

Palladium arenethiolates with intramolecularly coordinating nitrogen Lewis bases

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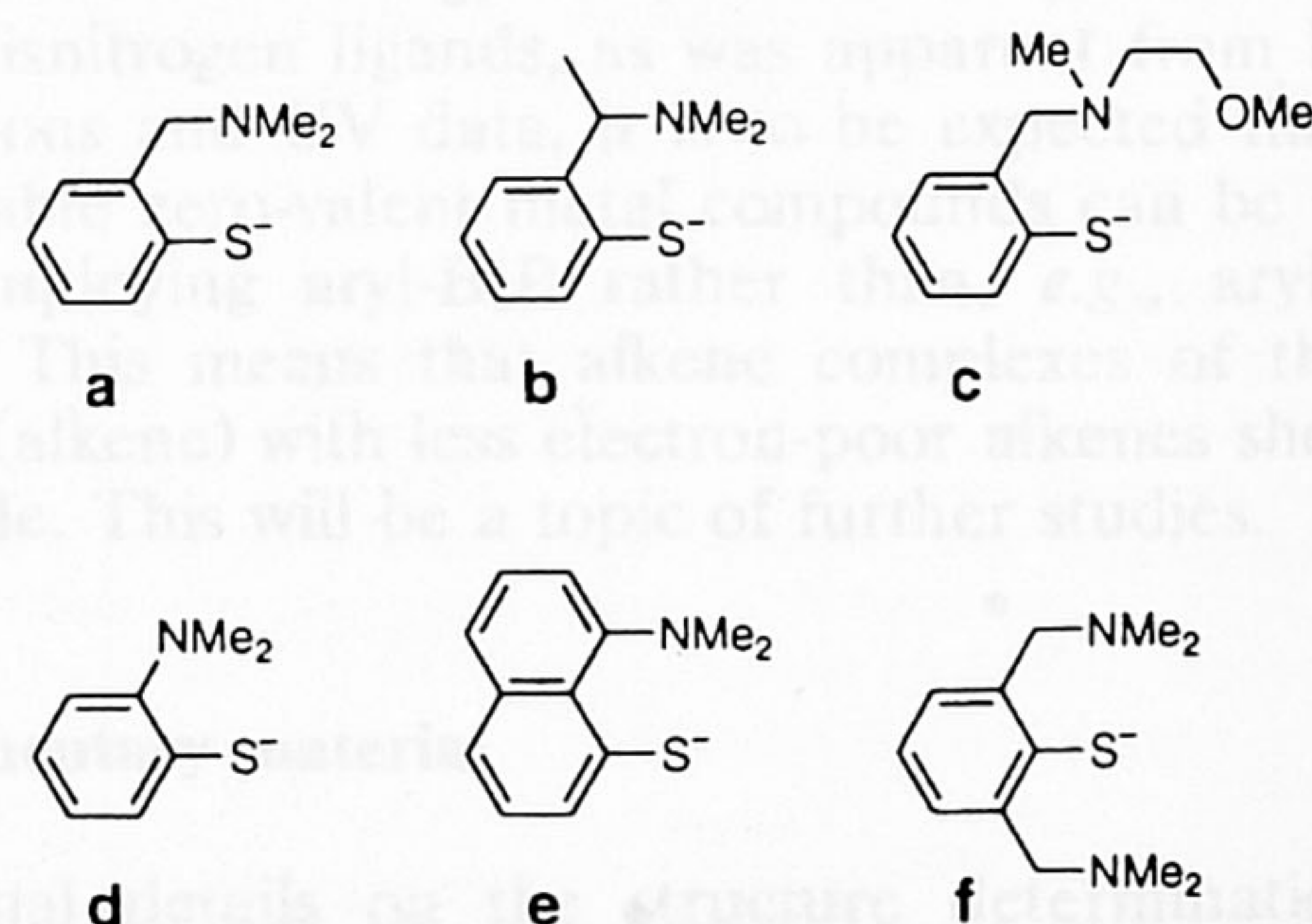
Abstract. The reaction of $[\text{PdCl}_2(\text{MeCN})_2]$ with one or two equivalents of $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2$ -2 in toluene affords the mono(arenethiolate) complex $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2-2)]$ (**1**) or the bis(arenethiolate) complex $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2-2)_2]$ (**2**), respectively, in high yields. $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2-2)]$ (**1**) exists as a tetramer in the solid state (X-ray) while $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2-2)_2]$ (**2**) is a monomer both in the solid state and in solution (cryoscopy, NMR). The X-ray structure determination of tetrameric **1** shows arenethiolate ligands bridging between PdCl units to form a unique eight-membered U-shaped Pd_4S_4 ring. Crystals of **1** are tetragonal, space group $P\bar{4}2_1c$, with $a = b = 12.0495(10)$ Å, $c = 16.672(1)$ Å, $V = 2420.6(3)$ Å³, $Z = 2$, and final $R = 0.029$, $wR = 0.034$ and $S = 1.42$ for 1174 reflections with $I > 2.5 \sigma(I)$ and 111 variables. The X-ray structure determination of **2** shows it to be monomeric in the solid state. The palladium has a square-planar geometry that results from coordination by two *S,N*-chelating arenethiolate ligands with a *trans* S and *trans* N arrangement of the donor atoms. Crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 8.9923(5)$ Å, $b = 9.2472(5)$ Å, $c = 11.5933(6)$ Å, $V = 825.93(9)$ Å³, $Z = 2$, and final $R = 0.025$, $wR = 0.047$ and $S = 0.53$ for 3603 reflections with $I > 2.5 \sigma(I)$ and 226 variables.

Introduction

In order to explore a new synthetic approach to metal arenethiolates in general¹, and to understand the coordination behaviour of arenethiolate ligands with potentially intramolecularly coordinating *ortho* substituents (see Scheme 1) to various metals, we have studied the synthesis, structure and reactivity of copper(I)², zinc(II)³ and lithium arenethiolate⁴ complexes.

The importance of the copper(I) and zinc(II) complexes stems from the fact that they represent a new type of (pre)catalyst for homogeneous metal-catalyzed organic synthesis. For example, copper(I) arenethiolates derived from ligands **a**, **b**, **d** and **e** (Scheme 1) are excellent catalysts for selective group transfer from Grignard reagents to various enone substrates. More specifically, selective conjugate 1,4-⁵ and 1,6-additions⁶ to cyclic or acyclic α,β -unsaturated enones and conjugated alkynylones as well as selective α - or γ -alkylation of allylic substrates⁷ have been achieved. Furthermore, zinc(II) arenethiolate complexes derived from ligand **b** (Scheme 1) are efficient catalysts in the enantioselective addition of diorganozinc(II) reagents to various aldehydes³. The function of the arenethiolate ligand in such catalytic systems is to bring together two different metal centres (Cu, Li; Cu, Mg; Zn, Zn) via the bridging S donor atom while the N donor atom can coordinate to the metal centre with the highest Lewis acidity.

The reasons for our current interest in palladium complexes with arenethiolate ligands are twofold. Firstly, although palladium(II) thiolate complexes with or without coordinating ligands (mostly neutral N, or P donor atom ligands) are known in the literature⁸, reports concerning palladium arenethiolate complexes with *ortho* substituents having intramolecularly coordinating donor atoms are scarce^{9,10}. Secondly, organopalladium complexes are often employed in organic reactions (*e.g.* co-polymerization of CO and ethene¹¹, biaryl coupling¹²) and there has recently been much interest in thiolate ligands in metal-mediated or catalyzed reactions^{1-3,5-7,13}. Therefore, in order to see whether the potentially *S,N* bidentate ligands **a–e** (Scheme 1) can afford palladium thiolate pre-catalysts with different or new catalytic behaviour, we are now investigating synthetic routes to such complexes.



Scheme 1. Arenethiolate ligands with potentially intramolecularly coordinating amine groups.

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In this report we show that synthesis of palladium arenethiolate complexes with an intramolecularly coordinating *ortho*-(dimethylamino) group on the arene ring is possible, and that the complexes $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2-2)]_4$ and $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2-2)_2]$ have interesting structural features.

Results

Synthesis

The reaction of equimolar amounts of $[\text{PdCl}_2(\text{MeCN})_2]$ with 2-[(trimethylsilyl)thio]-*N,N*-dimethylaniline, $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2-2$, affords the (chloro)palladium arenethiolate complex $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2-2)]_4$ (**1**) which has been isolated in 81% yield as an orange air-stable solid (Scheme 2).

The reaction of either **1** with a second equivalent of $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2-2$ or the direct reaction of two equivalents of $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2-2$ with $[\text{PdCl}_2(\text{MeCN})_2]$ results in the quantitative formation of the bis(arenethiolate) complex $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2-2)_2]$ (**2** see Scheme 2). Attempted conversion of **2** into **1** by reacting it with one equivalent of palladium dichloride in benzene at 25°C or acetonitrile, both at 25°C and at reflux, unfortunately did not succeed.

The palladium arenethiolate complexes **1** and **2** are air-stable orange-red solids which are slightly hygroscopic, and which are thermally stable at room temperature. Complex **1** decomposes at 158°C to afford a black solid, whereas complex **2** is more stable and does not melt or decompose below 200°C.

The (chloro)palladium arenethiolate **1** is very soluble in chlorinated hydrocarbons (CH_2Cl_2 or CHCl_3) or coordinating solvents such as pyridine and 4-methylpyridine, but is less soluble in aromatic solvents (benzene, toluene). The bis(arenethiolate) complex **2** is very soluble in both chlorinated hydrocarbons and aromatic solvents. Both **1** and **2** are insoluble in alkanes such as pentane and hexane.

Structure of (chloro)palladium arenethiolate **1** in the solid state

To investigate the nuclearity and coordination geometry of palladium in **1**, the solid-state structure of this complex was determined in an X-ray crystallographic study (Figure 1). Selected bond lengths and bond angles are listed in Table I. This study shows complex **1** to have an unprecedented tetrameric structure which is based on four $\text{PdCl}(\text{SAr})$ entities that are related by a crystallographic 4-fold inversion axis. In the structure of **1**, each 2-(dimethylamino)-benzenethiolate ligand is S,N-chelate-bonded to palladium and the bite angle S1-Pd1-N1 of $87.6(3)^\circ$ fits the expected square-planar geometry of a palladium(II) centre almost perfectly. At the same time, the S atom of the arenethiolate ligand is also bridge-bonded to a neighbouring Pd atom. In this way, each palladium atom, which is also bonded to one

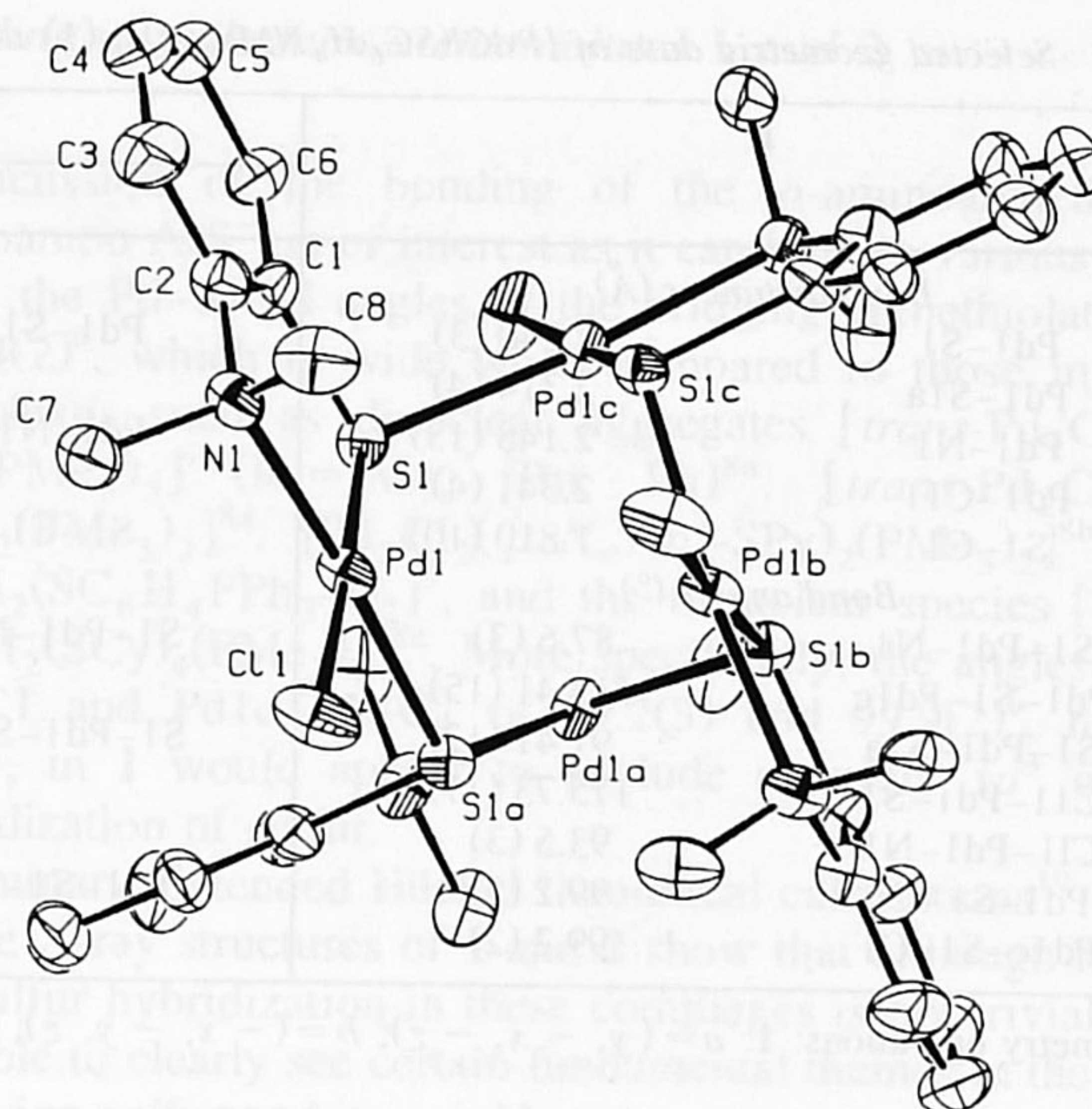
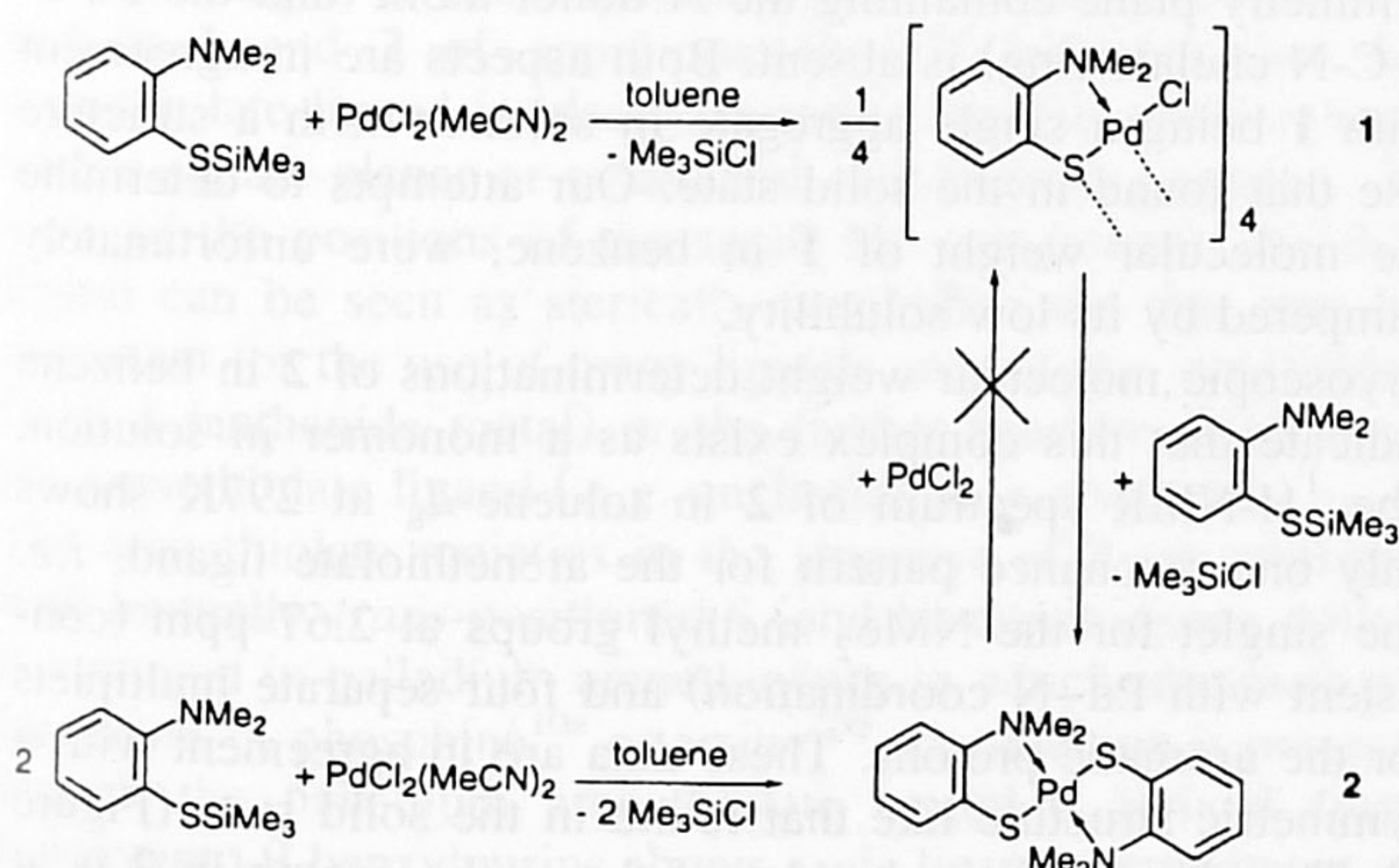


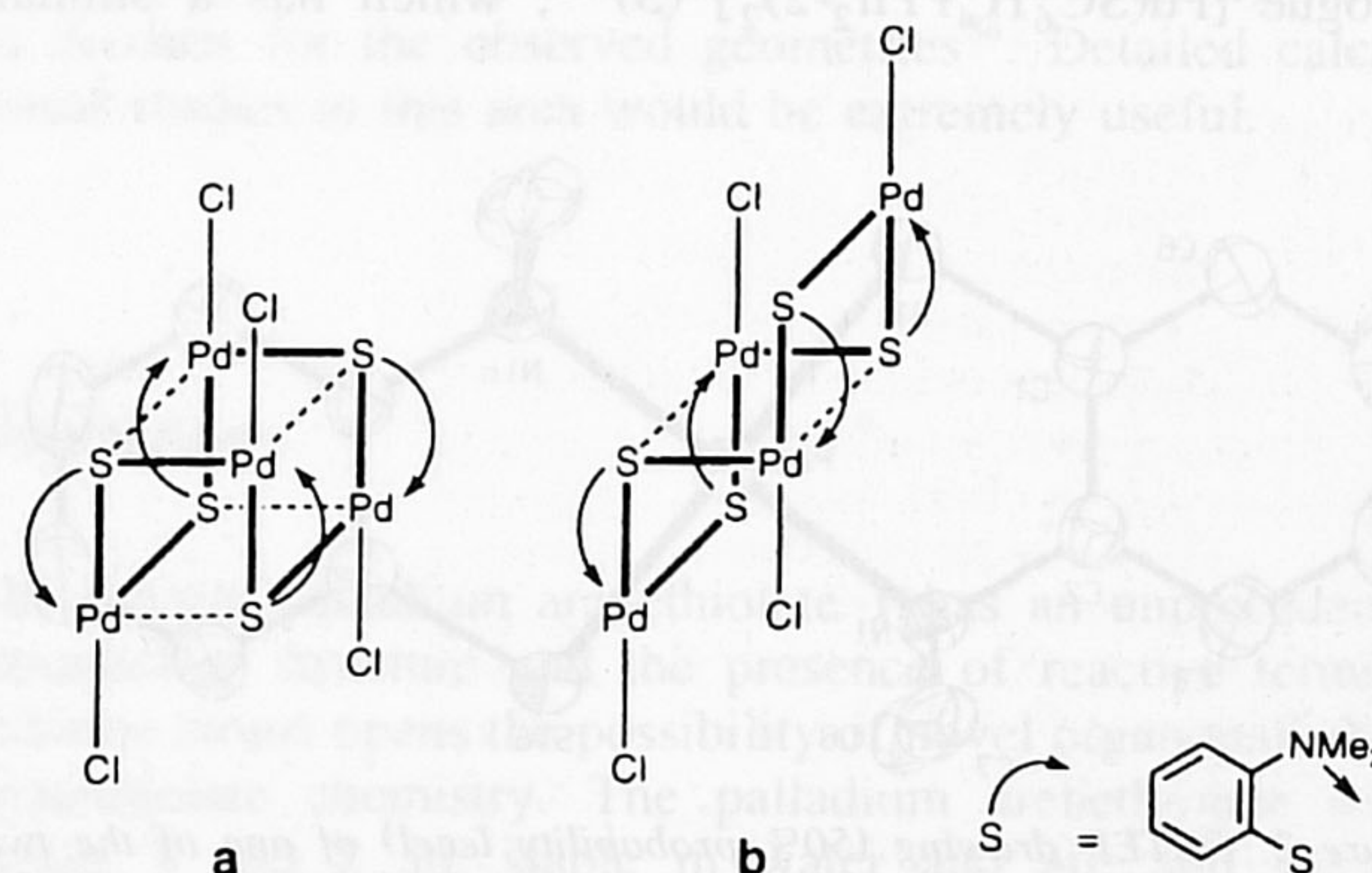
Figure 1. ORTEP drawing (30% probability level) of $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2-2)]_4$ (**1**) with the adopted atom-labelling scheme. Hydrogen atoms have been omitted for clarity.

terminal chlorine atom, completes its coordination sphere with an S atom of a neighbouring arenethiolate ligand. The geometric arrangement is such that the terminal chlorine atom is *trans* to the S atom of the internally chelating arenethiolate ligand, while the S atom of a second arenethiolate ligand is *trans* to the coordinated nitrogen atom [Pd1-N1 2.148(13) Å]¹⁴. As can be seen from Figure 1 and the schematic structure in Scheme 3a, the tetramer contains an unprecedented eight-membered U-shaped Pd_4S_4 ring with alternating Pd and S atoms.

The Pd-S distances of 2.240(3) Å (Pd1-S1, within chelate) and 2.314(4) Å (Pd1-S1a, thiolate bridge) are a little shorter than those in palladium arenethiolate complexes with intermolecularly coordinating phosphine ligands, but are similar to those in other palladium halide arenethiolate aggregates⁸. The Pd-S-Pd' angles of $114.4(2)^\circ$ are wide when compared to that of $95.7(1)^\circ$ found in $[\text{trans-Pd}_2\text{Cl}_2(\mu\text{-SPh})_2(\text{PMe}_3)_2]$ ^{8a}, and as a result the eight-membered Pd_4S_4 ring is folded to create a cube-like overall structure in which the bridging S atoms also come close to a third Pd atom [$\text{Pd}\cdots\text{S}$ is 3.3983(17) Å]. The magnitude of the latter distance, as well as that the fact that the $\text{Pd}\cdots\text{S}$ vector makes an angle of $61.58(17)^\circ$ with the Pd coordination plane, points to a possible positive attractive interaction between empty Pd(hybrid) orbitals and S electron pairs (sum of the Van der Waals radii is 3.71 Å). The cube-like structure of **1** is apparently more stable than the more open alternative step structure shown in Scheme 3b, in which two of the four Cl atoms are close to a neighbouring Pd atom.



Scheme 2. Synthesis of palladium arenethiolates **1** and **2**.



Scheme 3. (a) Schematic representation of (chloro)palladium arenethiolate **1**. (b) Alternative step structure of **1**.

Table 1 Selected geometric data of $[PdCl(SC_6H_4NMe_2-2)]_4$ (**1**) and $[Pd(SC_6H_4NMe_2-2)_2]$ (**2**)^a

1		2			
		Molecule 1		Molecule 2	
<i>Bond distances (Å)</i>					
Pd1-S1	2.240 (3)	Pd1-S1	2.2945 (6)	Pd2-S2	2.2895 (6)
Pd1-S1a	2.314 (4)				
Pd1-N1	2.148 (13)	Pd1-N1	2.1018 (18)	Pd2-N2	2.1043 (19)
Pd1-C11	2.341 (4)				
S1-C1	1.810 (10)	S1-C1	1.748 (3)	S2-C11	1.747 (3)
<i>Bond angles (°)</i>					
S1-Pd1-N1	87.6 (3)	S1-Pd1-N1	87.00 (6)	S2-Pd2-N2	86.91 (5)
Pd1-S1-Pd1c	114.41 (15)				
S1-Pd1-S1a	91.41 (12)	S1-Pd1-S1a	180	S2-Pd2-S2a	180
C11-Pd1-S1	175.73 (17)				
C11-Pd1-N1	93.5 (3)				
Pd1-S1-C1	99.2 (3)	Pd1-S1-C1	98.79 (10)	Pd2-S2-C11	98.96 (8)
Pd1c-S1-C1	99.2 (2)				

^a Symmetry operations: **1**: $a = (y, -x, -z)$; $b = (-x, -y, z)$; $c = (-y, x, -z)$; **2**: $a = (-x, -y, -z)$.

Terminal chlorine atoms in polynuclear Pd structures such as tetrameric **1** are not unusual and reported instances include the dinuclear structures of $[trans-Pd_2Cl_3(\mu-SR)(PMe_3)_2]$ ($R = Me, ^iBu, Ph$)^{8a}, $[trans-Pd_2Cl_2(\mu-SPh)_2(PMe_3)_2]$ ^{8a}, $[Pd_2Cl_2(\mu, N, S, -\eta^2-SPy)_2(PMe_3)_2]$ ^{8b} as well as the trinuclear structure of $[trans-Pd_3Cl_2(SCy)_4(PMe_3)_2]$ ^{8c}. Terminal iodine atoms are present in the dinuclear structure of $[Pd_2I_2(SC_6H_4PPh_2-2)_2]$ ⁹. These structures and that of **1** exemplify a common observation that anionic S donor atoms more readily form bridges than halide atoms. The palladium-to-chlorine bond length of 2.341(4) Å in **1** is normal and lies in the range 2.3–2.4 Å usually encountered for such bonds⁸.

Structure of **2** in the solid state

A crystal structure determination of **2** by X-ray diffraction techniques shows it to be a monomeric species in the solid state (Figure 2).

Complex **2** affords crystals having the space group $P\bar{1}$ and the asymmetric unit of **2** contains two crystallographically independent, monomeric, $[Pd(SC_6H_4NMe_2)_2]$ molecules whose palladium atoms are positioned on a crystallographic inversion centre. Selected bond lengths and bond angles of the two molecules are listed in Table I. There are only very small geometrical differences between the two unique molecules and therefore only one will be discussed. The two monoanionic arenethiolate ligands are both *S,N*-chelate-bonded to a single Pd centre which has an almost perfect square-planar coordination geometry with the S donor (and N donor) atoms mutually *trans*-positioned. The bite angle of the 2-(dimethylamino)benzenethiolate ligand in the structure of **2** is 87.00(6)° and is similar to that found in **1**.

The Pd–S distance Pd1–S1 of 2.2945(6) Å in **2** is slightly longer than the corresponding chelate Pd–S distance in **1** [2.240(3) Å] and is comparable to those in the phosphine analogue $[Pd(SC_6H_4PPh_2-2)_2]$ (**3**)^{10a}, which has a similar

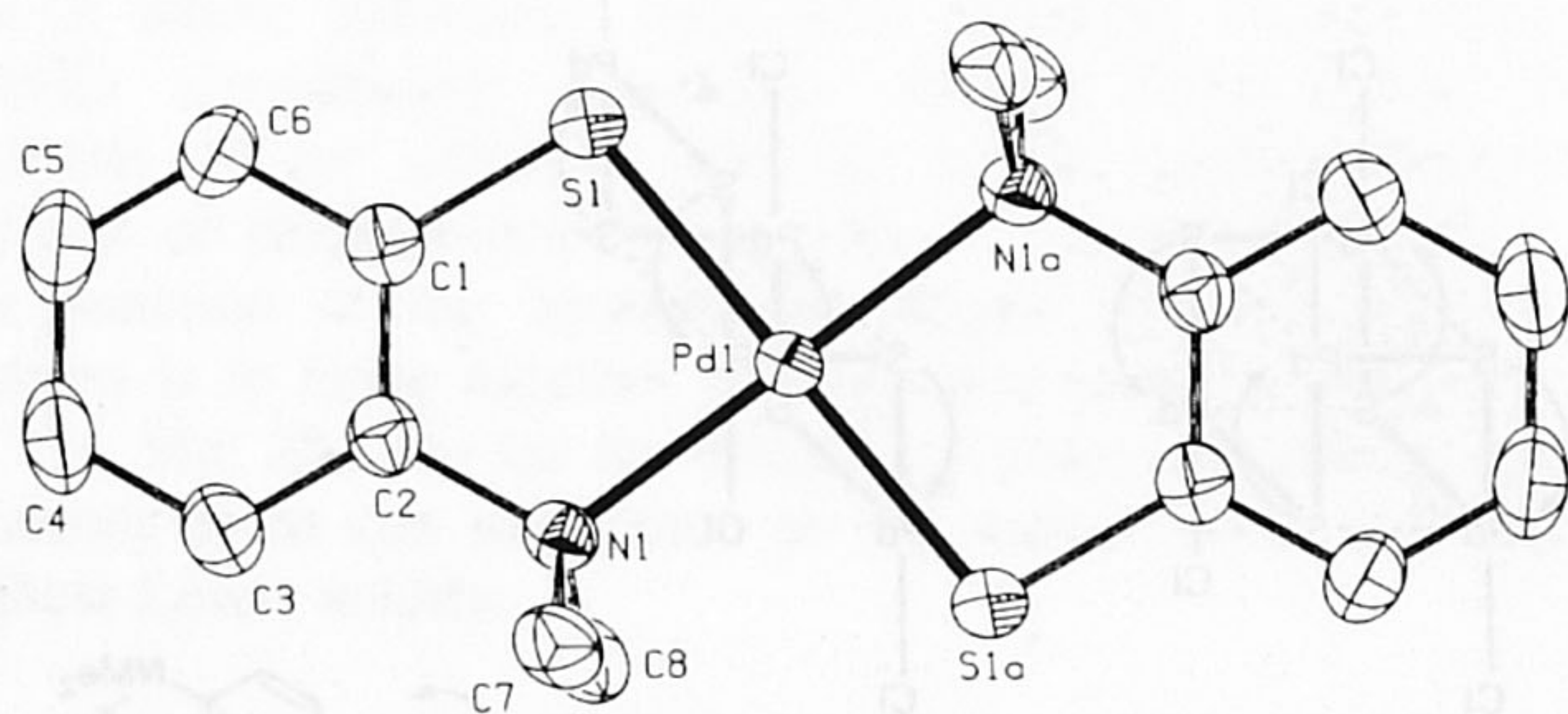


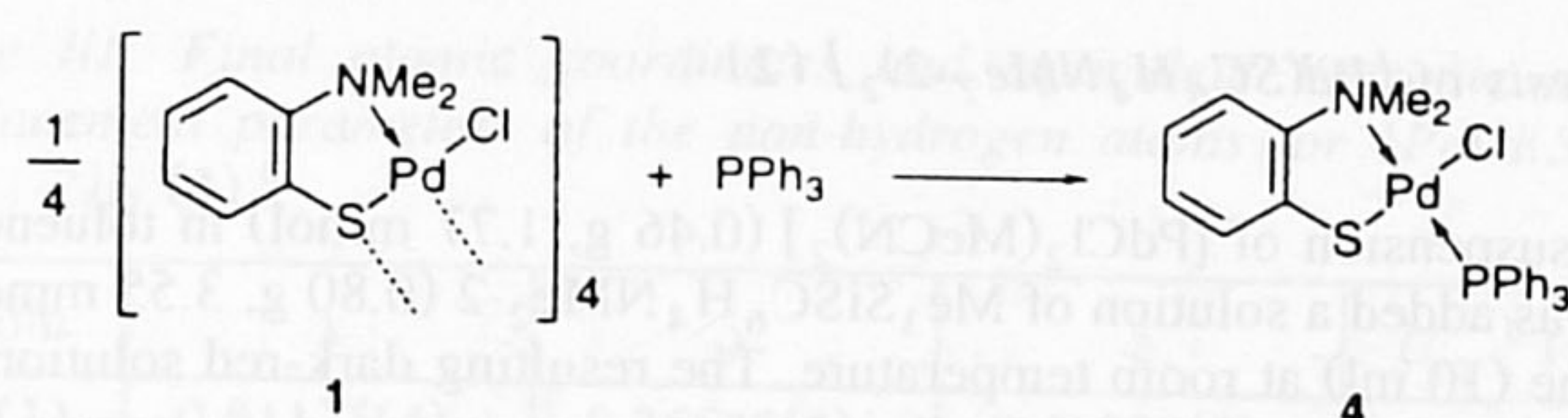
Figure 2. ORTEP drawing (50% probability level) of one of the two crystallographically independent molecules of $[Pd(SC_6H_4NMe_2-2)_2]$ (**2**) with the adopted atom-labelling scheme. Hydrogen atoms have been omitted for clarity.

trans configuration of the S donor atoms as well as a five-membered Pd–S–C–C–X chelate ring [$X = NMe_2$ (**2**), PPh_2 (**3**)]. It is interesting to note that, although the Pd–N distance in **2** [Pd–N 2.1018(18) Å] is significantly shorter than the Pd–P distance in **3** [Pd–P 2.291(1) Å], the bite angles in **2** and **3** are comparable [**2**: 87.00(6)°; **3**: 86.6(1)°]. The Pd–N distances in **2** [Pd1–N1 2.1018(18); Pd2–N2 2.1043(19) Å] are similar to those in **1** [Pd1–N1 2.148(13) Å], *i.e.* the *trans* influence of a *trans* N donor in **2** is like that of a bridging S atom on the Pd–N bonding in **1**. The observation that the Pd–S(bridge) distance is longer than the Pd–S(chelate) distance underlines this conclusion. Finally, it is interesting to see in both **1** and **2** that the aryl rings, the N and S donor atoms and the palladium centre are all almost in one plane [largest deviations: 0.013(8) Å for C1 and C2 in **1**, 0.0309(8) Å for Pd1 in **2**], *i.e.* the five-membered Pd–S–C–C–N chelate ring lacks any significant puckering which is so characteristic for isoelectronic $[2-[(dimethylamino)methyl]phenyl]palladium$ structural units¹⁵. Accordingly, both NMe groups in **1** and **2** are almost symmetrically oriented above and below the plane through the chelate ring and the aryl system.

Structure of palladium arenethiolates **1** and **2** in solution

The ¹H- and ¹³C-NMR spectra of **1** and **2** are both temperature independent in the range 213 to 353 K. The ¹H-NMR spectrum of **1** in toluene-*d*₈ at 297 K comprises one single ligand pattern: two singlets at 2.65 and 3.68 ppm for the NMe₂ groups and four separate multiplets for the aromatic protons, with the low-field doublet at 8.92 ppm being assigned to H-6 *ortho* to the sulfur atom; this low-field chemical shift for an aromatic proton is characteristic for arenethiolate complexes. Since the NMe groups are diastereotopic, one can conclude not only that there is coordination of the amine functionality to palladium (Figure 1), but also that a molecular symmetry plane containing the N donor atom (and the Pd–S–C–C–N chelate ring) is absent. Both aspects are in agreement with **1** being a single aggregate in solution with a structure like that found in the solid state. Our attempts to determine the molecular weight of **1** in benzene, were unfortunately hampered by its low solubility.

Cryoscopic molecular weight determinations of **2** in benzene indicate that this complex exists as a monomer in solution. The ¹H-NMR spectrum of **2** in toluene-*d*₈ at 297K shows only one resonance pattern for the arenethiolate ligand, *i.e.* one singlet for the NMe₂ methyl groups at 2.67 ppm (consistent with Pd–N coordination) and four separate multiplets for the aromatic protons. These data are in agreement with a symmetric structure like that found in the solid state (Figure 2). The characteristic doublet of the *ortho* proton in **2** is at 7.46 ppm and is thus at a much higher field position than that

Scheme 4. Reaction of **1** with PPh_3 ; formation of **4**.

in **1**. This difference can be explained by this proton being positioned in empty space in complex **2**, but being close to the terminal chlorine atom of a neighbouring $\text{PdCl}(\text{SAr})$ moiety in **1** [$\text{H61} \cdots \text{Cl1}$ is $3.600(8) \text{ \AA}$]¹⁶.

Reactivity of palladium arenethiolates **1** and **2**

The tetranuclear aggregate of the (chloro)palladium arenethiolate **1** does not react with Lewis bases such as pyridine or 4-methylpyridine. However, **1** does react with triphenylphosphine to afford a coordination complex tentatively identified as $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2\text{-2})(\text{PPh}_3)]$ (**4**) (Scheme 4). In the $^1\text{H-NMR}$ spectrum of **4** the NMe_2 unit affords one singlet at 3.02 ppm, *i.e.* the NMe groups are enantiotopic, and the NMe_2 and PPh_3 proton integrals are consistent with the formation of a complex with a 1:1 PPh_3 to arenethiolate ratio. Furthermore, the positions of the *ortho* proton H-6 (7.24 ppm, 3J 7 Hz) and the NMe_2 group (3.02 ppm) which are similar to those found in **1**, suggest that complex **4** likewise has the Cl atom *trans* to the S donor and *cis* to the NMe_2 grouping. Based on these data we conclude that PPh_3 breaks down the aggregate structure of **1** (with stereogenic palladium centres) to form species **4**, which must have a molecular symmetry plane containing the N donor atom and which is most probably mononuclear.

Preliminary experiments show that **1** reacts with AgOTf in acetonitrile to form the cationic species $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2\text{-2})\text{OTf}]$ (**5**) (OTf = trifluoromethanesulfonate). Complexes **4** and **5** form the successful basis for a new area of palladium arenethiolate chemistry and further characterization and catalytic studies with these and analogous complexes are in progress.

Discussion

Structures of palladium arenethiolates **1** and **2**

Complex **1** is the first structurally characterized example of a tetranuclear palladium arenethiolate complex. Interestingly, the cube-like Pd_4S_4 entity in **1** is like the Pd_4O_4 moiety in the *N*-ligated palladium phenoxide bis[(*R*)-*N*-(α -methylbenzyl)salicylideneaminato-*N,O*] palladium(II)¹⁷. When ligands are not capable in themselves of saturating the palladium coordination then polynuclear aggregates can be formed, an example is the trimeric palladium complex $[\text{Pd}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})]_3$ ¹⁸.

The bite angle of the 2-(dimethylamino)benzenethiolate ligand in **1** and **2** of approximately 87° indicates that the arenethiolate ligand is ideally suited to bind to metal centres with a square-planar or octahedral coordination geometry. In view of the positions of the small Me substituents, the S,N ligand can be seen as sterically non-bulky and this may be important for the use of many ligands around one metal atom (*e.g.* a lanthanide metal) or the further functionalization of the arenethiolate ligand (*e.g.* anchoring to a polymer).

The arenethiolate moieties in the structure of **2** are arranged with mutually *trans*-positioned S (and N) donor atoms, which is common in palladium arenethiolates in which intramolecular amine^{10c}, phosphine^{10a} or arsine^{10d} coordination is present, though the palladium arenethiolate complex derived from 6-mercapto-9-benzylpurine shows a *cis* ligand arrangement of the arenethiolate ligands^{10b}.

Bonding in palladium arenethiolates **1** and **2**

A discussion of the bonding of the *o*-aminoarenethiolate monoanion ArS^- is of interest as it can bind in various ways. In **1**, the Pd-S-Pd angles of the bridging arenethiolates are $114.4(2)^\circ$, which is wide when compared to those in other complexes such as dinuclear aggregates [*trans*- $\text{Pd}_2\text{Cl}_3(\mu\text{-SR})(\text{PMe}_3)_2$] ($\text{R} = \text{Me}, ^t\text{Bu}, \text{Ph}$)^{8a}, [*trans*- $\text{Pd}_2\text{Cl}_2(\mu\text{-SPh})_2(\text{PMe}_3)_2$]^{8a}, [$\text{Pd}_2\text{Cl}_2(\mu, N, S-\eta^2\text{-SPy})_2(\text{PMe}_3)_2$]^{8b}, and [$\text{Pd}_2\text{I}_2(\text{SC}_6\text{H}_4\text{PPh}_2\text{-2})_2$]⁹, and the trinuclear species [*trans*- $\text{Pd}_3\text{Cl}_2(\text{SCy})_4(\text{PMe}_3)_2$]^{8c}. More specifically, the angles Pd1-S1-Cl and Pd1c-S1-Cl of $99.2(3)$ and $99.9(2)^\circ$, respectively, in **1** would appear to exclude a purely sp^3 or sp^2 hybridization of sulfur.

Preliminary Extended Hückel theoretical calculations¹⁹ based on the X-ray structures of **1** and **2** show that although indeed the sulfur hybridization in these complexes is not trivial, it is possible to clearly see certain fundamental themes in the MOs involving sulfur and its neighbouring atoms.

In complex **1**, in which the S atom is engaged in bridge-bonding to two Pd atoms, the sulfur 3s orbital plays an important role in building the σ -bond to carbon. Furthermore, the 3p orbitals contribute significantly as p^3 hybrids to some of the highest occupied MOs which are bonding between Pd and S. This type of p^3 hybridization is not unusual: standard text books state that it is the most common hybridization of three-coordinate atoms with a trigonal bipyramidal shape²⁰. In fact, although the sulfur atoms in **1** only have connections to three atoms (Pd1, Pd1c, Cl) the observed angles are consistent with a trigonal-bipyramidal form in which the two palladium atoms are in the trigonal plane [$\text{Pd1-S1-Pd1c} = 114.41(5)^\circ$] and the carbon atom is in an apical position [Pd1-S1-Cl and Pd1c-S1-Cl are $99.2(2)$ and $99.9(3)^\circ$, respectively, Figure 1].

For monomeric complex **2**, our calculations show a different hybridization pattern. As in **1**, the sulfur 3s orbital is involved in MOs that are involved in the σ -bond to carbon. However, the sulfur atom also forms MOs that have contributions based on varying degrees of s, sp, p^2 and sp^2 character, with sp^3 being to all intents and purpose absent. In this complex one p orbital of S contributes little to the interatomic bonding and, with its lobes above and below the metal coordination plane, is a dominant contributor to the HOMO. In general terms, these results are consistent with the commonly found p^2 hybridization of two-coordinate atoms with a bent geometry²⁰. Because the S-C(aryl) bond in both complexes is dominated by a combination of a sulfur 3s and a carbon sp^2 hybrid orbital, the geometrical positioning of C_{ipso} (aryl) with respect to sulfur is not restricted on symmetry grounds and, as a consequence, a wide variation in Pd-S-C angles is to be anticipated. This is indeed what we find in the X-ray structures.

The hybridization of sulfur in many metal arenethiolate complexes has been a subject of discussion and several authors have proposed mixing of s and p (and sometimes d) orbitals to account for the observed geometries^{8a}. Detailed calculational studies in this area would be extremely useful.

Conclusions

The (chloro)palladium arenethiolate **1** has an unprecedented tetranuclear structure and the presence of reactive terminal chlorine atoms opens the possibility of novel organopalladium arenethiolate chemistry. The palladium arenethiolate complexes **1** and **2** are stable in water and air, and we are currently exploring the application of these complexes in catalytic reactions.

Experimental

Syntheses involving organolithium compounds or the hydrolysis-sensitive (trimethylsilylthio)arenes were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Toluene, benzene and hexane were dried and distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from calcium hydride. Commercial BuLi (1.67 M in hexane) was used. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC-200P or a Bruker AC-300P spectrometer. FAB-MS analyses (FAB = fast atomic bombardment) were carried out at the Analytical Chemical Laboratory of the University of Utrecht. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Cryoscopy of **2** was carried out in C_6H_6 at a concentration of approximately 3 mg/g C_6H_6 with naphthalene as internal reference. $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2$ -2 was prepared from 2-bromo *N,N*-dimethylaniline, BuLi, elemental sulfur and Me_3SiCl in a procedure analogous to that used for the preparation¹ of $\text{Me}_3\text{SiSC}_6\text{H}_4[\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{OMe}]$ -2; full details will be published elsewhere^{2b}.

Synthesis of $[\text{PdCl}(\text{SC}_6\text{H}_4\text{NMe}_2)_2]_4$ (**1**)

To a suspension of $[\text{PdCl}_2(\text{MeCN})_2]$ (0.50 g, 1.93 mmol) in toluene (10 ml) was added a solution of $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2$ -2 (0.44 g, 1.95 mmol) in toluene (3 ml) at room temperature. The resulting dark red reaction mixture was warmed to ca. 40°C and after stirring for 4 h all volatiles were removed *in vacuo* affording crude, almost pure, **1** as an orange solid. Slow diffusion of pentane into a solution of **1** in CH_2Cl_2 affords the analytically pure complex in a crystalline form (suitable for X-ray analysis); yield 0.46 g (81%, 1.56 mmol); T_{dec} 158°C. ^1H -NMR (CDCl_3 , 297K, 200.13 MHz) δ in ppm: 3.26 (s, 3H, NMe), 3.67 (s, 3H, NMe), 7.1–7.35 (m, 3H, ArH), 8.56 (d, 1H, 3J 6.4 Hz, ArH-6). ^1H -NMR (toluene- d_8 , 297K, 200.13 MHz) δ in ppm: 2.86 (s, 3H, NMe), 3.69 (s, 3H, NMe), 6.39 (d, 1H, 3J 8 Hz, ArH-3), 6.65 (t, 1H, 3J 8 Hz, ArH-4), 6.82 (t, 1H, 3J 8 Hz, ArH-5), 8.92 (d, 1H, 3J 8 Hz, ArH-6). Signals from Ar-4 and Ar-5 have been tentatively assigned. ^{13}C -NMR (CDCl_3 , 297K, 50.32 MHz) δ in ppm: 54.98 (NMe), 56.30 (NMe), 122.44, 128.52, 129.04, 134.66, 134.88, 154.68 (Ar). Anal. calcd. for $\text{C}_{32}\text{H}_{40}\text{Cl}_4\text{N}_4\text{Pd}_4\text{S}_4 \cdot \text{CH}_2\text{Cl}_2$: C 31.42, H 3.36, N 4.44; found: C 31.76, H 3.38, N 4.58%.

Synthesis of $[\text{Pd}(\text{SC}_6\text{H}_4\text{NMe}_2)_2]$ (**2**)

To a suspension of $[\text{PdCl}_2(\text{MeCN})_2]$ (0.46 g, 1.77 mmol) in toluene (15 ml) was added a solution of $\text{Me}_3\text{SiSC}_6\text{H}_4\text{NMe}_2$ -2 (0.80 g, 3.55 mmol) in toluene (10 ml) at room temperature. The resulting dark-red solution was stirred for 17 h after which all volatiles were removed *in vacuo*; yield 0.73 g (100 %) of crude product. Pure **2** could be obtained by crystallization on slow diffusion of pentane into a solution of **2** in CH_2Cl_2 ; mp > 200°C. ^1H -NMR (CDCl_3 , 297K, 200.13 MHz) δ in ppm: 3.25 (s, 6H, NMe₂), 6.82–6.94 (m, 1H, ArH), 6.96–7.08 (m, 2H, ArH), 7.22–7.34 (m, 1H, ArH). ^1H -NMR (toluene- d_8 , 297K, 200.13 MHz) δ in ppm: 2.67 (s, 6H, NMe₂), 6.36 (d, 1H, 3J 8 Hz, Ar-3), 6.59 (t, 1H, 3J 8 Hz, Ar-4), 6.60 (t, 1H, 3J 8 Hz, Ar-5), 7.46 (d, 1H, 3J 8 Hz, Ar-6). Signals from Ar-4 and Ar-5 have been tentatively assigned. ^{13}C -NMR (CDCl_3 , 297K, 50.32 MHz) δ in ppm: 56.48 (NMe₂), 119.57, 122.95, 128.19, 129.98, 140.98, 154.03 (Ar). Anal. calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{PdS}_2$: C 46.77, H 4.91, N 6.82; found: C 46.88, H 4.95, N 6.86%.

Structure determination and refinement of **1** and **2**

X-ray data were collected on an Enraf-Nonius CAD4T rotating anode diffractometer for an orange (**1**) or a red (**2**) crystal glued on top of a glass fibre. Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 25 well-centred reflections (SET4)²¹ in the range $11^\circ < \theta < 14^\circ$. The unit-cell parameters were checked for the presence of higher lattice symmetry²². Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied (DIFABS)²³. The structures were solved by Patterson methods (SHELXS86)²⁴ and subsequent difference Fourier techniques. Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76)²⁵. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were introduced at calculated positions (C–H 0.98 Å) and refined riding on their carrier atoms. Neutral-atom scattering factors were taken from Cromer and Mann²⁶, anomalous dispersion corrections from Cromer and Liberman²⁷. An empirical extinction parameter was refined for **2**. Geometrical calculations and illustrations were performed with PLATON²⁸; all calculations were performed on a Microvax II and on a DEC5000 cluster. The solvate molecules in the structure of **1** which could not be located unambiguously

Table II Experimental data for the X-ray diffraction studies of **1** and **2**

	1	2
Formula	$\text{C}_{32}\text{H}_{40}\text{Cl}_4\text{N}_4\text{Pd}_4\text{S}_4$ ^a	$\text{C}_{16}\text{H}_{20}\text{N}_2\text{PdS}_2$
Formula weight	1176.45 ^a	410.90
Temperature (K)	298	298
Crystal system	tetragonal	triclinic
Space group	$P\bar{4}2_1c$	$P\bar{1}$
<i>a</i> (Å)	12.0495(10)	8.9923(5)
<i>b</i> (Å)	—	9.2472(5)
<i>c</i> (Å)	16.6720(10)	11.5933(6)
α (°)	—	110.420(4)
β (°)	—	111.665(4)
γ (°)	—	91.596(4)
Volume (Å ³)	2420.6(3)	825.93(9)
<i>Z</i>	2	2
ρ_{calcd} (g·cm ⁻³)	1.614 ^a	1.652
<i>F</i> (000) (electrons)	1152 ^a	416
μ (MoK α) (cm ⁻¹)	18.6 ^a	13.5
crystal size (mm)	0.25 × 0.25 × 0.25	0.43 × 0.43 × 0.43
Radiation (Å)	MoK α (0.71073) ^b	MoK α (0.71073) ^b
θ^{max} (°)	27.50	27.50
Scan ($\omega/2\theta$ mode) (°)	1.00 + 0.35 · tan(θ)	0.55 + 0.35 · tan(θ)
Horizontal aperture (mm)	4.75	3.00
Vertical aperture (mm)	4.00	4.00
Reference reflections(s)	2,3,1; 3,2,1; 3,0,2	−2,3,0; 0,2,3; −2,3,2
Decay, X-ray time	30%, 22 h.	< 1 %, 14 h.
<i>h</i> ; <i>k</i> ; <i>l</i> (min, max)	0, 15; −15, 15; 0, 21	−10, 11; −11, 11; −15, 14
Total/unique reflections	4647, 1566 (R_{av} 0.024)	4126, 3773
Observed reflections	1174 [$I > 2.5 \sigma(I)$]	3603 [$I > 2.5 \sigma(I)$]
N_{ref} , N_{par}	1174, 111	3603, 226
<i>R</i> , <i>w</i> · <i>R</i> , <i>S</i>	0.029, 0.034, 1.42	0.025, 0.047, 0.53
Weight (w^{-1})	$\sigma^2(F)$	$\sigma^2(F)$
Min., max. resd. dens. (e/Å ³)	−0.30, 0.37	−0.73, 0.77

^a Excluding the contribution of the disordered solvent (see experimental).

^b Graphite monochromator.

Table III Final atomic coordinates and equivalent isotropic atomic displacement parameters of the non-hydrogen atoms for $[PdCl(SC_6H_4NMe_2-2)]_4$ (1)^a

Atom	x	y	z	U_{eq}^b (Å ²)
Pd(1)	0.51175(4)	0.35561(4)	0.41223(2)	0.0425(2)
Cl(1)	0.42550(16)	0.3562(2)	0.28647(10)	0.0765(8)
S(1)	0.58684(13)	0.34437(13)	0.53480(9)	0.0423(5)
N(1)	0.6633(5)	0.2870(5)	0.3665(3)	0.053(2)
C(1)	0.7178(6)	0.2860(6)	0.5089(5)	0.051(3)
C(2)	0.7447(6)	0.2656(6)	0.4290(5)	0.055(3)
C(3)	0.8509(7)	0.2195(7)	0.4128(6)	0.082(3)
C(4)	0.9227(7)	0.2004(7)	0.4706(6)	0.079(3)
C(5)	0.8994(7)	0.2212(6)	0.5509(6)	0.076(3)
C(6)	0.7942(6)	0.2641(6)	0.5679(5)	0.062(3)
C(7)	0.6308(6)	0.1781(6)	0.3257(5)	0.075(3)
C(8)	0.7077(7)	0.3681(8)	0.3068(4)	0.077(3)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

^b $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized U tensor.

from difference Fourier maps were taken into account in the structure factor and refinement calculations by direct Fourier transform of the electron density in the cavity of 113.7 Å³ centered at $\frac{1}{2}$, 0, 0.109, following the BYPASS²⁹ procedure. The number of electrons integrated over the cavity area amounts to 35 electrons, consistent with one CH₂Cl₂ molecule per void or four solvent molecules in the unit cell. Crystal data and numerical details of the data collection and refinement of **1** and **2** are listed in Table II. Fractional coordinates and equivalent isotropic atomic displacement parameters of the structures of **1** and **2** are listed in Tables III and IV, respectively. Selected bond distances and bond angles for **1** and **2** are listed in Table I. Supplementary material may be obtained from one of the authors (A.L.S.).

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Table IV Final atomic coordinates and equivalent isotropic atomic displacement parameters of the non-hydrogen atoms for $[Pd(SC_6H_4NMe_2-2)]_2$ (2)^a

Atom	x	y	z	U_{eq}^b (Å ²)
<i>Molecule 1</i>				
Pd(1)	1	0	0	0.0255(1)
S(1)	0.96258(7)	0.22567(7)	-0.03925(6)	0.0383(2)
N(1)	0.84652(19)	0.0571(2)	0.10233(17)	0.0296(5)
C(1)	0.8421(3)	0.2951(3)	0.0494(2)	0.0343(7)
C(2)	0.7934(3)	0.2100(2)	0.1114(2)	0.0329(6)
C(3)	0.6964(3)	0.2662(3)	0.1795(3)	0.0462(8)
C(4)	0.6455(4)	0.4091(4)	0.1872(4)	0.0583(10)
C(5)	0.6946(4)	0.4947(3)	0.1263(3)	0.0581(10)
C(6)	0.7924(3)	0.4399(3)	0.0589(3)	0.0443(8)
C(7)	0.6992(3)	-0.0692(3)	0.0278(3)	0.0418(7)
C(8)	0.9338(3)	0.0597(3)	0.2403(2)	0.0418(7)
<i>Molecule 2</i>				
Pd(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0288(1)
S(2)	0.37045(7)	0.25386(7)	0.34338(6)	0.0448(2)
N(2)	0.6991(2)	0.3956(2)	0.57485(17)	0.0338(5)
C(11)	0.5228(3)	0.1487(3)	0.3937(2)	0.0365(6)
C(12)	0.6720(3)	0.2238(3)	0.5005(2)	0.0346(7)
C(13)	0.7922(3)	0.1378(3)	0.5377(3)	0.0449(8)
C(14)	0.7665(3)	-0.0218(3)	0.4680(3)	0.0500(9)
C(15)	0.6191(3)	-0.0974(3)	0.3621(3)	0.0504(9)
C(16)	0.4978(3)	-0.0137(3)	0.3238(3)	0.0469(8)
C(17)	0.7336(3)	0.4276(3)	0.7191(2)	0.0505(8)
C(18)	0.8452(3)	0.4710(3)	0.5695(3)	0.0493(8)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

^b $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized U tensor.

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Atom	x	y	z	Occupancy
1 Pd	0.0000	0.0000	0.0000	1.000000
2 S	0.0000	0.0000	0.0000	1.000000
3 C	0.0000	0.0000	0.0000	1.000000
4 C	0.0000	0.0000	0.0000	1.000000
5 C	0.0000	0.0000	0.0000	1.000000
6 C	0.0000	0.0000	0.0000	1.000000
7 C	0.0000	0.0000	0.0000	1.000000
8 C	0.0000	0.0000	0.0000	1.000000
9 C	0.0000	0.0000	0.0000	1.000000
10 C	0.0000	0.0000	0.0000	1.000000
11 C	0.0000	0.0000	0.0000	1.000000
12 C	0.0000	0.0000	0.0000	1.000000
13 C	0.0000	0.0000	0.0000	1.000000
14 C	0.0000	0.0000	0.0000	1.000000
15 C	0.0000	0.0000	0.0000	1.000000
16 C	0.0000	0.0000	0.0000	1.000000
17 C	0.0000	0.0000	0.0000	1.000000
18 C	0.0000	0.0000	0.0000	1.000000
19 C	0.0000	0.0000	0.0000	1.000000
20 C	0.0000	0.0000	0.0000	1.000000
21 C	0.0000	0.0000	0.0000	1.000000
22 C	0.0000	0.0000	0.0000	1.000000
23 C	0.0000	0.0000	0.0000	1.000000
24 C	0.0000	0.0000	0.0000	1.000000
25 C	0.0000	0.0000	0.0000	1.000000
26 C	0.0000	0.0000	0.0000	1.000000
27 C	0.0000	0.0000	0.0000	1.000000
28 C	0.0000	0.0000	0.0000	1.000000
29 C	0.0000	0.0000	0.0000	1.000000
30 C	0.0000	0.0000	0.0000	1.000000
31 C	0.0000	0.0000	0.0000	1.000000
32 C	0.0000	0.0000	0.0000	1.000000
33 C	0.0000	0.0000	0.0000	1.000000
34 C	0.0000	0.0000	0.0000	1.000000
35 C	0.0000	0.0000	0.0000	1.000000
36 C	0.0000	0.0000	0.0000	1.000000
37 C	0.0000	0.0000	0.0000	1.000000
38 C	0.0000	0.0000	0.0000	1.000000
39 C	0.0000	0.0000	0.0000	1.000000
40 C	0.0000	0.0000	0.0000	1.000000
41 C	0.0000	0.0000	0.0000	1.000000
42 C	0.0000	0.0000	0.0000	1.000000
43 C	0.0000	0.0000	0.0000	1.000000
44 C	0.0000	0.0000	0.0000	1.000000
45 C	0.0000	0.0000	0.0000	1.000000
46 C	0.0000	0.0000	0.0000	1.000000
47 C	0.0000	0.0000	0.0000	1.000000
48 C	0.0000	0.0000	0.0000	1.000000
49 C	0.0000	0.0000	0.0000	1.000000
50 C	0.0000	0.0000	0.0000	1.000000
51 C	0.0000	0.0000	0.0000	1.000000
52 C	0.0000	0.0000	0.0000	1.000000
53 C	0.0000	0.0000	0.0000	1.000000
54 C	0.0000	0.0000	0.0000	1.000000
55 C	0.0000	0.0000	0.0000	1.000000
56 C	0.0000	0.0000	0.0000	1.000000
57 C	0.0000	0.0000	0.0000	1.000000
58 C	0.0000	0.0000	0.0000	1.000000
59 C	0.0000	0.0000	0.0000	1.000000
60 C	0.0000	0.0000	0.0000	1.000000
61 C	0.0000	0.0000	0.0000	1.000000
62 C	0.0000	0.0000	0.0000	1.000000
63 C	0.0000	0.0000	0.0000	1.000000
64 C	0.0000	0.0000	0.0000	1.000000
65 C	0.0000	0.0000	0.0000	1.000000
66 C	0.0000	0.0000	0.0000	1.000000
67 C	0.0000	0.0000	0.0000	1.000000
68 C	0.0000	0.0000	0.0000	1.000000
69 C	0.0000	0.0000	0.0000	1.000000
70 C	0.0000	0.0000	0.0000	1.000000
71 C	0.0000	0.0000	0.0000	1.000000
72 C	0.0000	0.0000	0.0000	1.000000
73 C	0.0000	0.0000	0.0000	1.000000
74 C	0.0000	0.0000	0.0000	1.000000
75 C	0.0000	0.0000	0.0000	1.000000
76 C	0.0000	0.0000	0.0000	1.000000
77 C	0.0000	0.0000	0.0000	1.000000
78 C	0.0000	0.0000	0.0000	1.000000
79 C	0.0000	0.0000	0.0000	1.000000
80 C	0.0000	0.0000	0.0000	1.000000
81 C	0.0000	0.0000	0.0000	1.000000
82 C	0.0000	0.0000	0.0000	1.000000
83 C	0.0000	0.0000	0.0000	1.000000
84 C	0.0000	0.0000	0.0000	1.000000
85 C	0.0000	0.0000	0.0000	1.000000
86 C	0.0000	0.0000	0.0000	1.000000
87 C	0.0000	0.0000	0.0000	1.000000
88 C	0.0000	0.0000	0.0000	1.000000
89 C	0.0000	0.0000	0.0000	1.000000
90 C	0.0000	0.0000	0.0000	1.000000
91 C	0.0000	0.0000	0.0000	1.000000
92 C	0.0000	0.0000	0.0000	1.000000
93 C	0.0000	0.0000	0.0000	1.000000
94 C	0.0000	0.0000	0.0000	1.000000
95 C	0.0000	0.0000	0.0000	1.000000
96 C	0.0000	0.0000	0.0000	1.000000
97 C	0.0000	0.0000	0.0000	1.000000
98 C	0.0000	0.0000	0.0000	1.000000
99 C	0.0000	0.0000	0.0000	1.000000
100 C	0.0000	0.0000	0.0000	1.000000