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FULL PAPER

Synthesis, X-ray and solid state NMR studies on silver(I) silanethiolates. Crystal structure of bis[(triphenylphosphine)-(tri-*o*-tolylsilanethiolato)silver(I)]–toluene(1/2), $[\{Ag[SSi(C_6H_4\text{-}Me\text{-}o)_3](PPh_3)\}_2]\cdot 2C_6H_5Me$ †

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A series of silver(I) trialkoxysilanethiolates $[Ag(SSiR_3)(PPh_3)_2]$, R = Bu^{t}O, Bu^{s}O or Pr^{i}O, and triarylsilanethiolates $[Ag(SSiR'_3)(PPh_3)]$, R′ = *o*-MeC$_6$H$_4$ or Ph, were obtained by reaction of $[Ag(acac)(PPh_3)_2]$ with the respective silanethiols. Products were studied by ^{1}H NMR, CP MAS ^{31}P and ^{29}Si NMR in solution and/or in the solid state. A single-crystal X-ray structural analysis was carried on for $[\{Ag[SSi(C_6H_4Me\text{-}o)_3](PPh_3)\}_2]\cdot 2C_6H_5Me$.

Introduction

The thiolato group RS$^-$ is widely recognized as a basic type of ligand, and a huge number of copper group metal thiolates has been obtained up to now. However, owing to the strong tendency of sulfur to bridge metal centers and consequently form insoluble polymers, their detailed characterization has proved very difficult in many cases. The most common approaches to overcome the irregular polymerization problem have been increasing the steric demand of the thiol substituent R and/or incorporation of heteroligands on the metal atom. To increase the bulk of silicon containing thiols, for example triorganosilyl substituted thiophenols[2] or (triorganosilyl)methanethiols $(R_3Si)_nCH_{3-n}SH$,[3] were used as ligand sources. These however are still based on a common ≡C–SH theme.

Our continuing interest in silicon–sulfur compounds prompted us to introduce a novel type of ligand where the thiolate function rather than on carbon is bonded directly to silicon. The first metal silanethiolate we obtained and characterized structurally was the silver(I) complex $[\{AgSSi(OBu^t)_3\}_4]$.[4] This was followed by several other neutral tri-*tert*-butoxysilanethiolates, which were invariably molecular. Among them were also copper(I) and gold(I) derivatives, $[\{MSSi(OBu^t)_3\}_4]$ (where M = Cu or Au).[5,6] Later we found that tetrameric copper(I) tri-*tert*-butoxysilanethiolate reacts with triphenylphosphine giving a neutral, heteroleptic copper(I) complex, $[Cu\{SSi(OBu^t)_3\}(PPh_3)_2]$.[7] So far our investigations have been limited to tri-*tert*-butoxysilanethiol $(Bu^tO)_3SiSH$, as the source of silanethiolate ligand. It has one great advantage over other silanethiols. Owing to the great steric hindrance caused by three bulky *tert*-butoxy substituents bonded to silicon, under normal conditions it does not undergo hydrolysis in which silanethiols more or less easily decompose to the corresponding silanol and hydrogen sulfide.[8] Now we present some results of our investigations on the synthesis and properties of heteroleptic silver complexes where also other trialkoxysilanethiols, $(Bu^sO)_3SiSH$, $(Pr^iO)_3SiSH$, and triarylsilanethiols, Ph_3SiSH and $(o\text{-}MeC_6H_4)_3SiSH$, have been used. Triphenylphosphine was bound as the second ligand.

Results and discussion

For the preparation of phosphine ligated silver silanethiolates three methods may be of interest. (1) Direct reaction between silanethiol, silver salt and phosphine. The reaction between silver nitrate, phosphine and tri-*tert*-butoxysilanethiol under heterogeneous conditions (water–CHCl$_3$) in the presence of sodium acetate gave the pure compound $[Ag\{SSi(OBu^t)_3\}(PPh_3)_2]$ **1** in good yield. This simple procedure could not however be applied for the other four silanethiols. Even the more stable of them, $(o\text{-}MeC_6H_4)_3SiSH$,[8] was easily hydrolysed and Ag$_2$S precipitated from the reaction mixture. (2) Reaction of homoleptic silver silanethiolate with phosphine. The procedure is of limited importance because of its requirement for homoleptic silver silanethiolates, which besides $[\{AgSSi(OBu^t)_3\}_4]$ are still unknown. (3) Reaction of a silanethiolate ligand source with an appropriate silver phosphine complex. The reaction of tri-*tert*-butoxysilanethiol (in the presence of Et$_3$N) with different triphenylphosphine complexes of silver, $[Ag(PPh_3)_4]NO_3$, $[Ag_2Br_2(PPh_3)_4]$ or $[\{AgI(PPh_3)\}_4]$, gave invariably **1** which is obviously the preferred product.

The only method which could be used for all silanethiols was that utilizing silver phosphine complexes as substrates. The complexes mentioned above required the presence of a base for neutralization of the strong acid produced. However, too basic conditions promote hydrolysis of silanethiols.[9] Since silanethiols are more acidic than organic thiols[10,11] a method with substitution of a stronger acid for a weaker one was envisaged. The preparation of phosphine ligated silver(I) silanethiolates was best accomplished by the use of bis(triphenylphosphine)silver(I) acetylacetonate, eqn. (1). Besides **1** the following new

$$[Ag(acac)(PPh_3)_2] + R_3SiSH \longrightarrow R_3SiSAg(PPh_3)_n + Hacac + (2-n)PPh_3 \quad (1)$$

complexes were obtained: $[Ag\{SSi(OPr^i)_3\}(PPh_3)_2]$ **2**, $[Ag\{SSi(OBu^s)_3\}(PPh_3)_2]$ **3**, $[Ag\{SSi(C_6H_4Me\text{-}o)_3\}(PPh_3)]$ **4** and $[Ag(SSiPh_3)(PPh_3)]$ **5**. Contrary to trialkoxysilanethiols, triarylsilanethiols gave complexes with a silver : phosphine ratio of

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† Contributions to the chemistry of silicon–sulfur compounds. Part 71.[1]

Supplementary data available: preparations. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3063/, otherwise available from BLDSC (No. SUP 57613, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

Table 1 Selected bond lengths (Å) and angles (°) for $[\{Ag[SSi(C_6H_4Me\text{-}o)_3](PPh_3)\}_2]\cdot 2C_6H_5Me$ **4**

Ag(1)–S(2)	2.4680(9)	P(3)–C(32)	1.822(2)
Ag(1)–S(2^1)	2.6376(8)	P(3)–C(38)	1.824(2)
Ag(1)–P(3)	2.3845(12)	Si(4)–C(5)	1.899(2)
S(2)–Si(4)	2.1060(12)	Si(4)–C(12)	1.896(2)
P(3)–C(26)	1.815(2)	Si(4)–C(19)	1.883(2)
S(2^1)–Ag(1)–S(2)	91.98(4)	C(26)–P(3)–Ag(1)	113.06(9)
Ag(1^1)–S(2)–Ag(1)	88.02(4)	C(32)–P(3)–Ag(1)	114.65(8)
P(3)–Ag(1)–S(2)	145.90(3)	C(38)–P(3)–Ag(1)	115.11(8)
P(3)–Ag(1)–S(2^1)	122.12(3)	C(5)–Si(4)–S(2)	108.63(8)
Si(4)–S(2)–Ag(1^1)	121.98(4)	C(12)–Si(4)–S(2)	110.11(8)
Si(4)–S(2)–Ag(1)	105.34(5)	C(19)–Si(4)–S(2)	111.84(8)
Torsion angles			
S(2^1)–Ag(1)–S(2)–Ag(1^1)	0.0^a	Ag(1)–P(3)–C(26)–C(31)	−42.8(3)
P(3)–Ag(1)–S(2)–Ag(1^1)	−179.01(3)	Ag(1)–P(3)–C(32)–C(33)	−51.3(2)
P(3)–Ag(1)–S(2)–Si(4)	−56.32(5)	Ag(1)–P(3)–C(38)–C(39)	−37.7(2)
S(2)–Ag(1)–P(3)–C(26)	149.79(9)	S(2)–Si(4)–C(5)–C(10)	−4.3(2)
S(2)–Ag(1)–P(3)–C(32)	−89.85(9)	S(2)–Si(4)–C(12)–C(13)	−61.5(2)
S(2)–Ag(1)–P(3)–C(38)	30.22(9)	S(2)–Si(4)–C(19)–C(20)	−52.2(2)

Atoms related by the center of symmetry are indicated by superscript 1. ^{a} Flat Ag_2S_2 ring.

only 1 : 1, *i.e.* one phosphine molecule was eliminated from silver during the reaction. Compounds **1**–**5** form colorless crystals characterized by sharp melting points.

Compound **1** is stable and can be stored without special precautions. It is readily soluble in $CHCl_3$, tetrahydrofuran and benzene, sparingly soluble in heptane, acetone, acetonitrile and practically insoluble in methanol or butan-1-ol. Solutions in more polar solvents (THF or $CHCl_3$) are not stable and multiple crystallization leads to separation of PPh_3 and the known $[\{Ag[SSi(Bu^tO)_3]\}_4]$.[4] The mass spectrum of **1** (FAB; *m*-nitrobenzyl alcohol matrix, NBA): positive ions, *m*/*z* 1270 ($Ag_2(PPh_3)_4^+$, 65), 1019 ($Ag_2SR(PPh_3)_2^+$, 10), 633 ($Ag(PPh_3)_2^+$, 100) and 370 ($Ag(PPh_3)_2^+$, 92%); negative ions, *m*/*z* 279 (RS^-, 45), 539 ($Ag(NBA)SR^-$, 30), 667 ($Ag(SR)_2^-$, 30) also 1053 ($Ag_2(SR)_3^-$, <2) and 1301 ($Ag_2(PPh_3)_2(SR)_2^-$, <2%); where $R = SSi(OBu^t)_3$. The cited intensities are given for the most intense peaks because of the wide isotropic profile of each signal. All the profiles are consistent with the proposed formulas.

The two other trialkoxysilanethiolates **2** and **3** are much less stable and should be stored under a dry neutral atmosphere. Under normal laboratory conditions the crystals underwent visible decomposition within a few days, even in a refrigerator, with formation of Ag_2S. Their solubilities are similar to that of **1** but in solutions, especially in more polar solvents, the compounds decompose quite easily. The tri-*o*-tolylsilanethiolate **4** can be dissolved in aromatic hydrocarbons and, as shown by a subsequent structure determination, the crystals obtained from toluene contained the solvent. The triphenylsilanethiolate **5** is completely insoluble in all common organic solvents and as such may be a polymer. Its elemental analysis suggests a benzene solvate. This was the reason why we turned to the more bulky tri-*o*-tolylsilanethiol as substrate.

Molecular structures

The different types of stoichiometric formulas found for the trialkoxy- and triaryl-silanethiolate complexes of silver called for elucidation and attempts have been made to determine their structures. Good quality single crystals were obtained for **1**, **2** and **4**, but **2** survived only two days under X-ray radiation at room temperature. Despite numerous efforts the crystals of **5**, although well shaped, grew too small to be considered for X-ray measurements. The compound is hard to characterize because of its very low solubility in all popular solvents. No solution spectral data are available. Elemental analysis and solid state NMR data suggest its structure is similar to that of its *o*-tolyl homologue **4**.

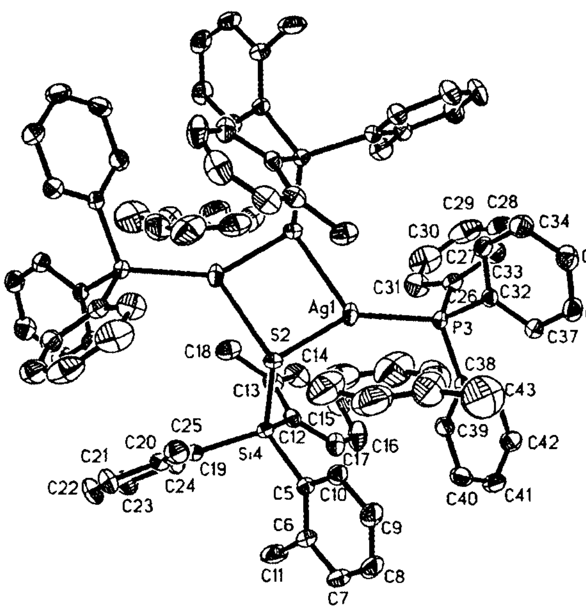

Fig. 1 Molecular structure of $[\{Ag[SSi(C_6H_4Me\text{-}o)_3](PPh_3)\}_2]\cdot 2C_6H_5Me$ **4**. General shape of the dimer part and atom numbering scheme (toluene atom numbers and all hydrogen atoms omitted, thermal ellipsoids 20%).

$[Ag\{SSi(OBu^t)_3\}(PPh_3)_2]$ 1. Details of the measurement, complete set of positional parameters and view of the molecule have been reported.[12] There are no silver complexes that could be directly compared with **1**. From the geometric point of view the closest related structure is represented by $[Ag(PPh_3)_2(Hpymt)]NO_3$ (Hpymt = pyrimidine-2-thione) reported recently.[13] However, this complex is ionic with Ag co-ordinated by thione sulfur and thus having a much longer Ag–S bond 2.573(1) as compared to 2.4495(11) Å found in **1**. It is worthy to note that the Si–S bond shortens on going from homoleptic $[\{AgSSi(OBu^t)_3\}_4]$, 2.119(8) Å where sulfur is three-bonded to heteroleptic silanethiolate, to **1** with sulfur two-bonded, 2.0738(14) Å. The same type of shortening was observed previously for the pair $[\{CuSSi(OBu^t)_3\}_4]$[5] and $[Cu\{SSi(OBu^t)_3\}(PPh_3)_2]$.[7]

$[\{Ag[SSi(C_6H_4Me\text{-}o)_3](PPh_3)\}_2]$ 4. Bis[(triphenylphosphine)(tri-*o*-tolylsilanethiolato)silver(I)–toluene (1/2) crystallizes in the triclinic system as colorless prisms. Selected bond lengths and angles are given in Table 1 and the molecular structure and atom numbering scheme are illustrated in Fig. 1. Alternating

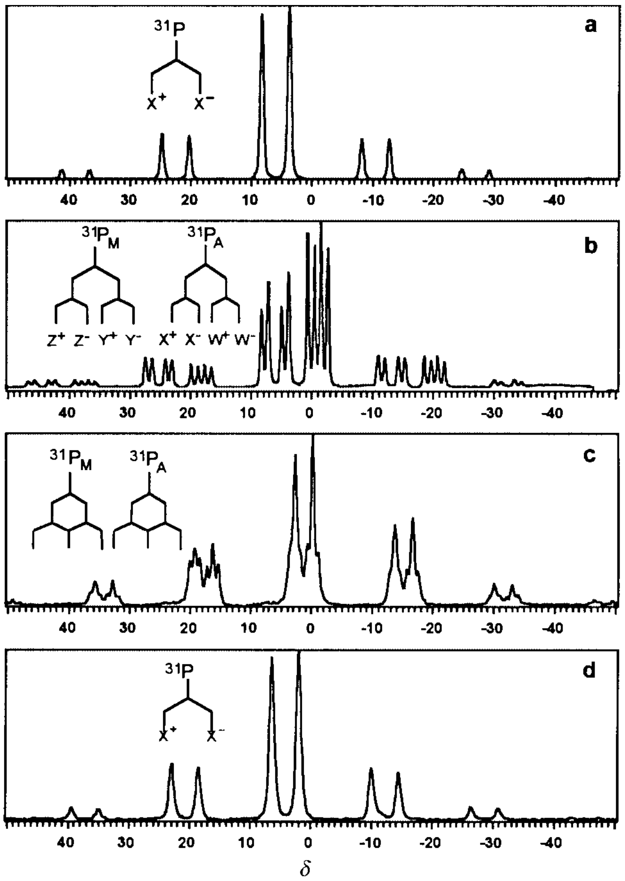

Fig. 2 The 121.49 MHz ^{31}P CP MAS NMR spectra of (a) compound **4**, $\nu_{rot} = 2.0$ kHz, (b) **1**, $\nu_{rot} = 2.33$ kHz, (c) **2**, $\nu_{rot} = 2.0$ kHz and (d) **5**, $\nu_{rot} = 2.0$ kHz. The spectra have 4K data points, a contact time of 1 ms and 100 scans.

silver and sulfur atoms in the central Ag_2S_2 core of the molecule form a structure close to a rectangle. The two Ag–S bond lengths are different and the two inside angles are close to the right angle: 92.0 and 88.0°. The molecule, consisting of two monomer units, possesses a center of symmetry in the middle of the Ag_2S_2 ring. Both Ag–P bonds are in the ring plane, whereas the silanethiolate groups are above and below the plane. Well ordered toluene molecules are trapped in the structure at niches in the vicinity of the silanethiolate groups. One dimeric silanethiolate molecule and two solvent molecules are present in the unit cell.

The Ag–S bond lengths in compound **4** (2.468 and 2.638 Å) are comparable with that (2.449 Å) found in **1**. They are longer than values usually observed for two-co-ordinated silver (2.38–2.40 Å), *e.g.* $[\{AgSSi(OBu^t)_3\}_4]$,[5] $[(AgSBu^t)_{14}(PPh_3)_4]$,[14] $[\{AgSC(SiMe_3)_3\}_4]$ and $[\{AgSCH(SiMe_3)_2\}_8]$,[3] $[(AgSC_6H_{11})_{12}]$[3] or $[\{AgSC_6H_4SiMe_3\text{-}o\}_4]$[2] and are close to the values of *ca.* 2.50 Å observed in complexes where Ag is three-co-ordinated, *e.g.* $[Ag_4(SPh)_4(PPh_3)_4]$[15] or $[(AgSCMeEt_2)_8(PPh_3)_2]$ and $[(AgSBu^t)_{14}(PPh_3)_4]$.[14]

The Ag–P bond in compound **4** (2.3845(12) Å) is significantly shorter than both such bonds in **1** (2.4950(12) and 2.4470(9) Å), however the compounds differ in the type of co-ordination. There are some remarkable features in the structure of **4**. Its bimetallic central Ag_2S_2 ring is rare among neutral thiolates. We can recall here two similar copper-group complexes. One is neutral, $[Cu_2(SPh)_2(PPh_3)_4]$, with a central Cu_2S_2 core.[16] The two copper atoms have tetrahedral environments with two phosphines attached to each and both bridging thiolate groups are coplanar with the central Cu_2S_2 ring which precludes more detailed comparisons. A recently reported silver thiolate, of some resemblance to **4**, is a derivative of *o*-carboranethiol, 1-(SH)-1,2-$C_2B_{10}H_{11}$. The molecule of $[Ag_4(\mu_3\text{-}SC_2B_{10}H_{11})(\mu\text{-}O_3SCF_3)_2(PPh_3)_4]$[17] also contains an Ag_2S_2 core with two more (exocyclic) silver atoms held together not only by sulfur bridges but also by triflate (O_3SCF_3) groups. In fact **4** seems to be the only known neutral bimetallic silver thiolate complex with only three-co-ordinating metal centers.

Table 2 Coupling constants for compounds **1**, **2**, **4** and **5** and phosphorus–silver bond lengths

Compound	$^1J_{P\text{-}Ag}$/Hz	$^2J_{P\text{-}P}$/Hz	$d_{P\text{-}Ag}$/Å
4	549.3	—	2.3844
1	268.6	146.5	2.4939
	390.6	—	2.4475
2	354.0	109.9	—
5	538.0	—	—

Solid state NMR studies

High-resolution ^{31}P solid state NMR spectra of silver(I) silanethiolates **1**, **2**, **4** and **5** are shown in Fig 2. The ^{31}P CP MAS spectra present different patterns owing to the changes in indirect spin–spin coupling *J*. The sample **4** (Fig. 2a), in the isotropic part of spectrum, exhibits a simple AX doublet due to strong phosphorus–silver splitting ($^1J_{P\text{-}Ag} = 549$ Hz) (Table 2). At natural abundance silver has two $I = 1/2$ isotopes, ^{107}Ag (51.82%) and ^{109}Ag (48.18%), and their magnetogyric ratios are similar in magnitude [$\gamma(^{107}Ag)/\gamma(^{109}Ag) = 0.87$]. Thus, the resulting spectrum should show two doublets in which the separate couplings of ^{31}P to the ^{107}Ag and ^{109}Ag nuclei are resolved. Such coupling pattern is often observed for silver(I) complexes of phosphorus donor ligands in solution. The difference between $^1J_{^{31}P\text{-}^{107}Ag}$ and $^1J_{^{31}P\text{-}^{109}Ag}$ is of the order of 40 Hz. For solid state samples the spectral resolution is usually below 40 Hz and the separate splitting due to the ^{107}Ag and ^{109}Ag nuclei is not observed. Only in a few cases such a distinction was reported in the solid phase.[18]

The ^{31}P CP MAS spectrum of sample **1** (Fig. 2b) shows a more complex pattern compared to that of **4**. Eight well resolved lines in the isotropic part correspond to an AMX spin system in which two crystallographically and magnetically non-equivalent phosphorus ligands are geminally split and further split by silver. The origin of the splitting pattern is indicated by the stick diagram above the spectrum. The $^2J_{^{31}P\text{-}^{31}P}$ coupling is found to be 146 Hz and is in the range for other silver(I) complexes of phosphorus donor ligands. Of interest is the significant difference in $^1J_{P\text{-}Ag}$ couplings for **1** (269 and 391 Hz). Moreover these values are much smaller than that of **4**. The question of the relationship between the magnitude of $^1J_{P\text{-}Ag}$ and geometrical parameters of phosphorus–silver(I) complexes was discussed by several research groups.[19] For phosphole–silver(I) compounds Attar *et al.*[20] have shown the simple relationship between the inverse cube of the Ag–P bond length (*d*) and $^1J_{P\text{-}Ag}$: $1/(d/\text{Å})^3 = (AJ/\text{Hz}) + B$ where *A* and *B* are constants dependent on the class of complexes. It is apparent that a similar correlation will be valid for phosphinesilver(I) silanethiolates. The values of *J* and corresponding Ag–P distances are collected in Table 2.

Fig. 3 shows the trend in $^1J_{P\text{-}Ag}$ *versus* the phosphorus–silver bond length. It is obvious that for a quantitative description of this relationship a larger experimental database is necessary. Nevertheless, it is worthy of note that even with such a limited data set the *A* and *B* parameters (3.32×10^{-5} and 5.54×10^{-2}, respectively) are very similar to those reported elsewhere.[20]

Owing to the lack of X-ray data for compounds **2** and **5** their structures were deduced from analysis of NMR parameters. The ^{31}P CP MAS spectrum of **2** (Fig. 2c) displays triplet like patterns which are due to partial overlap of AMX spin systems. Such coupling confirms that two phosphine ligands are bonded to silver. The geminal $^2J_{^{31}P\text{-}^{31}P}$ splitting is 110 Hz. Moreover, only one value of the $^1J_{P\text{-}Ag}$ coupling constant equal to 354 Hz is

Table 3 The ^{31}P principal elements of effective dipolar/chemical shift tensors for compounds **1**, **2**, **4** and **5**

Compound	Spin	δ_{iso}	T_{11}/ppm	T_{22}/ppm	T_{33}/ppm	Ω/ppm	κ
4	X^+	8.3	33	12	−20	53	0.21
	X^-	3.8	29	8	−25	54	0.23
1	Z^+	8.2	46	8	−29	75	0.00
	Z^-	7.1	39	7	−24	63	0.00
	Y^+	4.9	41	5	−31	72	0.00
	Y^-	3.8	34	4	−26	60	0.00
	X^+	0.6	29	−7	−20	49	−0.46
	X^-	−0.5	27	−8	−21	48	−0.47
	W^+	−1.6	26	−9	−21	47	−0.47
	W^-	−2.7	24	−9	−24	48	−0.40
2	X^+	2.6	39	2	−33	72	−0.03
	X^-	−0.3	36	−2	−35	71	−0.07
5	X+	6.4	33	9	−22	55	0.14
	X−	2.0	28	5	−27	55	0.16

Estimated errors in T_{11}, T_{22} and T_{33} are ±2 ppm; errors in δ_{iso} are ±0.2 ppm. The principal components of the chemical shift tensor are $T_{11} > T_{22} > T_{33}$. The isotropic chemical shift is given by $\delta_{iso} = (T_{11} + T_{22} + T_{33})/3$.

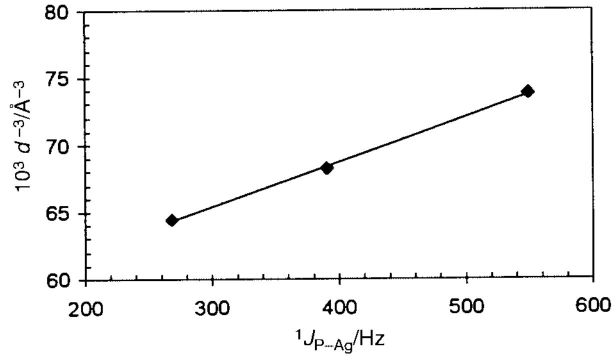

Fig. 3 Plot of the reciprocal of cube of the distance *d*(Ag–P) *vs.* coupling constant $^1J_{P\text{-}Ag}$.

found. Hence, these results suggest that *d*(Ag–P) for both ligands are similar and according to the proposed equation should be *ca.* 2.46 Å. Sample **5** (Fig. 2d) exhibits an AX doublet. The line shape and magnitude of $^1J_{P\text{-}Ag}$ are very similar to those observed for complex **4**. Thus the structural resemblance of these two compounds is apparent.

Interesting information about the molecular structure of complexes **1**, **2**, **4**, **5** can be obtained from an analysis of chemical shift tensor elements (δ_{ii}) and chemical shift tensor parameters, span (Ω) and skew (κ). The static ^{31}P NMR solid state spectra of phosphinesilver(I) silanethiolates **1**, **2**, **4**, **5** are relatively broad (*ca.* 9 kHz). With sample spinning higher than 9 kHz the broad lines can be narrowed to isotropic signals. Under slow MAS condition (*ca.* 2 kHz) the isotropic lines are symmetrically flanked by spinning sidebands, which can be further used to calculate chemical shift anisotropy and other NMR parameters. However, for the systems under investigation several precautions have to be taken. It is apparent that for spectra of dipolar-coupled $I = 1/2$ spin pairs the relationship between sample spin rotation, dipolar coupling and chemical shift anisotropy is crucial for the analysis of MAS spectra. Dipolar interaction constants R_{DD} expressed by $[(\gamma_P\gamma_{Ag}h)/2\pi]\langle r_{P\text{-}Ag}{}^{-3}\rangle(\mu_0/4\pi)$ are dependent only on the inverse cube of the separation of phosphorus and silver. The R_{DD} values calculated using the P–Ag distances taken from X-ray crystallographic data were found to be for ^{109}Ag from −146.8 Hz to −168.1 Hz and for ^{107}Ag from −127.6 to −146.0 Hz. The homonuclear ^{31}P–^{31}P dipolar coupling effect for sample **1** was also considered. With a phosphorus–phosphorus separation equal to 4.3074 Å the R_{DD} is 247 Hz. For static spectra when the ***J*** and ***D*** tensors are collinear the dipolar coupling constant is diminished in effect by one third of the anisotropy of the *J* coupling, $R_{eff} = R_{DD} - (\Delta J/3)$, or increased if the anisotropy has a negative value. It is known, however, that *J* anisotropy is in the range of the isotropic *J* coupling value and in our case this effect should not influence the dipolar phosphorus–silver coupling. As the line shape and spinning sideband pattern are affected by chemical shift and dipolar interactions, according to the notation used by Zilm and Grant[21] the effective dipolar/chemical shift tensor components are labeled as T_{ii}. Subsequent analysis of the sideband intensities gives principal values of the tensors T_{ii+} and T_{ii-}. The values of δ_{iso} and of the isotropic coupling constants J_{iso} can be obtained directly. Unfortunately, it is not possible to obtain the details of the T_{ii} orientation with respect to the principal axis system. The calculated values of the ^{31}P principal components T_{ii}, span Ω and skew κ are given in Table 3.

The accuracy of calculation was confirmed by comparison of experimental and theoretical spectra. Deconvolution of individual lines for sample **2** was impossible due to partial overlap of resonances in AMX multiplets. However, with line broadening of 110 Hz the $^2J_{^{31}P\text{-}^{31}P}$ splitting was not observed. Only the AX subspectrum was used for further calculation.

The span parameter reflects the distortion of the geometry from ideal tetrahedral or cubic symmetry. The values found for compounds **1**, **2**, **4**, **5** (48–75 ppm) are in the range typical for silver(I) complexes with phosphine ligands. The skew parameter reflects the distribution of electron density around the nuclei under investigation. It ranges from −1 for $\delta_{22}(T_{22}) = \delta_{33}(T_{33})$ to +1 for $\delta_{11}(T_{11}) = \delta_{33}(T_{33})$. The κ magnitudes, established for silver(I) silanethiolates, indicate that electron density is not localized in any particular bond but is spread over the entire tetrahedron. On the other hand, of interest is the linear correlation between κ and $^1J_{P\text{-}Ag}$. As shown in Fig. 4 for a large coupling constant the skew is positive, becoming zero for intermediate values and is negative for small values of $^1J_{P\text{-}Ag}$. There is not such tendency for the span parameter. Compared to other silver(I) complexes, silver(I) silanethiolates provide an additional, attractive probe for structural studies, which allow extended application of the NMR technique. Silicon-29, for the samples under investigation, is considered as an isolated nucleus. Splitting by the ^{107}Ag, ^{109}Ag and ^{31}P nuclei is below the detectable limit. Experimental ^{29}Si CP MAS NMR spectra for **4**, **1**, **5** samples are displayed in Fig. 5. The calculated values of the ^{29}Si principal components of the chemical shift tensor δ_{ii}, span Ω and skew κ are collected in Table 4.

Inspection of ^{29}Si data provides interesting information about significant distinction of the local environment of the silicon centers in **4**, **5** and **1**. The isotropic chemical shift δ_{iso} is extremely sensitive to the character of the substituent. For sample **1** the δ_{iso} is upfield by about 55 ppm compared to **4** and **5**. Moreover, the span parameter for **1** is over 20 ppm larger compared to **4** and **5**. The differences in Ω are very likely related with distortion of the tetrahedral geometry around silicon. For

Table 4 The ^{29}Si principal elements of chemical shift tensors for complexes **1**, **4** and **5**

Compound	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω	κ
4	−2.6	23	10	−41	64	0.59
1	−57.6	−20	−42	−111	91	0.51
5	−2.1	23	10	−40	63	0.58

Estimated errors in δ_{11}, δ_{22} and δ_{33} are ±2 ppm; errors in δ_{iso} are ±0.2 ppm. The principal components of the chemical shift tensor are $\delta_{11} > \delta_{22} > \delta_{33}$. The isotropic chemical shift is given by $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

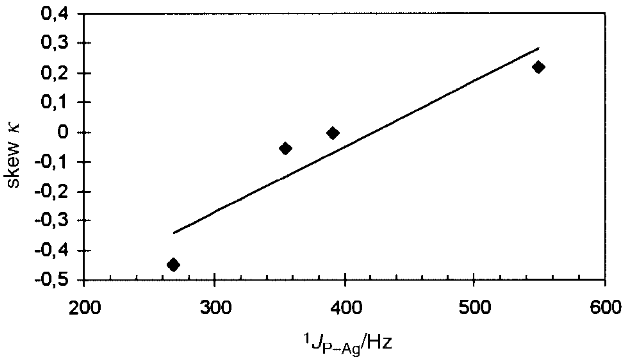

Fig. 4 Plot of skew *vs.* coupling constant $^1J_{P\text{-}Ag}$.

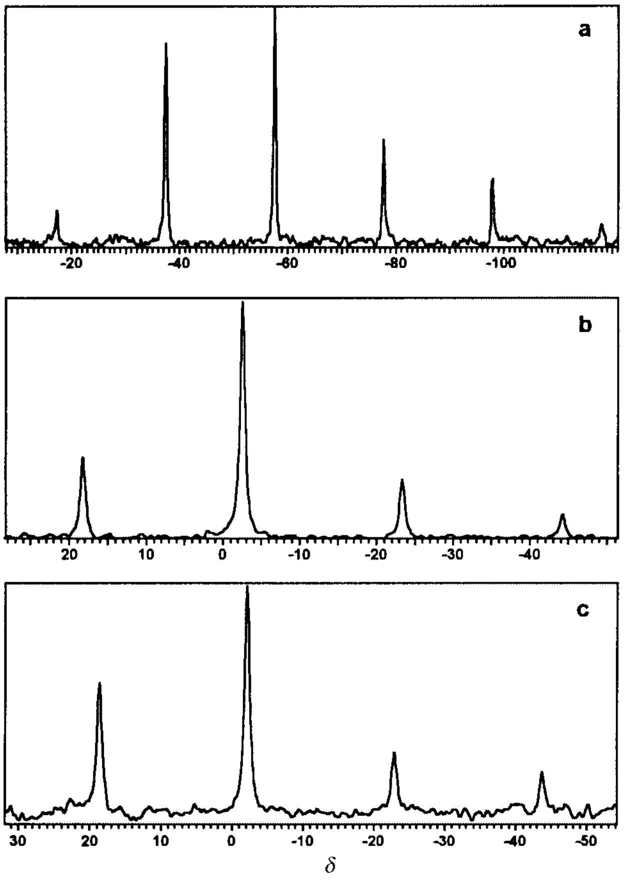

Fig. 5 The 59.63 MHz ^{29}Si CP MAS NMR spectra of (a) compound **4**, ν_{rot} = 1.24 kHz, (b) **1**, ν_{rot} = 1.20 kHz and (c) **5**, ν_{rot} = 1.24 kHz. The spectra have 4K data points, a contact time of 1 ms and 400 scans.

1 the S–Si–O valence angles are 107.41, 112.64 and 115.78° while for **4** the corresponding S–Si–C valence angles are 108.62, 110.09 and 111.80°. The spread of valence angles for **1** is much larger. This is probably a result of the steric hindrance of the *tert*-butyl groups. The resemblance of ^{29}Si δ_{ii} parameters for **4** and **5** provides further evidence in support of the hypothesis from ^{31}P CP MAS data about the similarity of their structures. The effect of ^{29}Si chemical shift anisotropy is not observed for sample **2**. This complex exhibited single resonance at spinning rate 1 kHz. The δ_{iso} is found to be −43.5 ppm.

The preliminary, ^{29}Si CP MAS NMR results presented in this work unambiguously show that this technique is potentially useful in structural studies of silver(I) silanethiolate complexes.

Experimental

Miscellaneous

Trialkoxysilanethiols (Bu^{t}O)$_3$SiSH, (Bu^{s}O)$_3$SiSH and (Pr^{i}O)$_3$SiSH were obtained by alcoholysis of SiS$_2$ as described previously.[22,23] Triarylsilanethiols were obtained by insertion of elemental sulfur into silanes.[24] Acetylacetonatobis(triphenylphosphine)silver(I), [Ag(acac)(PPh$_3$)$_2$], was prepared by reaction of Ag$_2$O with 2,5-pentanedione and triphenylphosphine according to the literature procedure[25] (developed for fluorinated analogues). The crude product was purified by passing its toluene solution through a short (4 cm) silica gel layer. Thin layer chromatography was performed on silica gel plates, Silufol (Kavalier): mobile phase, hexane–benzene (4:1, v/v); developers, iodine vapors or hydrogen sulfide.

Preparation of compounds

[Ag{SSi(OBu^t)$_3$}(PPh$_3$)$_2$] 1. The compound [Ag(acac)(PPh$_3$)$_2$] (366 mg) was dissolved in 15 ml of toluene and a solution of 140 mg of tri-*tert*-butoxysilanethiol in 15 ml of toluene was added. The reagents were allowed to react for 15 min, then most of the solvent was removed. Upon layering of hexane 470 mg of crude product deposited. Recrystallization from hexane–ethanol (7:5) yielded 310 mg (68%) of **1**. Found: C, 63.26; H, 6.27; S, 3.39. $C_{48}H_{57}AgO_3P_2SSi$ requires C, 63.22; H, 6.30; S, 3.52%). NMR: δ_H (C_6D_6) 1.58 (27 H, s), 7.0–7.1 (18 H, m, *m*- and *p*-H of Ph) and 7.3–7.5 (12 H, m, *o*-H of Ph), (CDCl$_3$) 1.40 (27 H, s) and 7.37 (30 H, m, Ph); δ_C (C_6D_6) 32.126 (s, Me), 62 (s, *C*Me$_3$), 128.73, 128.86, 128.94, 133.98, 134.37 and 137 [d, *J*(C–P) 15 Hz, Ph]; δ_P (CDCl$_3$) 3.083 (s, PPh$_3$), ν(1/2) = 20 Hz; at −60 °C 4.849 (s, PPh$_3$), ν(1/2) = 400 Hz. Single crystals of **1** suitable for diffraction measurements were obtained by recrystallization from octane solution to which a few drops of chloroform were added. Other synthetic procedures leading to **1** are given in SUP 57613.

[Ag{SSi(OPr^i)$_3$}(PPh$_3$)$_2$] 2. To a solution of [Ag(acac)(PPh$_3$)$_2$] (1 mmol) in 15 ml of benzene 0.260 ml of 80% tri-*iso*-propoxysilanethiol was added. The contents turned light brown and were allowed to react for 30 min. The solvent was evaporated to a volume of about 3 ml and then 4 ml of hexane were slowly added. The deposit was filtered off, washed with hexane, dried and weighed. The procedure yielded 700 mg (80%) of compound **2**; mp 161–162 °C. Found: Ag, 12.5. $C_{45}H_{51}AgO_3P_2SSi$ requires Ag, 12.4%. The product is not stable and gradually darkens in the air at ambient temperatures as well as in a refrigerator. NMR: δ_H (C_6D_6) 1.26 (18 H, d, *J* = 6, C*H*$_3$), 4.63 (3 H, septet, *J* = 6 Hz, C*H*), 7.0–7.1 (18 H, m, *m*- and *p*-H of Ph) and 7.45–7.6 (12 H, m, *o*-H of Ph).

[Ag{SSi(OBu^s)$_3$}(PPh$_3$)$_2$] 3. Preparation was analogous to that of compound **2** except the use of half of the substrates (mp 126 °C). Compound **3** is not stable in the air and gradually darkens during storage.

[{Ag[SSi(C$_6$H$_4$Me-*o*)$_3$](PPh$_3$)}$_2$]·2C$_6$H$_5$Me 4. To a solution of 340 mg of [Ag(acac)(PPh$_3$)$_2$] in 15 ml of toluene a solution of 167 mg of (*o*-MeC$_6$H$_4$)$_3$SiSH in 5 ml of toluene was added. After 15 min of reaction 2 ml of hexane were added, then another 4 ml after half an hour. On the next day the tiny crystals were filtered off and recrystallized from 10 ml of hot

Table 5 Summary of crystal data, intensity collection and structure refinement for compound **4**

Chemical formula	$C_{46}H_{44}AgPSSi$
Formula weight	795.80
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.824(3)
b/Å	13.667(3)
c/Å	14.524(3)
α/°	115.15(3)
β/°	99.76(3)
γ/°	107.71(3)
V/Å^3	2059.0(8)
T/K	293(2)
Z	2
μ/mm^{-1}	0.638
Number of reflections, measured	8402
unique	8111
$R1$, $wR2$ for $I > 2\sigma(I)$	0.0267, 0.0716
all reflections	0.0927, 0.0899

toluene giving crystals suitable for the X-ray study. Yield 305 mg (75%) of compound **4**, mp 183 °C. NMR: δ_H (C_6D_6) 2.1 (s, $C_6H_4CH_3$) and 6.85–7.2 (m, aryl).

[{Ag(SSiPh$_3$)(PPh$_3$)}$_2$]·2C$_6$H$_6$ 5. To a solution of 370 mg of [Ag(acac)(PPh$_3$)$_2$] in benzene a solution of 150 mg of Ph_3SiSH in 5 ml of benzene was added. Immediately a microcrystalline, colorless product deposited (345 mg, 75%). In order to obtain bigger crystals the reaction was carried out in a special test-tube with a capillary narrowing at its middle. One substrate solution was placed in the lower part of the tube and the second in the upper part. This considerably slowed the mixing rate and should slow the reaction rate and eventually the crystallization process. Nevertheless, the crystals (mp 164–166 °C), although bigger, were unsuitable for an X-ray study. Found: C, 67.7; H, 4.8; Ag, 14.4; S, 4.2. $C_{42}H_{36}AgPSSi$ requires C, 68.2; H, 4.9; Ag, 14.58; S, 4.3%.

Crystal structure determination

Diffraction measurements were carried on using a KUMA KM4 diffractometer with Mo-Kα radiation (λ 0.71073 Å) at ambient temperature. The crystal structure was solved and refined using the SHELX-97 program package[26,27] with full-matrix least-squares refinement based on F^2. Crystal data are given in Table 5.

CCDC reference number 186/1572.

See http://www.rsc.org/suppdata/dt/1999/3063/ for crystallographic files in .cif format.

NMR Spectroscopy

Spectra of compounds in solutions (^{1}H, ^{31}P and ^{13}C) were recorded on Gemini 200 (200 MHz) or Unity Plus (500 MHz) spectrometers; C_6D_6 or $CDCl_3$ was used as solvent. Cross-polarization magic-angle spinning solid state ^{31}P and ^{29}Si NMR spectra were recorded on a Bruker 300 MSL instrument with high-power proton decoupling at 121.496 MHz for ^{31}P and 59.627 MHz for ^{29}Si. Powder samples were placed in a cylindrical rotor and spun at 2.0–4.5 kHz. For the ^{31}P experiments the field strength for ^{1}H decoupling was 1.05 mT, a contact time of 5 ms, a repetition of 6 s and spectral width of 50 kHz were used and 8 K data points represented the free induction decay (FID). Spectra were accumulated 100 times which gave a reasonable signal-to-noise ratio. The ^{31}P chemical shifts were calibrated indirectly through bis(dineopentoxythiophosphoryl) disulfide at δ 84.0 as secondary reference; 85% H_3PO_4 was used as primary reference for ^{31}P and set at 0 ppm. For the ^{29}Si experiments the field strength for ^{1}H decoupling was 1.05 mT, a contact time of 3 ms, a repetition of 10 s and spectral width of 50 kHz were used and 8 K data points represented the FID. Spectra were accumulated 100 times. The Hartman–Hahn match was set up using Q_8M_8 standard (Bruker). The ^{29}Si chemical shifts were calibrated indirectly through TMS set at 0.0 ppm. The principal elements of the ^{31}P and ^{29}Si chemical shift tensor and shielding parameters were calculated employing WIN-MAS program. The details describing the method and accuracy of calculations are exhaustively discussed elsewhere.[28,29] The principal components δ_{ii} were used for calculation of the chemical shift parameters: $\Omega = \delta_{11} - \delta_{33}$ and $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$.

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