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Electrochemical synthesis and crystal structure of silver(I) complexes with some heterocyclic thiones

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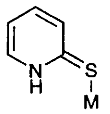
Two silver(I) complexes, $[\{Ag(SR)\}_6]$ [R^1SH = 6-(*tert*-butyldimethylsilyl)pyridine-2-thione **1**, R^2SH = 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione **2**], have been synthesized by electrochemical oxidation of the metal in an acetonitrile solution of the neutral heterocyclic thiones. The reaction of equimolar amounts of dppm [bis(diphenylphosphino)methane] with complexes **1** and **2** in dichloromethane resulted in the formation of $[Ag_4Cl_4(dppm)_2]$ **3** and the elimination of $RSCH_2SR$. Single-crystal X-ray analyses were performed for compounds **1**, **3** and $R^2SCH_2SR^2$.

Interest in the co-ordination chemistry of metal–sulfur complexes arises, in part, from their potential relevance to active sites in metalloenzymes, and also from to their ability to adopt geometries of variable nuclearities and great structural diversity.[1–3] The last features are the result of the tendency of thiolates to bridge metal centres to yield oligo- or poly-meric species. Recently, it has been established[4] that the extent of association depends intimately on both the reaction conditions and the nature of the thiolates. Moreover, these association phenomena may be further affected by providing steric constraints through appropriate design or the introduction of coligands to block a number of co-ordination sites. Recently, much effort has been made[5] to modify the thiolate through the introduction of solubilizing groups or a bulky substituent that might modify such aggregation processes.

As a result of our continuing interest in the chemistry of sterically hindered thiolates,[6] and of the paucity of known structures of neutral homoleptic species $[Ag(SR)]_n$,[4a,7] we report in this paper the electrochemical synthesis and characterization of silver(I) complexes with 3-(*tert*-butyldimethylsilyl)pyridine-2-thione and 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione ligands which have bulky silyl groups close to the sulfur atom that might modify the extent of aggregation as a result of steric constraints. In addition, these ligands are most versatile, since they can act as (*a*) a neutral monodentate *via* the sulfur atom[8–11] or as a bridge through S[11,12] and (*b*) as an anion, in which case they can act as a monodentate donor through the sulfur atom,[13,14] as a chelate[15–17] and/or as a bridge between two [(**E**),[13,18] (**F**)[9,10,16,19] and (**G**)[17,20]] or three metal atoms [(**H**)[10,21]].

In contrast to the mono- or di-nuclear adducts found in the reaction between other polynuclear thiolato complexes and different neutral compounds,[6a,22] in which some of the co-ordination sites tend to be blocked [2,2′-bipyridine, 1,10-phenanthroline, bis(diphenylphosphine)methane (dppm) and 1,2-bis(diphenylphosphine)ethane], the crystalline solid obtained by treating the present thiones with dppm in CH_2Cl_2 was the tetranuclear complex $[Ag_4Cl_4(dppm)_2]$.



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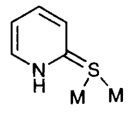

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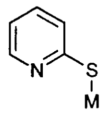

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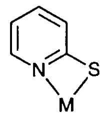

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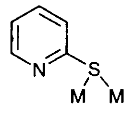

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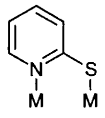

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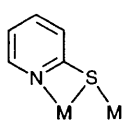

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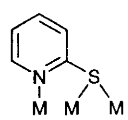

H

Experimental

Materials

tert-Butylchlorodimethylsilane, bis(diphenylphosphine)methane, acetonitrile and other solvents were commercial products used without further purification. *n*-Butyllithium and 2 mol dm^{-3} lithium diisopropylamide were obtained from Aldrich as solutions in hexane. Silver (Ega Chemie) was used as plates (*ca.* 2 × 2 cm).

Synthesis of triorganosilyl pyridine-2-thiones

The silylated compounds were prepared following a modified literature method.[5a] In an argon atmosphere and at room temperature, $Li[NPr^i_2]$ (54 cm^3, 11.45 g, 107 mmol) was added slowly to a solution of pyridine-2-thione [6 g, 54 mmol, in 60 cm^3 tetrahydrofuran (thf)]. The mixture was stirred for 5 min, then cooled to −78 °C. *n*-Butyllithium (54 mmol; 22 cm^3 of a 2.5 mol dm^{-3} solution in hexane) and thf (40 cm^3) were slowly added, and the reaction was allowed to reach room temperature. The solution was stirred at this temperature for 4 h. It was again cooled to −78 °C and *tert*-butylchlorodimethylsilane (16 g, 106 mmol) was slowly added. The final solution was allowed to react at room temperature with stirring for 12 h. After this time water (25 cm^3) was slowly added and the solution was then evaporated to dryness. The resultant yellow oil was dissolved in diethyl ether (250 cm^3), and water (300 cm^3) was added. The aqueous phase was extracted with ether (3 × 50 cm^3) and the organic phase dried with anhydrous Na_2SO_4. Ether was evaporated, the crude material dissolved in a small amount of hexane, and subjected to flash chromatography on silica gel (hexane–ethyl acetate). This resulted in the isolation of 3-(*tert*-butyldimethylsilyl)pyridine-2-thione (0.38 g) {IR (KBr, cm^{-1}): 3136m [ν(N–H)], 1570s [ν(C=C)], 1550s [ν(C=N)], 825vs [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 13.88 (s, NH), 7.31 (d, H^4), 6.50 (dd, H^5), 7.38 (d, H^6), 0.77 (s, CCH$_3$) and 0.20 (s, SiCH$_3$); ^{13}C, δ 181.76 (C^2), 146.58 (C^6), 137.41 (C^4), 142.77 (C^3), 113.33 (C^5), 28.15 (*C*CH$_3$), 18.62 (*C*CH$_3$) and −3.30 (SiCH$_3$)}, 6-(*tert*-butyldimethylsilyl)pyridine-2-thione (0.98 g) {IR (KBr, cm^{-1}): 3177 (br) [ν(NH)], 1580s [ν(C=C)], 1560s [ν(C=N)] and 835vs [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 10.37 (s, NH), 7.28 (d, H^3), 7.04 (t, H^4), 6.56 (d, H^5), 0.72 (s, CCH$_3$) and 0.14 (s, SiCH$_3$); ^{13}C, δ 179.80 (C^2), 152.73 (C^6), 135.73 (C^4), 134.28 (C^3), 121.09 (C^5), 26.41 (C*C*H$_3$), 17.11 (*C*CH$_3$) and −6.85 (SiCH$_3$)} and 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione (6.0 g) {IR (KBr, cm^{-1}): 3167 (br) [ν(NH)], 1564s [ν(C=C)], 1552s [ν(C=N)] and 839s [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 10.34 (s, NH), 7.46 (d, H^4), 6.72 (d, H^5), 0.94, 0.91 (s, CCH$_3$), 0.47, 0.41 (s, SiCH$_3$); ^{13}C, δ 184.77 (C^2), 152.80 (C^6), 144.23 (C^4), 142.90 (C^3), 120.14 (C^5), 26.48, 28.15 (C*C*H$_3$), 17.11, 18.57 (*C*CH$_3$), −6.56, −3.53 (SiCH$_3$)}.

Preparation of the complexes

The electrochemical method used in the synthesis of the Ag(SR) complexes was similar to that described previously by Tuck and co-workers.[23] The cell was a beaker (100 cm^3) fitted with a rubber bung through which the electrochemical leads entered. The silver anode was suspended from a platinum wire in a solution of the corresponding thione in acetonitrile and the cathode was a platinum wire. Direct current was obtained from a purpose-built d.c. power supply. The cells can be summarized as: Pt(−)|MeCN + RSH|Ag(+).

[{Ag(SR^1)}$_6$] 1 (R^1 = 6-*tert*-butyldimethylsilyl-2-pyridyl). The electrochemical oxidation of silver in a solution of 6-(*tert*-butyldimethylsilyl)pyridine-2-thione (R^{1}SH) (0.17 g, 0.75 mmol) in acetonitrile (60 cm^3) containing a small amount of tetramethylammonium perchlorate (20 mg) as supporting electrolyte for 2 h at 19 V and 10 mA resulted in the loss of 79 mg silver from the anode (E_f = 0.98 mol F^{-1}). A white crystalline precipitate formed immediately at the anode and hydrogen was evolved at the cathode. The solid was collected and dissolved in Pr^{i}OH. Crystals of [{Ag(SR^1}] suitable for X-ray diffraction studies were isolated from the final solution by evaporation at room temperature (Found: C, 40.7; H, 5.9; N, 4.3; S, 9.6. Calc. for $C_{72}H_{124}Ag_6N_6O_2S_6Si_6$: C, 40.9; H, 5.9; N, 4.0; S, 9.1%). IR (KBr, cm^{-1}): 1550s [ν(C=C)], 1540s [ν(C=N)] and 830vs [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 7.32 (d, H^3), 6.95 (t, H^4), 6.76 (d, H^5), 0.49 (s, CCH$_3$) and 0.38 (s, SiCH$_3$); ^{13}C, δ 165.96 (C^2), 162.81 (C^6), 130.25 (C^4), 125.14 (C^3), 123.12 (C^5), 24.51 (C*C*H$_3$) and 14.93 (*C*CH$_3$).

[{Ag(SR^2)}$_6$] 2 [R^2 = 3,6-bis(*tert*-butyldimethylsilyl)-2-pyridyl]. A similar experiment (25 V, 10 mA, 2 h) with silver as anode and 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione (0.25 g, 0.74 mmol) in acetonitrile (50 cm^3), dissolved 77 mg silver (E_f = 0.96 mol F^{-1}) to yield a yellow solution. The solution was filtered to remove any solid impurities and the filtrate left to concentrate by evaporation at room temperature. The precipitate formed was collected, washed with acetonitrile and diethyl ether, dried *in vacuo* and identified as [{Ag(SR^2)}$_6$] (Found: C, 45.5; H, 7.3; N, 3.4; S, 7.1. Calc. for $C_{17}H_{32}AgNSSi_2$: C, 45.7; H, 7.2; N, 3.1; S, 7.2%). IR (KBr, cm^{-1}): 1550s [ν(C=C)], 1540s [ν(C=N)] and 835vs [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 7.32 (d, H^4), 6.95 (t, H^5), 0.96 (s), 0.69 (s) (CCH$_3$), 0.49 (s), 0.38 (s) (SiCH$_3$); ^{13}C, δ 173.82 (C^2), 162.12 (C^6), 142.02 (C^4), 131.66 (C^3), 128.78 (C^5), 26.91, 27.52 (C*C*H$_3$), 16.99, 18.60 (*C*CH$_3$), −3.24, −6.17 (SiCH$_3$).

[Ag$_4$Cl$_4$(dppm)$_2$] 3. This compound was obtained by treating **1** (0.1 g, 0.30 mmol) and dppm (0.15 g, 0.39 mmol) in acetonitrile–dichloromethane (50 cm^3, 1 : 1). This mixture was refluxed for 48 h, and the recovered solid crystallized from methanol. X-Ray diffraction studies identified it as [Ag$_4$Cl$_4$(dppm)$_2$] **3** (Found: C, 44.3; H, 3.1. Calc. for $C_{50}H_{44}Ag_4Cl_4P_4$: C, 44.7; H, 3.3%). IR (KBr, cm^{-1}): 1450s [ν(C=C)], 1645s, 1460s and 1127s (bands due to dppm). NMR (CDCl$_3$): ^{1}H, δ 7.17–7.26 (aromatic) and 3.48 (CH$_2$); ^{13}C, δ 132–128 (aromatic C of dppm) and 26.7 (CH$_2$); ^{31}P, δ 22.96.

R^{2}SCH$_2$SR^2. A mixture of dppm (0.10 g, 0.26 mmol) and complex **2** (0.12 g, 0.27 mmol) was refluxed in acetonitrile–dichloromethane (30 cm^3) until a clear solution was obtained; concentration at room temperature afforded colourless crystals identified as R^{2}SCH$_2$SR^2 by X-ray diffraction studies (Found: C, 61.1; H, 9.9; N, 4.3; S, 9.2. Calc. for $C_{35}H_{66}N_2S_2Si_4$: C, 60.9; H, 9.6; N, 4.1; S, 9.3%). IR (KBr, cm^{-1}): 1550s [ν(C=C)], 1540s [ν(C=N)] and 835vs [ν(Si–C)]. NMR (CDCl$_3$): ^{1}H, δ 7.41 (d, H^4), 7.13 (d, H^5), 0.96 (s), 0.80 (s) (CCH$_3$), 0.28 (s), 0.33 (s) (SiCH$_3$) and 2.16 (s, CH$_2$); ^{13}C, δ 166.14 (C^2), 163.12 (C^6), 141.98 (C^4), 130.41 (C^3), 125.23 (C^5), 27.53, 27.20 (C*C*H$_3$), 18.53, 17.31 (*C*CH$_3$), −3.22, −5.83 (SiCH$_3$) and 32.78 (CH$_2$).

Physical measurements

Microanalyses were done using a CHN Carlo Erba 1108 elemental analyser. The IR spectra were obtained as KBr pellets at 298 K on a Perkin-Elmer 180 spectrophotometer, ^{1}H, ^{13}C and ^{31}P NMR spectra for chloroform solutions of the compounds using a Bruker WM 250 MHz spectrometer.

X-Ray crystallography

Crystals of complexes **1**, **3** and compound R^{2}SCH$_2$SR^2 were mounted on glass fibres on a Rigaku AFC5S diffractometer and intensity data were collected with Mo-Kα radiation (λ = 0.710 73 Å, graphite monochromator) at 213 K using the ω-scan technique. Three standard reflections monitored every 150 showed no significant variation. Corrections for Lorentz and polarization effects and an empirical absorption correction were applied. The crystal data and a summary of the data collection and structure refinement for these compounds are given in Table 1.

The crystallographic program system was the Siemens SHELXTL PLUS (PC version).[24] The structures were solved by direct methods and refined on F by full-matrix least squares. In the final cycles of refinement, hydrogen atoms placed at idealized positions were included. The function minimized was $\Sigma w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated structure factors. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + 0.0002F^2$ (**1**, R^{2}SCH$_2$SR^2) and $\sigma^2(F) + 0.0011F^2$ (**3**). Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were those of Cromer.[26]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Compounds of general formula [Ag(SR)] were readily prepared in high yield and good purity by using an electrochemical procedure. This method represents a simple route to silver thiolate compounds and is a good alternative to other standard chemical procedures. The electrochemical efficiency, defined as the number of moles of metal dissolved per Faraday of charge, is close to 1. This and the evolution of hydrogen at the cathode is consistent with the mechanism in equations (1) and (2).

$$\text{Cathode: RSH} + e^- \longrightarrow \tfrac{1}{2}\text{H}_2(g) + \text{RS}^- \qquad (1)$$

$$\text{Anode: RS}^- + \text{Ag} \longrightarrow [\text{Ag(SR)}] + e^- \qquad (2)$$

Table 1 Summary of crystal data for compounds **1**, **3** and $R^2SCH_2SR^2$

	1	**3**	$R^2SCH_2SR^2$
Empirical formula	$C_{72}H_{124}Ag_6N_6O_2S_6Si_6$	$C_{50}H_{44}Ag_4Cl_4P_4$	$C_{35}H_{66}N_2S_2Si_4$
M	2113.9	1342.1	691.4
Colour, habit	Yellow block	Colourless cube	Colourless block
Crystal size/mm	0.15 × 0.17 × 0.15	0.25 × 0.20 × 0.25	0.30 × 0.40 × 0.50
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$C2/c$
a/Å	15.139(3)	17.400(3)	23.955(5)
b/Å	17.298(3)	15.945(3)	15.818(3)
c/Å	18.074(4)	17.666(4)	12.327(2)
β/°	98.25(3)	—	115.04(3)
U/Å^3	4684(2)	4901(2)	4232(2)
Z	2	4	4
D_c/g cm^{-3}	1.499	1.095	1.085
μ(Mo-Kα)/mm^{-1}	1.481	1.958	0.263
Scan type	ω–2θ	ω–2θ	2θ–ω
Scan rate/° min^{-1}	2–8	2–8	8
2ω Range/°	2.0–45.0	2.0–45.0	2.0–50.0
No. reflections collected	6116	3209	3721
No. independent reflections (R_{int} = 0.00)	6116	3209	3721
No. unique data [$F > 6.0\sigma(F)$]	4634	2567	2854
F(000)	1076	660	1512
R	0.0639	0.0475	0.0357
R'	0.0749	0.0789	0.0484
Goodness of fit	2.53	1.77	1.46

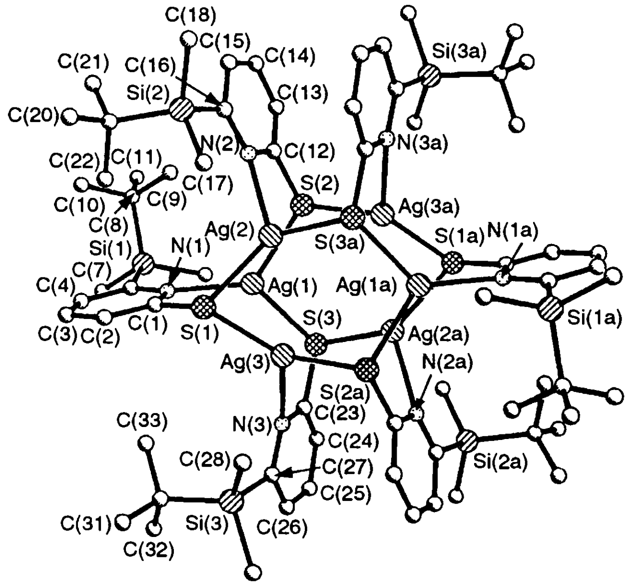

Fig. 1 An ORTEP view of the structure of $[\{Ag(SR^1)\}_6]$ **1** viewed parallel to the pseudo-three-fold axis passing through the centroids of the Ag_3S_3 rings

X-Ray diffraction studies show the compounds to be hexameric. They were treated with dppm to ascertain whether the hexamers could be depolymerized. Reaction in acetonitrile and in other commom solvents gave the initial silver complexes, presumably due to insolubility in these solvents. Only the presence of chlorinated solvents such as dichloromethane allows the solid to be dissolved in the presence of the phosphine. Consequently, the reactions were repeated in a mixture of acetonitrile and dichloromethane. X-Ray diffraction studies on crystals of the solid recovered show it to be $[Ag_4Cl_4(dppm)_2]$. This compound was probably formed by electrophilic atack of the silver atom of [Ag(SR)] on a chlorine atom of dichloromethane. Such a mechanism is consistent with the fact that in the case of $[\{Ag(SR^2)\}_6]$ **2** in addition to the silver compound another solid was isolated. X-Ray diffraction on crystals of this compound show it to be $R^2SCH_2SR^2$ the expected product from the above mechanism. This electrophilic attack appears to be general under the conditions used.

Structure of $[\{Ag(SR^1)\}_6]$ 1

An ORTEP[27] view of the molecular structure of $[\{Ag(SR^1)\}_6]$ with atom labelling is given in Fig. 1. Final atomic coordinates are listed in Table 2 and selected bond distances and angles, with estimated standard deviations, in Table 3. The complex crystallizes with two formula units and four Pr^{i}OH molecules in the cell.

The complex has an hexanuclear structure with the silver atoms in a highly distorted octahedral arrangement. The unit cell contains two molecules of $[\{Ag(SR^1)\}_6]$. Each has a centre of symmetry located at the centre of the entity Ag_6S_6. Intermetallic Ag ··· Ag distances among the silver atoms lie in the range 2.882(3)–4.034(3) Å. All are best considered as non-bonding,[3] although the shortest [2.882(3) and 2.901(2) Å] are very similar to those present in metallic silver (2.88 Å).[28] The overall pattern of metal–metal bond lengths is such that distances within two mutually *trans* faces, Ag(1)–Ag(2)–Ag(3) and Ag(1a)–Ag(2a)–Ag(3a), range from 2.882(3) to 3.159(2) Å, while the remaining six silver–silver bond lengths vary from 3.279(2) to 4.034(3) Å. Thus, the octahedron defining the silver system has two small (approximately) isosceles triangular faces and six larger triangular faces.

Each pyridine-2-thiolate ligand is bonded to three different metallic atoms defining a face of the octahedron, through the nitrogen atom and through the sulfur atom, which acts as a bridge. Two opposite faces of the octahedron are left exposed. Each silver atom is bonded to the sulfur atoms of two ligands and to the nitrogen atom of a further ligand, showing a distorted trigonal geometry, AgS_2N. The bond distances observed [Ag–S 2.479(4)–2.529(4) and Ag–N 2.271(11)–2.363(11) Å] are very similar to those found in other hexanuclear complexes of silver(I) with derivatives of pyridine-2-thione.[29] Although the structure of $[\{Ag(SR^1)\}_6]$ is related to that of the previously reported silver complex, there are some differences between them. Thus, the Ag–Ag distances within an Ag_3S_3 ring [3.157(2) Å] and between Ag_3S_3 rings [3.016(2) Å] in $[\{Ag(SR^3)\}_6]$ (R^3 = 3-dimethylphenylsilyl-2-pyridyl) are very different to those found in $[\{Ag(SR^1)\}_6]$.

Table 2 Atomic coordinates (× 10^4) for $[\{Ag(SR^1)\}_6]\cdot 2Pr^iOH$ **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	822(1)	1 161(1)	4 435(1)	C(13)	3 326(10)	−568(9)	4 613(9)
Ag(2)	1 204(1)	311(1)	5 827(1)	C(14)	4 099(11)	−694(9)	5 080(9)
Ag(3)	−634(1)	1 146(1)	5 302(1)	C(15)	4 178(11)	−454(9)	5 827(9)
S(1)	701(2)	1 628(2)	6 128(2)	C(16)	3 451(9)	−81(8)	6 074(8)
S(2)	1 598(2)	−100(2)	4 285(2)	C(17)	2 559(11)	325(10)	7 477(9)
S(3)	−669(2)	924(2)	3 640(2)	C(18)	4 395(13)	−377(11)	7 635(10)
Si(1)	2 317(3)	2 673(3)	3 732(2)	C(19)	4 112(11)	1 297(10)	7 077(9)
Si(2)	3 613(3)	295(3)	7 070(2)	C(20)	4 320(12)	1 587(11)	7 890(9)
Si(3)	−2 330(3)	2 840(3)	5 444(2)	C(21)	4 938(14)	1 318(13)	6 715(12)
N(1)	1 446(7)	2 252(7)	4 980(6)	C(22)	3 416(13)	1 863(12)	6 647(11)
N(2)	2 669(7)	15(7)	5 610(6)	C(23)	−1 550(9)	1 570(8)	3 747(8)
N(3)	−1 614(7)	1 853(7)	4 417(6)	C(24)	−2 153(10)	1 777(9)	3 110(9)
O(1)	10 958(6)	200(5)	2 028(7)	C(25)	−2 857(11)	2 247(10)	3 199(9)
C(1)	1 251(9)	2 355(8)	5 675(8)	C(26)	−2 926(11)	2 540(10)	3 897(9)
C(2)	1 472(10)	3 029(9)	6 078(9)	C(27)	−2 284(10)	2 348(9)	4 516(8)
C(3)	1 920(11)	3 616(10)	5 759(9)	C(28)	−1 882(11)	2 220(10)	6 259(9)
C(4)	2 107(11)	3 509(10)	5 053(9)	C(29)	−3 529(12)	3 053(11)	5 543(11)
C(5)	1 896(10)	2 815(9)	4 660(8)	C(30)	−1 669(10)	3 772(10)	5 428(9)
C(6)	1 603(10)	2 007(9)	3 088(9)	C(31)	−1 689(14)	4 225(12)	6 147(11)
C(7)	2 368(12)	3 631(10)	3 269(10)	C(32)	−2 045(15)	4 284(13)	4 774(12)
C(8)	3 484(10)	2 243(9)	3 955(9)	C(33)	−723(13)	3 589(12)	5 367(12)
C(9)	3 409(12)	1 440(10)	4 290(10)	C(34)	9 307(10)	755(9)	1 301(9)
C(10)	4 077(13)	2 754(12)	4 501(11)	C(35)	9 495(11)	−824(10)	1 673(9)
C(11)	3 902(12)	2 175(11)	3 258(10)	C(36)	9 784(16)	97(14)	1 907(13)
C(12)	2 611(9)	−229(8)	4 897(7)				

Table 3 Selected bond lengths (Å) and angles (°) for $[\{Ag(SR^1)\}_6]$ **1**

Ag(1) ··· Ag(2)	2.901(2)	Ag(1) ··· Ag(3)	2.882(2)	S(1)–C(1)	1.773(15)	S(2)–C(12)	1.772(13)
Ag(1)–S(2)	2.511(4)	Ag(1)–S(3)	2.529(4)	S(2)–Ag(3a)	2.504(4)	S(3)–C(23)	1.771(14)
Ag(1)–N(1)	2.271(11)	Ag(2) ··· Ag(3)	3.159(2)	S(3)–Ag(2a)	2.524(4)	N(1)–C(1)	1.343(18)
Ag(2)–S(1)	2.487(4)	Ag(2)–N(2)	2.363(11)	N(1)–C(5)	1.363(19)	N(2)–C(12)	1.346(17)
Ag(2) ··· Ag(3a)	3.279(2)	Ag(2)–S(3a)	2.524(4)	N(2)–C(16)	1.359(16)	N(3)–C(23)	1.324(18)
Ag(3)–S(1)	2.479(4)	Ag(3)–N(3)	2.361(11)	N(3)–C(27)	1.358(19)		
Ag(3) ··· Ag(2a)	3.279(2)	Ag(3)–S(2a)	2.504(4)				

Ag(2)–Ag(1)–Ag(3)	66.2(1)	Ag(2)–Ag(1)–S(2)	67.4(1)	N(3)–Ag(3)–Ag(2a)	83.9(3)	Ag(1)–Ag(3)–S(2a)	133.8(1)
Ag(3)–Ag(1)–S(2)	117.2(1)	Ag(2)–Ag(1)–S(3)	117.5(1)	Ag(2)–Ag(3)–S(2a)	96.1(1)	S(1)–Ag(3)–S(2a)	121.5(1)
Ag(3)–Ag(1)–S(3)	67.5(1)	S(2)–Ag(1)–S(3)	101.0(1)	N(3)–Ag(3)–S(2a)	103.9(3)	Ag(2a)–Ag(3)–S(2a)	61.2(1)
Ag(2)–Ag(1)–N(1)	91.5(3)	Ag(3)–Ag(1)–N(1)	94.3(3)	Ag(2)–S(1)–Ag(3)	79.0(1)	Ag(2)–S(1)–C(1)	111.7(5)
S(2)–Ag(1)–N(1)	126.6(3)	S(3)–Ag(1)–N(1)	131.6(3)	Ag(3)–S(1)–C(1)	110.9(4)	Ag(1)–S(2)–C(12)	114.7(5)
Ag(1)–Ag(2)–Ag(3)	56.6(1)	Ag(1)–Ag(2)–S(1)	72.3(1)	Ag(1)–S(2)–Ag(3a)	107.1(1)	C(12)–S(2)–Ag(3a)	102.2(5)
Ag(3)–Ag(2)–S(1)	50.4(1)	Ag(1)–Ag(2)–N(2)	92.3(3)	Ag(1)–S(3)–C(23)	117.4(4)	Ag(1)–S(3)–Ag(2a)	103.3(1)
Ag(3)–Ag(2)–N(2)	148.9(3)	S(1)–Ag(2)–N(2)	124.0(3)	C(23)–S(3)–Ag(2a)	101.8(5)	Ag(1)–N(1)–C(1)	112.5(9)
Ag(1)–Ag(2)–Ag(3a)	81.2(1)	Ag(3)–Ag(2)–Ag(3a)	91.3(1)	Ag(1)–N(1)–C(5)	127.7(9)	C(1)–N(1)–C(5)	119.5(12)
S(1)–Ag(2)–Ag(3a)	141.1(1)	N(2)–Ag(2)–Ag(3a)	84.2(3)	Ag(2)–N(2)–C(12)	107.0(8)	Ag(2)–N(2)–C(16)	132.7(10)
Ag(1)–Ag(2)–S(3a)	136.5(1)	Ag(3)–Ag(2)–S(3a)	100.6(1)	C(12)–N(2)–C(16)	119.0(12)	Ag(3)–N(3)–C(23)	107.8(8)
S(1)–Ag(2)–S(3a)	124.5(1)	N(2)–Ag(2)–S(3a)	103.9(3)	Ag(3)–N(3)–C(27)	130.2(9)	C(23)–N(3)–C(27)	120.6(11)
Ag(3a)–Ag(2)–S(3a)	61.1(1)	Ag(1)–Ag(3)–Ag(2)	57.2(1)	S(1)–C(1)–N(1)	121.2(10)	S(1)–C(1)–C(2)	116.5(11)
Ag(1)–Ag(3)–S(1)	72.8(1)	Ag(2)–Ag(3)–S(1)	50.6(1)	N(1)–C(1)–C(2)	122.2(13)	C(1)–C(2)–C(3)	119.3(15)
Ag(1)–Ag(3)–N(3)	94.7(3)	Ag(2)–Ag(3)–N(3)	151.8(3)	C(2)–C(3)–C(4)	118.0(15)	C(3)–C(4)–C(5)	121.8(16)
S(1)–Ag(3)–N(3)	127.8(3)	Ag(1)–Ag(3)–Ag(2a)	79.8(1)	N(1)–C(5)–C(4)	119.1(14)		
Ag(2)–Ag(3)–Ag(2a)	88.7(1)	S(1)–Ag(3)–Ag(2a)	138.8(1)				

The pyridine rings are essentially planar, with the sulfur atoms lying approximately in the plane of the pyridine ring to which they are bound. The average S–C and C–N bond distances, 1.772(13) and 1.349(19) Å, respectively, are similar to those found in bis(6-*tert*-butyldimethylsilyl)-2-pyridyl disulfide,[6b] 1.791(8) and 1.344(13) Å, indicating that the ligand is co-ordinating in a form that is closer to pyridine-2-thionate than to the thione form.

An alternative way of describing the structure of the compound is to consider the whole geometry as a paddlewheel in which the hub is formed by two rings of Ag_3S_3 and the six paddles are the fragments $C_5H_3N(SiMe_2Bu^t)$. The ligands act as bridges between two Ag_3S_3 rings, in such a way that three nitrogen atoms are in each ring. The sulfur atoms act as bridges between adjacent metallic atoms in an Ag_3S_3 ring. The trigonal geometry around each silver atom is completed by nitrogen atoms.

The metal cluster and Pr^iOH molecules are separated by normal van der Waals distances and there are no abnormally short intermolecular contacts. It should be emphasized that Pr^iOH is not incorporated into any silver atom co-ordination sphere.

Vibrational spectra

The band attributable to ν(N–H), which appears at 3190 cm^{-1} for the free ligand, is absent for complexes **1** and **2** indicating that the ligand is in the deprotonated form. The strong ligand bands in the range 1580–1550 cm^{-1}, due to ν(C=C) and ν(C=N), appear at 1550–1525 cm^{-1} for the metal complexes. This is compatible with the transformation of the thione ring to a heterocyclic aromatic one. The [Ag(SR)] complexes show in addition a broad and strong band around 830–810 cm^{-1} assignable to the vibration ν(Si–C).[5c]

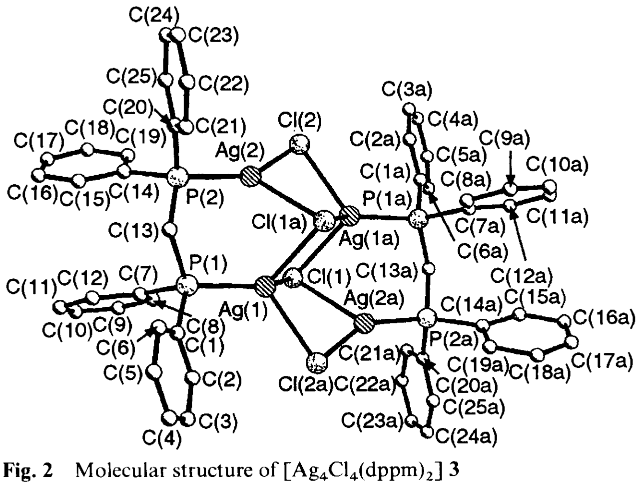

Fig. 2 Molecular structure of [$Ag_4Cl_4(dppm)_2$] **3**

Table 4 Atomic coordinates (× 10^4) for [$Ag_4Cl_4(dppm)_2$] **3**

Atom	*x*	*y*	*z*
Ag(1)	9 785(1)	138(1)	5 999(1)
Ag(2)	8 430(1)	−81(1)	4 745(1)
P(1)	8 755(1)	200(1)	6 884(1)
P(2)	7 487(1)	168(1)	5 682(1)
Cl(1)	10 401(1)	−1 083(1)	5 232(1)
Cl(2)	8 832(1)	−640(2)	3 538(1)
C(1)	8 987(4)	858(4)	7 691(4)
C(2)	9 676(6)	712(7)	8 033(6)
C(3)	9 905(7)	1 196(7)	8 629(6)
C(4)	9 503(6)	1 813(7)	8 889(5)
C(5)	8 829(9)	1 979(10)	8 562(8)
C(6)	8 564(8)	1 491(9)	7 936(8)
C(7)	8 474(4)	−780(5)	7 322(4)
C(8)	8 844(5)	−1 513(5)	7 101(5)
C(9)	8 647(6)	−2 262(6)	7 478(5)
C(10)	8 126(5)	−2 265(7)	8 017(5)
C(11)	7 755(6)	−1 563(6)	8 242(6)
C(12)	7 925(5)	−812(6)	7 891(5)
C(13)	7 864(4)	664(4)	6 526(4)
C(14)	6 907(5)	−694(5)	6 011(4)
C(15)	6 461(5)	−641(6)	6 657(5)
C(16)	5 999(6)	−1 318(7)	6 893(6)
C(17)	5 994(7)	−2 013(8)	6 446(6)
C(18)	6 382(6)	−2 081(8)	5 831(6)
C(19)	6 877(6)	−1 430(6)	5 581(6)
C(20)	6 784(4)	917(5)	5 307(4)
C(21)	6 803(5)	1 766(5)	5 457(4)
C(22)	6 298(5)	2 315(5)	5 113(4)
C(23)	5 766(5)	2 014(6)	4 603(5)
C(24)	5 735(6)	1 183(6)	4 450(5)
C(25)	6 244(5)	623(6)	4 793(5)

NMR spectra

The ^1H NMR spectrum of 6-(*tert*-butyldimethylsilyl)pyridine-2-thione shows a broad singlet at δ 10.37, due to NH. A nuclear Overhauser effect (NOE) experiment allows the assignments of the protons H^5, H^4 and H^3 to the signals appearing at δ 6.56, 7.04 and 7.28, respectively. A combination of distortionless enhancements by polarization transfer (DEPT) and ^1H–^{13}C correlation spectroscopy (COSY) allowed the assignment of the ^{13}C NMR spectrum (see Experimental section). The chemical shifts for 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione can also be found in the Experimental section.

The complexes [Ag(SR)] do not exhibit a signal attributable to the group NH, further indicating that deprotonation of the ligands has occurred, during the electrochemical reaction and consequently that the ligands bond to the metal in the thiolate form. In addition, the signals of the aromatic protons are slightly shifted to lower field. The ^{13}C NMR spectra show the characteristic signals of the free thiones, the most remarkable difference being the shift to higher field, about 10 ppm, of the signal due to C^2. This behaviour can be explained as the result of the reduction in the C–S bond order due to the transformation of thione to thiolate.[30]

Structure of [$Ag_4Cl_4(dppm)_2$]

The molecular structure of [$Ag_4Cl_4(dppm)_2$] is shown in Fig. 2, together with the atomic numbering scheme adopted; the final atomic coordinates, bond distances and angles are given in Tables 4 and 5 respectively. The compound consists of discrete neutral tetranuclear units with a centre of symmetry coinciding with a crystallographic centre and is best described as being based on a distorted parallelogram of four silver atoms. This structure is similar to that found in the centrosymmetric chair-like [$Ag_4I_4(PPh_3)_4$][31] although in this case the Ag···Ag distances in the parallelogram, 3.095(1) and 4.315(2) Å are very different to those observed in [$Ag_4Cl_4(dppm)_2$], Ag(1)···Ag(2) 3.254(1) and Ag(1)···Ag(2a) 3.374(1) Å. All these distances are considerably greater than the distance in metallic silver (2.88 Å)[28] showing that no significant metal–metal interaction exists. The distortion of the molecule is produced by the different metal–metal distances and the angles of 66.5(1)° for Ag(1)–Ag(2)–Ag(1a) and 113.5(1)° for Ag(2)–Ag(1)–Ag(2a), which are quite different from the ideal 90° for square-planar geometry.

On each of the short sides of the parallelogram two silver atoms are bridged by a dppm molecule, with very similar silver–phosphorus bonds lengths [Ag(2)–P(2) 2.366(2) and Ag(1)–P(1) 2.379(2) Å]. On each of the long sides the metallic atoms are bridged asymmetrically by one chlorine atom, Ag(2)–Cl(2) 2.414(2) and Ag(1a)–Cl(2) 2.665(2) Å. In addition, each of the other two chlorine atoms, above and below the plane of the parallelogram, bridges three metal atoms with distances Ag(1)–Cl(1) 2.602(2), Ag(2a)–Cl(1) 2.754(2) and Ag(1a)–Cl(1) 2.665(2) Å. The distance to the fourth silver atom is 4.816(6) Å. The geometry of the three-co-ordinated chlorine atoms can be described as a distorted pyramid with the chlorine atom at the apex and the three silver atoms in the triangular face of the base.

Two silver atoms, Ag(2) and Ag(2a), are co-ordinated by one phosphorus atom of one bridging dppm ligand and two bridging chlorine atoms (one doubly and the other triply bridging) to give a three-co-ordinated silver centre with a distorted trigonal-planar geometry [maximun deviation of the Ag atom from the best least-squares plane formed by the donor atoms, 0.200 Å; bond angles around the silver atom P(2)–Ag(2)–Cl(2) 151.8(1), P(2)–Ag(2)–Cl(1a) 112.9(1) and Cl(2)–Ag(2)–Cl(1a) 92.7(1)°]. Each of the other silver atoms is co-ordinated by one phosphorus atom of one dppm ligand and three chlorine atoms (one doubly and two triply bridging) resulting in a distorted-tetrahedral environment around the Ag. The deviation from perfect geometry is illustrated by the values of the angles around the Ag(2) atom which range from 90.7(1) to 133.1(1)°.

The Ag–P bond distances differ slightly, as the bond involving the four-co-ordinated silver atom is longer, Ag(1)–P(1) 2.379(2) Å, than that to the three-co-ordinated one, Ag(2)–P(2) 2.366(2) Å. Both distances are considerably shorter than Ag–P distances in the linear complex[32] [Ag{$P(C_6H_2Me_3$-2,4,6)$_3$}$_2$]$^+$, 2.461(6) Å, and even shorter than those in other silver–phosphine complexes, 2.411–2.524 Å if the metal is three-co-ordinated[33,34] or 2.417–2.746 if it is four-co-ordinated.[31,34–36] This suggests that in [$Ag_4Cl_4(dppm)_2$] the Ag–P bonds are relatively strong.

The digonal bridging Ag–Cl bonds are asymmetrical, with significantly different distances of 2.414(2) and 2.665(2). These are quite distinct from the terminal Ag–Cl bonds observed in [AgLCl],[35] L = 2,11-[bis(diphenylphosphino)methyl]benzo[*c*]phenanthrene [2.512(2) Å]. The longer Ag–Cl distance to the four-co-ordinated silver site is similar to those

Table 5 Bond lengths (Å) and angles (°) for [$Ag_4Cl_4(dppm)_2$] **3**

Ag(1) · · · Ag(2)	3.254(1)	Ag(1)–P(1)	2.379(2)	C(3)–C(4)	1.292(15)	C(4)–C(5)	1.335(18)
Ag(1)–Cl(1)	2.602(2)	Ag(1) · · · Ag(2a)	3.374(1)	C(5)–C(6)	1.429(20)	C(7)–C(8)	1.391(12)
Ag(1)–Cl(1a)	2.665(2)	Ag(1)–Cl(2a)	2.665(2)	C(7)–C(12)	1.387(11)	C(8)–C(9)	1.410(13)
Ag(2)–P(2)	2.366(2)	Ag(2)–Cl(2)	2.414(2)	C(9)–C(10)	1.315(14)	C(10)–C(11)	1.352(14)
Ag(2) · · · Ag(1a)	3.374(1)	Ag(2)–Cl(1a)	2.754(2)	C(11)–C(12)	1.380(13)	C(14)–C(15)	1.384(12)
P(1)–C(1)	1.816(7)	P(1)–C(7)	1.812(8)	C(14)–C(19)	1.398(12)	C(15)–C(16)	1.410(14)
P(1)–C(13)	1.831(7)	P(2)–C(13)	1.812(7)	C(16)–C(17)	1.360(16)	C(17)–C(18)	1.285(16)
P(2)–C(14)	1.801(8)	P(2)–C(20)	1.834(8)	C(18)–C(19)	1.419(15)	C(20)–C(21)	1.380(11)
Cl(1)–Ag(1a)	2.665(2)	Cl(1)–Ag(2a)	2.754(2)	C(20)–C(25)	1.387(12)	C(21)–C(22)	1.382(12)
Cl(2)–Ag(1a)	2.665(2)	C(1)–C(2)	1.361(12)	C(22)–C(23)	1.378(12)	C(23)–C(24)	1.353(14)
C(1)–C(6)	1.322(15)	C(2)–C(3)	1.365(15)	C(24)–C(25)	1.397(14)		
Ag(2)–Ag(1)–P(1)	84.7(1)	Ag(2)–Ag(1)–Cl(1)	82.2(1)	Ag(1)–P(1)–C(7)	116.7(3)	C(1)–P(1)–C(7)	102.9(3)
P(1)–Ag(1)–Cl(1)	133.1(1)	Ag(2)–Ag(1)–Ag(2a)	113.5(1)	Ag(1)–P(1)–C(13)	115.3(2)	C(1)–P(1)–C(13)	103.0(3)
P(1)–Ag(1)–Ag(2a)	161.8(1)	Cl(1)–Ag(1)–Ag(2a)	53.0(1)	C(7)–P(1)–C(13)	105.5(3)	Ag(2)–P(2)–C(13)	113.4(2)
Ag(2)–Ag(1)–Cl(1a)	54.4(1)	P(1)–Ag(1)–Cl(1a)	114.9(1)	Ag(2)–P(2)–C(14)	119.1(3)	C(13)–P(2)–C(14)	105.8(3)
Cl(1)–Ag(1)–Cl(1a)	92.7(1)	Ag(2a)–Ag(1)–Cl(1a)	79.0(1)	Ag(2)–P(2)–C(20)	108.6(2)	C(13)–P(2)–C(20)	104.8(3)
Ag(2)–Ag(1)–Cl(2a)	153.6(1)	P(1)–Ag(1)–Cl(2a)	117.7(1)	C(14)–P(2)–C(20)	103.9(4)	Ag(1)–Cl(1)–Ag(1a)	87.3(1)
Cl(1)–Ag(1)–Cl(2a)	90.7(1)	Ag(2a)–Ag(1)–Cl(2a)	45.3(1)	Ag(1)–Cl(1)–Ag(2a)	78.0(1)	Ag(1a)–Cl(1)–Ag(2a)	73.8(1)
Cl(1a)–Ag(1)–Cl(2a)	101.0(1)	Ag(1)–Ag(2)–P(2)	90.5(1)	Ag(2)–Cl(2)–Ag(1a)	83.1(1)	P(1)–C(1)–C(2)	116.4(6)
Ag(1)–Ag(2)–Cl(2)	115.5(1)	P(2)–Ag(2)–Cl(2)	151.8(1)	P(1)–C(1)–C(6)	125.0(7)	P(1)–C(7)–C(8)	118.6(6)
Ag(1)–Ag(2)–Ag(1a)	66.5(1)	P(2)–Ag(2)–Ag(1a)	156.4(1)	P(1)–C(7)–C(12)	121.8(6)	P(1)–C(13)–P(2)	114.5(4)
Cl(2)–Ag(2)–Ag(1a)	51.6(1)	Ag(1)–Ag(2)–Cl(1a)	51.9(1)	P(2)–C(14)–C(15)	122.2(6)	P(2)–C(14)–C(19)	119.1(6)
P(2)–Ag(2)–Cl(1a)	112.9(1)	Cl(2)–Ag(2)–Cl(1a)	92.7(1)	P(2)–C(20)–C(21)	123.6(6)	P(2)–C(20)–C(25)	117.8(6)
Ag(1a)–Ag(2)–Cl(1a)	49.0(1)	Ag(1)–P(1)–C(1)	111.9(2)				

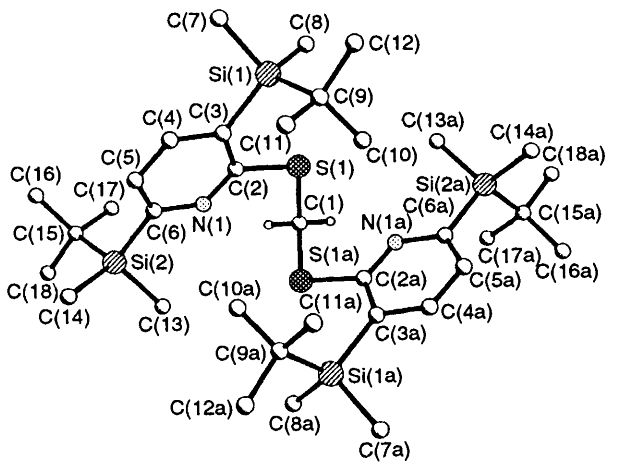

Fig. 3 Molecular structure of $R^2SCH_2SR^2$

found in [$Ag_2Cl_2\{Ph_2P(CH_2)_5PPh_2\}$][37] [2.671(26) Å] which exhibits doubly bridging chlorine and four-co-ordinated silver. The trigonally bridging Ag–Cl bonds are very different, 2.754(2), 2.602(2) and 2.665(2) Å. These distances do not show the systematic trend found in the chair-like complex [$Ag_4I_4(PPh_3)_4$] where the Ag–I bond lengths increase as the co-ordination number of the silver and iodine atoms increases. The bond angle and lengths in the dppm ligand are similar to those found in other dppm complexes, with P atoms tetrahedrally co-ordinated, 102.9(3)–116.7(3)° for P(1) and 103.9(4)–119.1(3)° for P(2). The C–P bond-lengths [P–C(sp^3) 1.812(7)–1.831(2), P–C(sp^2) 1.801(8)–1.834(8) Å] are normal.

The infrared spectrum of [$Ag_4Cl_4(dppm)_2$] shows bands attributed to the bonded diphosphine[38] at 1645, 1460 and 1130 cm^{-1}. The ^1H NMR spectrum shows signals at δ 7.1–7.3 assignable to the phenyl groups and at δ 3.48 assignable to the methylene groups. The ^{13}C NMR spectrum shows three signals at δ 132–128 due to the three types of carbon atoms of each phenyl group of the phosphine. In addition, the signal of the methylene group is found at δ 26.7. The ^{31}P NMR spectrum shows a signal at δ 22.96 (relative to external 85% H_3PO_4) which has shifted downfield from its position in the free dppm spectrum (δ −22.00). This downfield shift is characteristic of bridging dppm.[39]

Table 6 Atomic coordinates (× 10^4) for $R^2SCH_2SR^2$

Atom	*x*	*y*	*z*
S(1)	4435(1)	6652(1)	−3704(1)
Si(2)	4031(1)	6761(1)	244(1)
Si(1)	3449(1)	8266(1)	−5115(1)
N(1)	4119(1)	6851(1)	−1911(2)
C(1)	5000	6052(2)	−2500
C(2)	4023(1)	7155(1)	−2978(2)
C(3)	3636(1)	7846(1)	−3556(2)
C(4)	3363(1)	8226(1)	−2881(2)
C(5)	3473(1)	7943(2)	−1747(2)
C(6)	3846(1)	7239(1)	−1275(2)
C(7)	2677(1)	8781(2)	−5639(2)
C(8)	3376(1)	7406(2)	−6205(2)
C(9)	4038(1)	9084(2)	−5070(2)
C(10)	4676(1)	8693(2)	−4705(3)
C(11)	4089(2)	9777(2)	−4178(3)
C(12)	3829(2)	9472(2)	−6317(3)
C(13)	4794(1)	6231(2)	740(2)
C(14)	4062(1)	7633(2)	1285(2)
C(15)	3416(1)	5963(1)	121(2)
C(16)	2783(1)	6388(2)	−318(3)
C(17)	3388(1)	5267(2)	−758(2)
C(18)	3578(1)	5568(2)	1353(2)

Structure of bis[3,6-bis(*tert*-butyldimethylsilyl)-2-pyridylsulfanyl]methane

A perspective view of $R^2SCH_2SR^2$ is shown in Fig. 3; the final atomic coordinates, selected bond lengths and angles are given in Tables 6 and 7. This compound has C_2 symmetry with atom C(1) on a crystallographic two-fold axis.

The bond lengths and angles of the pyridine rings are similar and are in close agreement with those observed in di-2-pyridyl disulfide. The S(1)–C(1) distance 1.798(2) Å is within the accepted range for S–C single bonds.[40] The S(1)–C(2) distance 1.776(3) Å is shorter but is longer than that found in free pyridine-2-thione,[41] 1.68 Å, which is in the solid state in the thione form.

Each pyridine ring is planar, the maximum deviation of any atom from the best least-squares plane being 0.017 Å. Atom Si(2) lies approximately on the plane of the pyridine ring to which it is bound (0.008 Å). The other Si atom and the sulfur atom are both out of the plane of the pyridine to which they are bound [0.070 Å for Si(1) and 0.120 Å for S(1)]. The interplanar angle between the

Table 7 Selected bond lengths (Å) and angles (°) for $R^2SCH_2SR^2$

S(1)–C(1)	1.798(2)	S(1)–C(2)	1.776(3)
Si(2)–C(6)	1.890(2)	Si(2)–C(13)	1.864(3)
Si(2)–C(14)	1.863(3)	Si(2)–C(15)	1.896(3)
Si(1)–C(3)	1.899(2)	Si(1)–C(7)	1.870(3)
Si(1)–C(8)	1.867(3)	Si(1)–C(9)	1.898(3)
N(1)–C(2)	1.327(3)	N(1)–C(6)	1.360(3)
C(1)–S(1a)	1.798(2)	C(2)–C(3)	1.414(3)
C(3)–C(4)	1.395(4)	C(4)–C(5)	1.382(4)
C(5)–C(6)	1.393(3)	C(9)–C(10)	1.528(4)
C(9)–C(11)	1.520(4)	C(9)–C(12)	1.528(4)
C(15)–C(16)	1.532(4)	C(15)–C(17)	1.526(4)
C(15)–C(18)	1.531(4)		
C(1)–S(1)–C(2)	101.8(1)	C(2)–N(1)–C(6)	119.0(2)
S(1)–C(1)–S(1a)	116.3(1)	S(1)–C(2)–N(1)	115.9(2)
S(1)–C(2)–C(3)	118.6(2)	N(1)–C(2)–C(3)	125.5(2)
C(2)–C(3)–C(4)	114.0(2)	C(3)–C(4)–C(5)	121.8(2)
C(4)–C(5)–C(6)	119.7(3)	N(1)–C(6)–C(5)	120.0(2)
C(10)–C(9)–C(11)	108.4(2)	Si(1)–C(9)–C(12)	108.7(2)
C(10)–C(9)–C(12)	108.7(3)	C(11)–C(9)–C(12)	109.2(2)
C(16)–C(15)–C(17)	109.0(2)	C(16)–C(15)–C(18)	109.1(3)

two pyridine rings is 75.24(4)° whereas that between them and the S(1)–C(1)–S(1a) plane is 113.6(1)°. In each pyridine ring the planes Si(1)–C(3)–C(9) and C(15)–Si(2)–C(6) are almost parallel with a dihedral angle of 3.1(1)°. However, the *tert*-butyl groups are oriented in opposite directions and are approximately perpendicular to the pyridine ring, 86.1(1) and 87.90(8)°. On the other hand, the corresponding silyl groups of different pyridine rings are almost perpendicular, dihedral angle 92.63(6)°.

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