Cl, 7.2. Calc. for $C_{22}H_{21}S_2PdCl$: C, 53.8; H, 4.3; S; 13.1; Cl, 7.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00 (s, br, 4H, S—CH$_2$—Ph), 4.43 (s, br, 4H, S—CH$_2$—Ph), 6.80–7.50 (m, 13H, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 42.06, 44.70 (S—CH$_2$—Ph), 122.40, 124.84, 128.39, 128.98, 129.72, 134.40, 141.54, 141.78 (Ph).

[Pd(L^3)Cl] (**7**). The reactants were [Pd(CH$_3$CN)$_2$Cl$_2$] (0.10 g, 0.39 mmol) and HL^3 (0.13 g, 0.39 mmol). Refluxing time: 150 h. Yield: 80% (0.15 g). Found: C, 51.6; H, 3.6; S, 13.9; Cl, 7.9. Calc. for $C_{20}H_{17}S_2PdCl$: C, 52.0; H, 3.7; S; 13.8; Cl, 7.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.55 (s, br, S—CH$_2$—Ph), 6.91–7.79 (m, 13H, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 51.67 (S—CH$_2$—Ph), 122.22, 124.90, 129.63, 129.79, 131.43, 132.40, 146.00, 146.89 (Ph).

[Pd(L^4)Cl] (**8**). The reactants were [Pd(CH$_3$CN)$_2$Cl$_2$] (0.10 g, 0.39 mmol) and HL^4 (0.17 g, 0.39 mmol). Refluxing time: 150 h. Yield: 84% (0.19 g). Found: C, 50.0; H, 3.5; S, 10.8; Cl, 6.3. Calc. for $C_{24}H_{221}S_2O_4PdCl$: C, 49.7; H, 3.8; S; 11.1; Cl, 6.0%.

Method B. A suspension of **1**, **2**, **3** or **4** (0.10 mmol) in acetonitrile (50 cm^3) was refluxed until almost all the solid was dissolved (20 h for **1** and **2**, 100 h for **3** and **4**). After that the mixture was filtered and the clean solution was allowed to stand at room temperature until a yellow crystalline precipitate appeared which was filtered off and vacuum dried. Yields: 51% (0.02 g) for **5**, 81% (0.04 g) for **6**, 86% (0.04 g) for **7** and 78% (0.05 g) for **8**.

Crystallography

Single-crystal diffraction data of species **5**, **6** and **8** were collected at room temperature; unit cell parameters were determined from a least-squares refinement of the setting angles of 25 carefully centred reflections. Crystal data and data collection details for the compounds are presented in Table 1. During the data collection the stability of crystals was followed by measuring the intensity of three check reflections periodically. The data obtained were corrected for Lorentz and polarization effects and for dispersion. Corrections for empirical absorption (ψ scan; not for **6**) and secondary extinction (coefficient = 0.16995×10^{-5})[14] for **5** were also applied.

The structure of **5** was solved by direct methods using MITRIL.[15] Least-squares refinements and all subsequent calculations for this compound were performed using the TEXSAN[16a] crystallographic software package, which minimized the function $\Sigma w(\Delta F)^2$, where $w = 1/\sigma^2(F_o)$. Refinement of all anisotropic non-hydrogen atoms and hydrogen atoms with fixed isotropic temperature parameters (1.2 times B_{eq} of the carrying atom) reduced the R value to 0.023 (R_w = 0.030) for 197 parameters. Neutral atomic scattering factors were those included in the program. Structures were plotted with ORTEP.[16b]

The structure of **6** was solved by direct methods by using the SHELXS86 program.[17] Least-squares refinements and all subsequent calculations were performed using XTAL program system.[18] The asymmetric unit of **6** consists of one-half of the molecule having two-fold symmetry. After refinement of all non-hydrogen atoms anisotropically, a subsequent difference Fourier map revealed the approximate positions of all hydrogen atoms. Refinement of all atoms except H(4), with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, reduced the R value to 0.046 (R_w = 0.033) for 160 parameters. Neutral atomic scattering factors were those included in the programs. The structure of **8** was solved and refined with the same programs in a similar way as for **6**, yielding a final R value of 0.035 (R_w = 0.035) for 189 parameters. Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom coordinates, thermal parameters and remaining bonding parameters.

RESULTS AND DISCUSSION

Non-cyclopalladated complexes [Pd(HL)Cl$_2$] (**1–4**)

The reaction of equimolar amounts of [Pd(CH$_3$CN)$_2$Cl$_2$] and the corresponding ligands HL^1–HL^4 (Scheme 1) in acetonitrile at room temperature yielded complexes of stoichiometry [Pd(HL)Cl$_2$] (HL = HL^1–HL^4; Scheme 2). All these complexes are orange coloured, non-crystalline solids and their solubility strongly depends

Table 1. Crystal data for compounds [Pd(L^1)Cl] (**5**), [Pd(L^2)Cl] (**6**) and [Pd(L^4)Cl] (**8**)

	5	**6**	**8**
Formula	$C_{12}H_{17}ClPdS_2$	$C_{22}H_{21}ClPdS_2$	$C_{24}H_{21}ClO_4PdS_2$
M	367.24	491.36	579.38
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (no. 14)	*Pbcn* (no. 60)	$C2/c$ (no. 15)
$F(000)$	736	992	1168
a (Å)	10.336(1)	19.577(6)	9.601(1)
b (Å)	11.6028(9)	11.552(5)	14.637(3)
c (Å)	11.7285(6)	9.022(3)	16.050(3)
β (°)	90.863(6)		96.51(1)
U (Å^3)	1406.3(2)	2040(2)	2241.0(7)
D_c (g cm^{-3})	1.73	1.60	1.72
Z	4	4	4
Specimen size (mm^3)	$0.10\times0.26\times0.28$	$0.20\times0.16\times0.28$	$0.24\times0.20\times0.35$
μ_{Mo} (cm^{-1})	17.5	12.5	11.6
Diffractometer	Rigaku AFC5S	Nicolet P3F	Nicolet P3F
$2\theta_{max}$ (°)	55	55	55
Reflection range	$0\leqslant h\leqslant 13$	$0\leqslant h\leqslant 26$	$0\leqslant h\leqslant 12$
	$0\leqslant k\leqslant 15$	$0\leqslant k\leqslant 16$	$0\leqslant k\leqslant 19$
	$-15\leqslant l\leqslant 15$	$0\leqslant l\leqslant 12$	$-20\leqslant l\leqslant 20$
Unique reflections	3383	2693	2580
Refinement reflections	2723 [$I>2\sigma(I)$]	1662 [$F>2\sigma(F)$]	2355 [$F>2\sigma(F)$]
T_{max}(%)/T_{min}(%)	100/83		100/98
Parameters refined	197	160	189
Residual electron density (e Å^{-3})	−0.28/0.33	−0.9/0.5	−1.1/0.7
R^a	0.023	0.046	0.035
$R_w{}^b$	0.030	0.033	0.035

Details in common: graphite-monochromated Mo-K_α (0.7107 Å) radiation.
[a] $R(F_o)=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.
[b] $R_w(F_o)=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

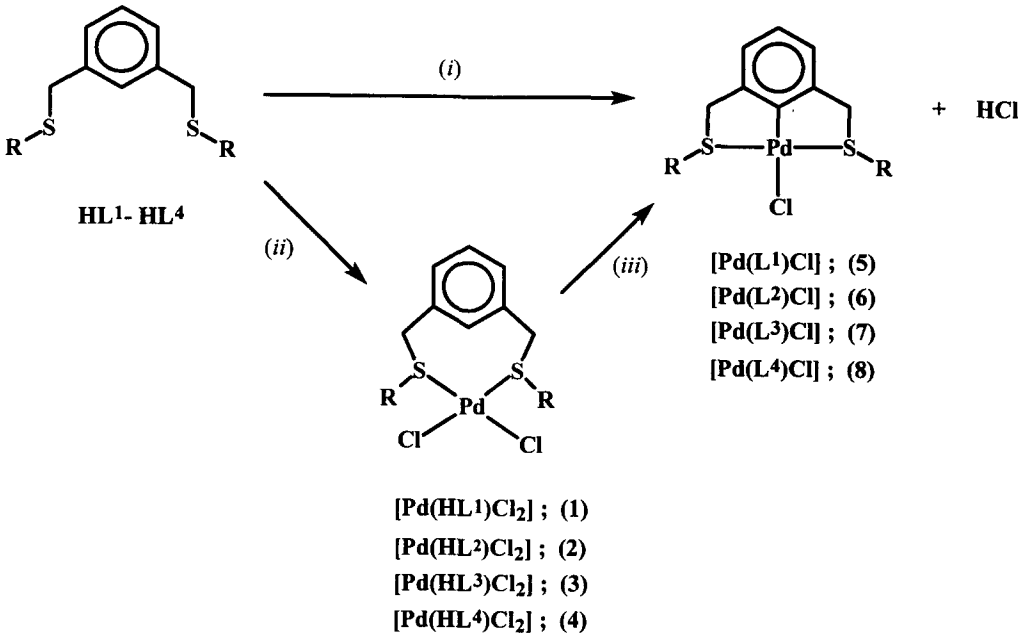
on the particular ligand. Complexes **1** and **2**, which incorporate S—Alif ligands, are slightly soluble in non-polar organic solvents ($CHCl_3$, acetone), but **3** and **4**, which include S—Ar ligands, are insoluble in most common non-coordinating solvents.

The ^{1}H NMR spectra of **1** and **2** display the same pattern of resonance lines as the free ligands, but the signals are shifted downfield by the effect of metal coordination. Taking into account the stoichiometry and the ^{1}H NMR equivalence of the benzylic hydrogen atoms of the 1,3-bis(thiomethyl)benzene unit in all the coordinated ligands, we assume that the two sulfur atoms of the ligands coordinate simultaneously to the palladium ion, defining monomeric species, as shown in Scheme 2.

Cyclopalladated complexes [Pd(L)Cl] (**5–8**)

Cyclopalladated complexes [Pd(L)Cl] (L = L^1–L^4) have been obtained by two different methods (Scheme 2). Method A involves the reaction of equimolar amounts of $[Pd(CH_3CN)_2Cl_2]$ and the corresponding ligands HL^1–HL^4 in a large volume of acetonitrile at refluxing temperature. In all cases, the previous formation of the non-cyclopalladated complex is evident. The more insoluble non-cyclopalladated complexes **3** and **4** first precipitate and later redissolve during the reaction, but for the more soluble ones (**1** and **2**) only a change of the solution colour, from yellow to orange, was observed.

In method B cyclopalladation of ligands HL^1–HL^4 was achieved by refluxing in a large volume of acetonitrile the previously isolated non-cyclopalladated complexes (**1–4**). In all cases the progression of the cyclopalladation reaction can be followed by the progressive change of colour of the solution and the release of HCl. Both methods produce the cyclopalladated compounds **6–8** in good yields (78–86%). Compound **5** is only obtained with a 47–51% yield, probably due to its great solubility in acetonitrile.



Scheme 2. Reaction conditions and reagents: all reactions were performed in acetonitrile. (i) $[Pd(CH_3CN)_2Cl_2]$, reflux; (ii) $[Pd(CH_3CN)_2Cl_2]$, room temperature; (iii) reflux.

The solubilities of cyclopalladated compounds present the same pattern as found in the non-cyclopalladated complexes. Compounds **5** and **6**, which include S—Alif ligands, are soluble in non-polar organic solvents, but compound **7**, which incorporates an S—Ar ligand, exhibits lower solubilities in the same solvents. Compound **8** is insoluble in most common non-coordinating solvents. As a general trend, excluding the complexes derived from the HL^4 ligand, the cyclopalladated complexes are more soluble than the corresponding non-cyclopalladated compounds.

In both methods, the reaction times required to obtain the cyclopalladated complexes depend on the type of ligand used. S—Alif ligands complete the cyclopalladation reaction in 20 h, while S—Ar ligands require 100–150 h in order to get similar yields. No appreciable differences in the reflux time required was observed between the members of the same group of ligands.

The ^1H and ^{13}C NMR spectra of **5–7** present similar groups of resonance lines as found in the free ligands, shifted downfield by the effect of metal coordination. In all cases the benzylic protons of the 1,3-bis(thiomethyl)benzene unit appear as broad signals in the ^1H NMR spectra at room temperature due to the fluxional behaviour of these compounds in solution. This effect is clearly evident in **6**, where ligand L^2 contains four additional benzylic protons that result from the incorporation of two benzyl sulfur substituents to the 1,3-bis(thiomethyl)benzene unit and that appear as a sharp singlet. This fluxional behaviour has been observed by Pfeffer *et al.* in the similar compound[9] [(S—Me)PdCl] (Scheme 1c) and was attributed to the pyramidal inversion of the sulfur atoms and/or to the inversion of the ring puckering of the cyclopalladated compounds, which has been shown to occur in many five-membered metallated rings. These two combined processes give rise to a dynamic equilibrium between two conformational isomers for [(S—Me)PdCl] that make the benzylic protons of the 1,3-bis(thiomethyl)benzene unit non-equivalent. Two broad signals corresponding to the four benzylic protons are observed at room temperature for [(S—Me)PdCl], with a coalescence temperature of *ca* 45°C. ^1H NMR spectra of **5–7** show only one broad signal at room temperature attributed to these benzylic protons, revealing that the coalescence temperature is significantly lower than that found for [(S—Me)PdCl], and consequently the two conformational isomers have a less energetic barrier between them. Unfortunately, our investigations on this fluxional behaviour were limited due to the insolubility and extensive precipitation of these complexes at low temperature.

It is well known that the reaction of benzylmethylthioether and methylcarbonylmanganese easily gives a five-membered *ortho*-metallated ring,[19] whereas the reaction of alkyl[7a] or aryl[7b] ben-

zylthioethers with $PdCl_2$ or $[PdCl_4]^{2-}$ yields non-cyclopalladated complexes. Some authors believed that S—Pd coordinaton in these compounds was so strong that electrophilic substitution at the phenyl group was inhibited.[5a,7b] Later works proved that this problem could be overcome by using other palladium salts without chloride atoms as starting material.[9] As it was pointed out, compounds containing the 1,3-bis(thiomethyl)benzene unit seem to promote cyclopalladation reactions as a consequence of the double activation induced in position 2 of the benzene ring by effect of the 1,3-substitution and/or to the extra stabilization introduced in the final cyclopalladated complex by the effect of the two chelating thioether rings formed. The compound[8] [(S—Bu^t)PdCl] (Scheme 1c) was easily obtained by reaction of the corresponding ligand and $[PdCl_4]^{2-}$ or $[Pd(CH_3CN)_2Cl_2]$, whereas [(S—Me)PdCl] was obtained by a ligand-exchange in high yield.[9] No reference has been made in these works to the non-cyclometallated derivatives, which may be a consequence of the synthetic strategies used. The reactions described here clearly show that non-cyclopalladated complexes of ligands HL^1–HL^4 are isolable intermediate products in the formation of cyclopalladated complexes, as was suggested in earlier works for thiobenzophenone-based ligands.[5a,20]

Cyclopalladation of ligands HL^1–HL^4 was achieved by refluxing their non-cyclopalladated complexes (**1**–**4**) in acetonitrile (method B) or by direct reaction of the starting materials with $[Pd(CH_3CN)_2Cl_2]$ in the same solvent at refluxing temperature (method A). It is accepted that these treatments promote the thermal activation of the C—H bond, facilitating electrophilic attack at the carbon atom of the Pd—C bond.[2] Method A produces cyclopalladated compounds with acceptable yields for ligands HL^1–HL^4 and it seems to indicate that this synthetic procedure could give similar results with related acyclic ligands containing the same 1,3-bis(thiomethyl)benzene unit. Synthetic methods based on ligand-exchange reactions seem to afford cyclopalladated complexes with this kind of ligand in better yields,[9] but the method reported here is advantageous, being a one-pot reaction.

Although all the tested ligands undergo cyclopalladation reactions in the aforementioned conditions, significant differences in the reaction times exist. The S—Ar ligands, HL^3 and HL^4, require longer reflux times than S—Alif in order to achieve similar yields. A possible explanation to this behaviour requires one to assume that the cyclopalladation mechanism involves an electrophilic attack of palladium on the aromatic carbon atom. In this sense, the presence of aromatic sulfur substituents in S—Ar non-cyclopalladate complexes could significantly decrease the electrophilic capability of the palladium ion, which would hinder the cyclopalladation. On the other hand, the different solubilities of S—Alif

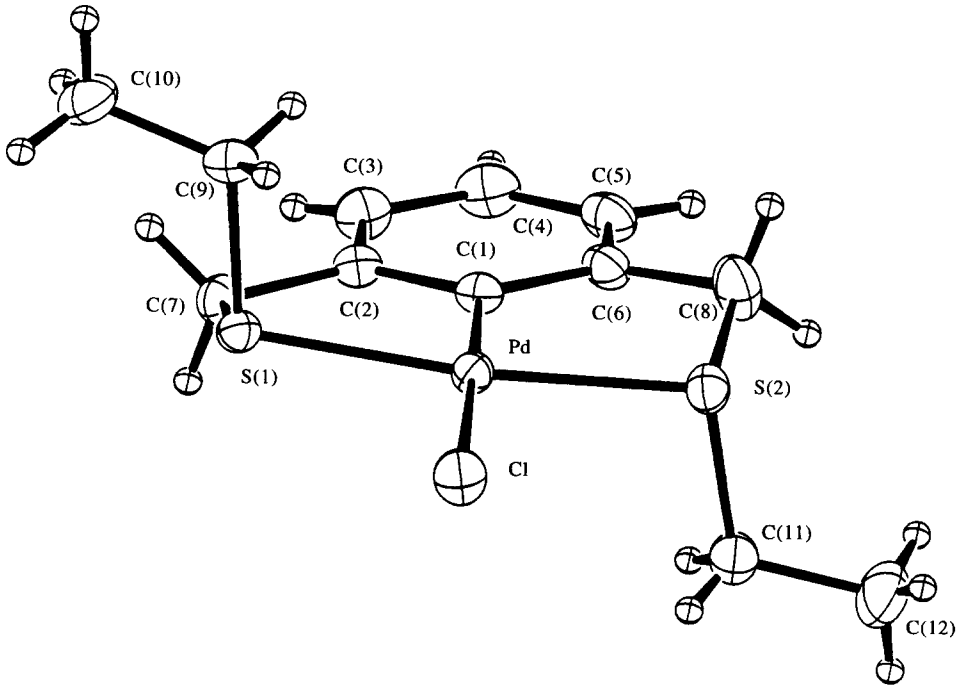


Fig. 1. Perspective view and atom numbering scheme for compound **5** in the form of an ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

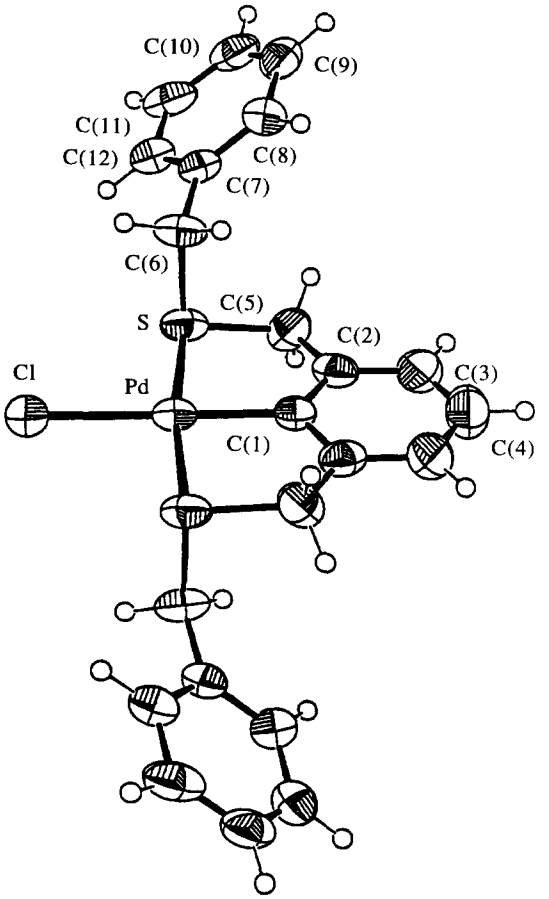


Fig. 2. Perspective view and atom numbering scheme for compound **6** in the form of an ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 50% probability level.

and S—Ar non-cyclopalladated complexes could also affect the reaction times.

Crystal structures of **5**, **6** *and* **8**

ORTEP drawings of complexes **5**, **6** and **8** are shown in Figs 1–3. Selected bonding parameters are given in Tables 2 and 3. All three complexes exhibit square planar geometry at the palladium centre with three donor atoms provided by the rigid S_2C chelating moiety of the 1,3-bis(thiomethyl)benzene unit. The Pd—S bond distances [2.2978(7)–2.301(1) Å] and Pd—C bond distances [1.968(1)–1.983(6) Å] are similar in all the structures and comparable with those observed in related cyclopalladated complexes with acyclic[8] or macrocyclic[10b,c] ligands containing the same 1,3-bis(thiomethyl)benzene unit. The fourth coordination site *trans* to the Pd—C bond is occupied in all cases by a chlorine atom. Pd—Cl distances are in the range 2.390(2)–2.4027(7) Å. Linear Cl—Pd—C(1) angles are found for compounds **6** and **8** and close to linear [177.76(7)°] for compound **5**. All complexes show distortion from ideal square planar geometry due to the two rigid five-membered chelating rings, which is evident in the observed values of the S—Pd—S bond angles [170.62(3)–171.81(4)°]. Complexes **6** and **8** show a two-fold symmetry axis going through Cl, Pd, C(1) and C(4) atoms that is absent in compound **5**. In this case the two ethyl groups bonded to the 1,3-bis(thiomethyl)benzene unit have slightly different orientations, probably due to packing forces in the

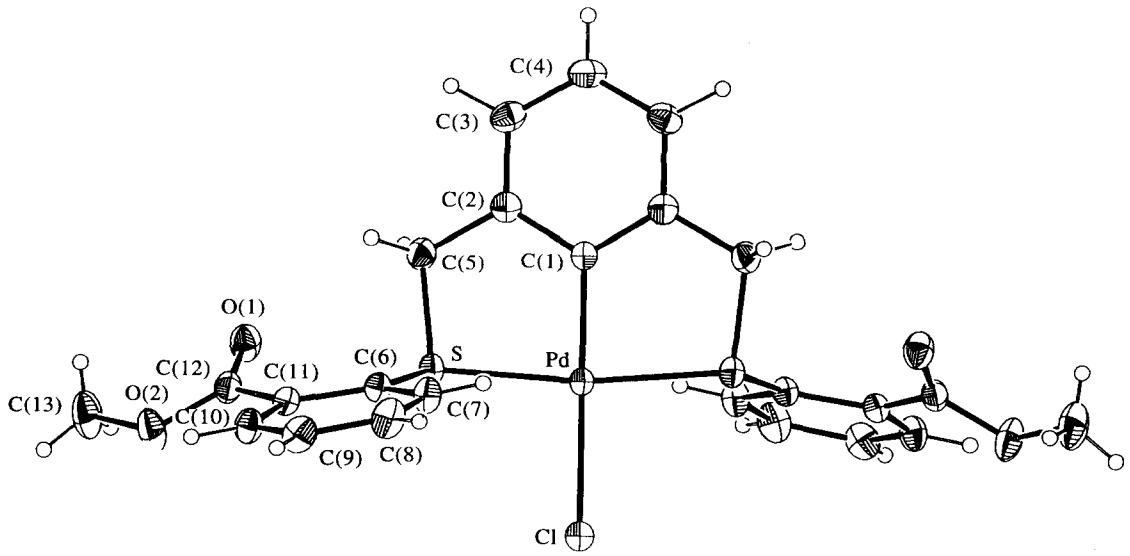


Fig. 3. Perspective view and atom numbering scheme for compound **8** in the form of an ORTEP drawing. Thermal ellipsoids are drawn with surfaces at the 30% probability level.

Table 2. Selected bond lengths (Å) and angles (°) with their e.s.d. values in parentheses for **5**

Pd—Cl	2.4027(7)	S(1)—C(9)	1.823(3)
Pd—S(1)	2.3016(7)	S(2)—C(8)	1.823(4)
Pd—S(2)	2.2978(7)	S(2)—C(11)	1.812(4)
Pd—C(1)	1.977(3)	C(1)—C(2)	1.404(4)
S(1)—C(7)	1.817(3)	C(1)—C(6)	1.408(3)
Cl—Pd—S(1)	93.95(2)	C(7)—S(1)—C(9)	102.4(1)
Cl—Pd—S(2)	95.04(3)	Pd—S(2)—C(8)	100.3(1)
Cl—Pd—C(1)	177.76(7)	Pd—S(2)—C(11)	102.9(1)
S(1)—Pd—S(2)	170.62(3)	C(8)—S(2)—C(11)	102.4(2)
S(1)—Pd—C(1)	85.41(7)	Pd—C(1)—C(2)	120.6(2)
S(2)—Pd—C(1)	85.71(7)	Pd—C(1)—C(6)	120.7(2)
Pd—S(1)—C(7)	100.08(9)	C(2)—C(1)—C(6)	118.7(2)
Pd—S(1)—C(9)	100.8(1)		

Table 3. Selected bond lengths (Å) and angles (°) with their e.s.d. values in parentheses for **6** and **8**

	6	**8**
Pd—Cl	2.390(2)	2.396(1)
Pd—S	2.301(1)	2.3011(7)
Pd—C(1)	1.983(6)	1.968(4)
S—C(5)	1.808(6)	1.823(4)
S—C(6)	1.833(5)	1.790(3)
C(1)—C(2)	1.407(5)	1.410(4)
Cl—Pd—S	94.50(3)	94.09(2)
Cl—Pd—C(1)	180.00	180.00
S—Pd—S#	170.99(5)	171.81(4)
Pd—S—C(5)	100.6(2)	100.9(1)
Pd—S—C(6)	102.0(2)	107.7(1)
C(5)—S—C(6)	1001.(3)	103.2(2)
Pd—C(1)—C(2)	120.3(3)	120.8(2)
C(2)—C(1)—C(2)#	119.4(5)	118.3(4)
S—C(5)—C(2)	111.9(4)	111.4(2)
S—C(6)—C(7)	112.1(4)	119.8(2)

Symmetry codes: # = $-x$, y, $0.5-z$ for **6** and $1-x$, y, $0.5-z$ for **8**.

crystal. In all cases the aliphatic or aromatic groups attached to the 1,3-bis(thiomethyl)benzene unit are oriented on opposite sides of the benzene plane.

Supplementary material available

Listing of positional parameters for non-hydrogen and hydrogen atoms, anisotropic thermal parameters, bond angles and torsion angles for non-hydrogen atoms and bond lengths for hydrogen atoms (27 pages). Listing of observed and calculated structure factors (44 pages) can be obtained from the author on request.

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