Crystallographic analysis of an intramolecularly stabilised organosilver tetramer, $[Ag(C_6H_4CH_2NMe_2\text{-}2)]_4$, and the first structurally characterised silver siloxide, $\{[Ag(PPh_3)]_2(\mu_4\text{-}OMe_2SiOSiMe_2O)\}_2$

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Recrystallisation of $[Ag(C_6H_4CH_2NMe_2\text{-}2)]_4$ **1** in the presence of PPh_3 has led to the isolation of a silver siloxide, $\{[Ag(PPh_3)]_2(\mu_4\text{-}OMe_2SiOSiMe_2O)\}_2$ **2**, from interaction with the silicone grease used to assemble the glassware. Both compounds have been characterised crystallographically, and **2** represents the first structurally characterised silver siloxide. The organometallic is a planar tetramer containing both four- and six-co-ordinate silver. The disiloxide adopts a dimeric 'step' structure incorporating trigonal PO_2Ag and tetrahedral PO_3Ag centres.

We have been investigating the synthesis of precursors for the chemical vapour deposition (CVD) of silver films,[1] and as part of this work have had cause to consider the use of intramolecularly stabilised organosilver species. Such species, although not new, complement both the stabilisation of organosilver compounds by using sterically demanding ligands, *e.g.* $Ag[C(SiMe)_3]_2^-$ (ref. 2) and $[Ag(C_6H_2Me_3\text{-}2,4,6)]_4$,[3,4] fluorinated ligands *e.g.* $Ag[CF(CF_3)_2](MeCN)$,[5] $Ag[CF(CF_3)_2]_2^-$,[5] $Ag[C(CF_3){=}CF_2]$[6] and $\{Ag[C(CF_3){=}C(F)CF_3]\}_4$,[7] and the use of soft phosphine donors to surround the metal centre *e.g.* $Ag(C{\equiv}R)(PMe_3)$ (R = Ph[8] or $SiMe_3$[9]). Known organosilver compounds which utilise ligands incorporating potential donor centres include $Ag[(CH_2)_3NMe_2]$,[10] $Ag(C_6H_4X\text{-}2)$ (X = NMe_2 or CH_2NMe_2)[11] and $Ag[C_6H_3(OMe)_2\text{-}2,6]$,[11] though crystallographic confirmation of the metal co-ordination sphere in all these cases is still outstanding. Moreover, in the case of $[Ag(C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)]_4$,[12] for which X-ray data are available, there appears to be no interaction between the pendant amine nitrogen and the silver and therefore such interactions cannot be assumed. It is pertinent, however, that $Ag(C_6H_4CH_2NMe_2\text{-}2)$ (m.p. 160–180 °C)[11] is more thermally robust than AgPh (m.p. 74 °C).[13]

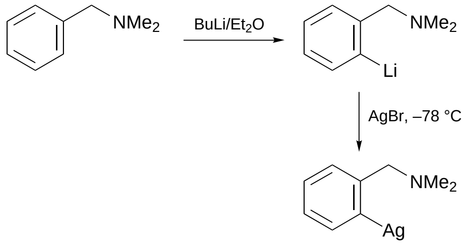
In this paper we report the crystal structure of $AgC_6H_4CH_2NMe_2\text{-}2$ **1** and show it to be a tetramer incorporating two distinct silver co-ordination spheres. In addition, recrystallisation of **1** from toluene in the presence of Ph_3P has led to the adventitious formation of the silver siloxide, $\{[Ag(PPh_3)]_2(\mu_4\text{-}OMe_2SiOSiMe_2O)\}_2$ **2** from silicone grease used in the joints of the crystallisation flask, which we have also characterised crystallographically.

Results and Discussion

The compound $Ag(C_6H_4CH_2NMe_2\text{-}2)$ **1** has been synthesized by the method of van Koten and co-workers[11] (Scheme 1) and its structure determined (Fig. 1, Table 1). It is tetrameric and contains a planar Ag_4 core (maximum deviation of Ag from the mean Ag_4 plane: ±0.01 Å) with adjacent pairs of silver atoms bridged by the *ipso*-carbon of the aryl groups. The core is not, however, a perfect square but distorted significantly into a parallelogram arrangement. The Ag–Ag–Ag angles are smaller where two-co-ordinate silver [Ag(1), Ag(3)] (see below) occupies the angle apex [Ag–Ag(1,3)–Ag 82.76(5), 82.22(5)°], while the angles around the four-co-ordinate silvers [Ag(2), Ag(4)] are appreciably larger [Ag–Ag(2,4)–Ag 97.41(5), 97.59(5)°]. Such a core is also found, for example, in $[Ag(C_6H_2Me_3\text{-}2,4,6)]_4$,[3,4] $[AgC(CF_3){=}C(F)CF_3]_4$[7] and $[Ag(C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)]_4$.[12]

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Ag(1)–Ag(2)	2.732(2)	Ag(1)–C(1)	2.161(13)
Ag(2)–Ag(3)	2.748(2)	Ag(1)–C(28)	2.157(12)
Ag(3)–Ag(4)	2.743(2)	Ag(2)–C(1)	2.402(13)
Ag(1)–Ag(4)	2.729(2)	Ag(2)–C(10)	2.410(12)
Ag(2)–N(1)	2.539(10)	Ag(3)–C(10)	2.134(12)
Ag(2)–N(2)	2.489(10)	Ag(3)–C(19)	2.166(13)
Ag(4)–N(3)	2.550(10)	Ag(4)–C(28)	2.351(11)
Ag(4)–N(4)	2.562(10)	Ag(4)–C(19)	2.359(13)
C(1)–Ag(1)–Ag(4)	132.8(4)	C(10)–Ag(3)–C(19)	173.4(4)
C(28)–Ag(1)–Ag(4)	56.1(3)	C(10)–Ag(3)–Ag(4)	129.3(3)
C(1)–Ag(1)–Ag(2)	57.4(4)	C(19)–Ag(3)–Ag(4)	56.0(3)
C(28)–Ag(1)–Ag(2)	128.2(3)	C(10)–Ag(3)–Ag(2)	57.5(3)
Ag(4)–Ag(1)–Ag(2)	82.76(5)	C(19)–Ag(3)–Ag(2)	129.0(3)
C(1)–Ag(1)–C(28)	171.0(5)	Ag(4)–Ag(3)–Ag(2)	82.22(5)
C(1)–Ag(2)–N(2)	101.0(4)	C(28)–Ag(4)–Ag(1)	49.6(3)
C(10)–Ag(2)–N(2)	77.3(4)	C(19)–Ag(4)–Ag(1)	136.5(3)
C(1)–Ag(2)–N(1)	76.7(4)	N(3)–Ag(4)–Ag(1)	136.4(2)
C(10)–Ag(2)–N(1)	98.1(4)	N(4)–Ag(4)–Ag(1)	88.9(2)
N(2)–Ag(2)–N(1)	119.1(3)	C(28)–Ag(4)–Ag(3)	136.5(3)
C(1)–Ag(2)–Ag(1)	49.3(3)	C(19)–Ag(4)–Ag(3)	49.5(3)
C(10)–Ag(2)–Ag(1)	136.0(3)	N(3)–Ag(4)–Ag(3)	86.5(3)
N(2)–Ag(2)–Ag(1)	135.8(3)	N(4)–Ag(4)–Ag(3)	137.0(2)
N(1)–Ag(2)–Ag(1)	88.5(2)	Ag(1)–Ag(4)–Ag(3)	97.59(5)
C(1)–Ag(2)–C(10)	173.1(4)	C(28)–Ag(4)–C(19)	173.3(4)
C(10)–Ag(2)–Ag(3)	48.3(3)	C(28)–Ag(4)–N(3)	99.7(4)
N(2)–Ag(2)–Ag(3)	87.4(2)	C(19)–Ag(4)–N(3)	76.8(4)
N(1)–Ag(2)–Ag(3)	133.8(2)	C(28)–Ag(4)–N(4)	77.7(4)
Ag(1)–Ag(2)–Ag(3)	97.41(5)	C(19)–Ag(4)–N(4)	98.7(4)
C(1)–Ag(2)–Ag(3)	138.5(3)	N(3)–Ag(4)–N(4)	117.1(3)



Scheme 1

Pendant CH_2NMe_2 groups bound to each of the aryl ligands additionally co-ordinate to only two of the silver atoms, resulting in two distinct silver environments: a two-co-ordinate, mildly distorted linear AgC_2 array [Ag(1) and Ag(3)] and a

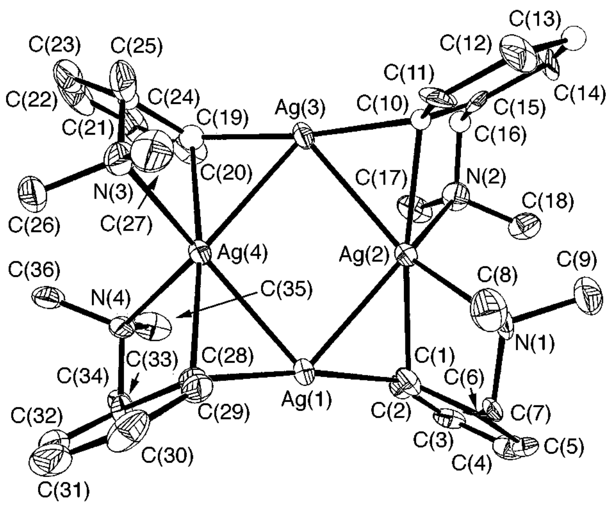


Fig. 1 The asymmetric unit of compound **1** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% probability level for both anisotropic (hatched spheres) and isotropic atoms (open spheres)

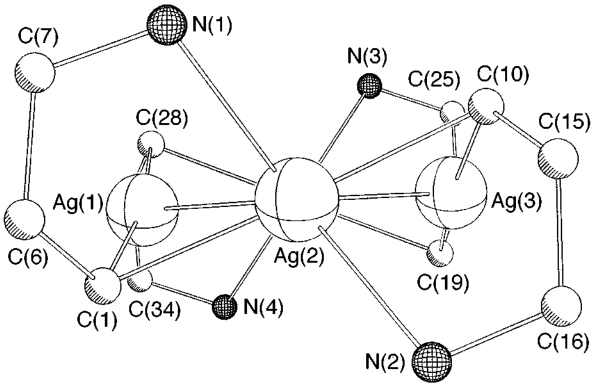


Fig. 2 The structure of compound **1** viewed along the Ag(2)–Ag(4) vector. Methyl groups and phenyl rings have been omitted for clarity

four-co-ordinate AgC_2N_2 seesaw [Ag(2) and Ag(4)] in which the carbon atoms are mutually *trans* to each other [C(1)–Ag(2)–C(10) 173.1(4), C(19)–Ag(4)–C(28) 173.3(4)°]. Distances within the core between adjacent silver atoms are relatively constant [Ag–Ag 2.729(2)–2.748(2) Å], and the mean Ag–Ag distance (2.738 Å) is slightly shorter than that observed in the metal (2.89 Å) which might indicate some weak interactions. The Ag–Ag separations are shorter in **1** than in the related $[AgC(CF_3)=C(F)CF_3]_4$ (2.761 Å)[7] and mesitylsilver (2.744 Å)[3,4] complexes although comparable to those in $[Ag(C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)]_4$ (2.740 Å).[12] If such contacts are included, the two observed geometries in **1** become a flattened seesaw C_2Ag_2Ag and octahedral *trans*-,*trans*-,*trans*-$C_2N_2Ag_2Ag$. The significance of d^{10}–d^{10} interactions in the chemistry of the coinage metals has been reviewed by Jansen.[14]

The aryl rings lie approximately perpendicular to the plane of the Ag_4 core. The bridging carbons do not lie in this plane but are displaced some 0.83–0.97 Å from it, arranged around the ring in an alternate up-down pattern (Fig. 2). The aryl groups bridging silver atoms are bound more strongly to the two-co-ordinate silvers [Ag–C 2.134(12)–2.166(13) Å] than to the four-co-ordinate centres [Ag–C 2.351(11)–2.410(12) Å].

Pendant CH_2NMe_2 groups on the aryl rings bind only to Ag(2) and Ag(4). The Ag–N distances in **1** are longer [Ag–N 2.489(10)–2.562(10) Å] than typical Ag–N distances found in donor adducts of silver iodide with morpholine (2.39 Å),[15] piperazine (2.32 Å)[16] and piperidine (2.329 Å),[17] but are comparable with those in AgN_3 (2.561 Å).[15] No Ag–N bonds are observed in related $[Ag(C_5H_3CH_2NMe_2\text{-}2)Fe(C_5H_5)]_4$ [Ag–N 2.94(2) Å][12] where silver adopts the same co-ordination as Ag(1,3) of **1**.

Compound **1** is unique among silver tetramers in having an unsymmetrical arrangement of metal centres. Overall, its structure may be visualised as two distorted linear $[R\text{–}Ag\text{–}R]^-$ anions [C–Ag(1,3)–C 171.0(5)–173.4(4)°] bridged by two base-stabilised Ag^+ cations. This visualisation has been used recently to describe the structure of the silver acetylide adduct $[Ag(C{\equiv}CPh)(PPh_3)]_4$.[9] In this latter case a central Ag_4 core is grossly distorted into a 'flat-butterfly' configuration and the $[AgR_2]^-$ and $[Ag(PPh_3)_2]^+$ units are easier to identify. The tetramer arrangement found in **1** is strikingly similar to that found in the aurate complex $[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ where $[AuR_2]^-$ anionic fragments are bridged by the lithium cations which in turn are each bonded to two CH_2NMe_2 groups.[18] Solution NMR studies on the analogous argentate complex suggest that it displays a similar arrangement in solution.[19]

While the tetrameric compound **1** crystallises from solution, previously reported molecular weight measurements are variable (880, 940, 1215; relative molar mass of **1**: 968.3)[11] and suggest the presence of other oligomers in solution. We have analysed **1** using FAB (liquid secondary ion mass spectrometry, SIMS) and found fragments which could be assigned to $Ag_7R_4 + 1$ (*m*/*z* 1286, based on ^{107}Ag), Ag_6R_3 (1044), $Ag_5R_4 - 1$ (1070), Ag_5 (535), Ag_4R_3 (830), Ag_4R (562), Ag_3 (321) and Ag_2R (348) among those observed, though interestingly not the parent ion Ag_4R_4.

In view of the limited stability of compound **1** in solution over long periods, an attempt was made to crystallise it in the presence of triphenylphosphine to generate a more stable low molecular weight adduct. After several weeks in the dark at −5 °C small crystals of the decomposition product, $\{[Ag(PPh_3)]_2[(\mu_4\text{-}OMe_2SiOSiMe_2O)]\}_2$ **2** were formed, presumably by interaction with components of the silicone grease used in the apparatus.* The formation of siloxides by this serendipitous method is not unique though documented examples are still rather scarce. Other species which have been obtained in this way, either intentionally or otherwise, are $[Tl_2(OSiMe_2)O]_n$,[20] $Yb(\eta^2\text{-}C_3N_2HMe_2\text{-}3,5)(\mu\text{-}\eta^1{:}\eta^2\text{-}OSiMe_2C_3N_2HMe_2\text{-}3,5)(\eta^5\text{-}C_5H_4Me)$,[21] $Sm(\eta^5\text{-}C_5Me_5)_2(thf)(\mu\text{-}OSiMe_2OSiMe_2O)$ (thf = tetrahydrofuran)[22] and the disordered species $[K^+]_{0.75}[K(Me_2SiO)_7^+]_{0.25}[InH(CH_2CMe_3)_3^-]$.[23] The generally adventitious nature of these reactions is illustrated by the samarium example which could not be prepared in a planned synthesis using dimethylsiloxane grease. Nonetheless, the characterisation of **2** represents the first structurally authenticated silver siloxide; indeed the literature contains only one earlier reference to such species, namely $Ag(OSiMe_3)(PMe_3)_n$ (*n* = 1, 2 or 3).[24] In the context of the formation of **2** it is notable that $[Ag(C_6H_2Me_3\text{-}2,4,6)]_4$ could not be crystallised in the presence of donors such as PPh_3, 2,2′-bipyridine or thf, but with $Ph_2PCH_2PPh_2$ generated $Ag_3(Ph_2PCHPPh_2)_3$ with concomitant loss of the aryl group (as $C_6H_3Me_3$) from silver.[3,4]

The centrosymmetric structure of compound **2** is shown in Fig. 3, and a simplified view of the molecular skeleton is given in Fig. 4. The structure consists of an Ag_4O_4 core arranged in a step conformation where oxygen atoms within the core are part of two equivalent bridging disiloxide ligands. The angle between adjacent Ag_2O_2 rings as measured by the angle between the Ag(1), Ag(2), O(1), O(2) and Ag(2), Ag(2′), O(2), O(2′) planes is 88.8(5)° and is presumably dictated by the bite of the disiloxide ligand. Additionally, each silver is bonded to a single triphenylphosphine molecule resulting in two distinct

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* Crystals of compound **2** were also found to contain two water and three toluene molecules per asymmetric unit by the usual Fourier-difference methods. These entities were well ordered but made no close contacts with the silver siloxide and are not discussed further. The water molecules are, however, hydrogen bonded to each other, O · · · O 2.35 Å.

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Ag(1)–O(1)	2.025(12)	Ag(1)–P(2)	2.247(5)
Ag(1)–O(2′)	2.297(11)	Ag(2)–P(1)	2.265(7)
O(2)–Ag(1′)	2.297(11)	Si(1)–O(1)	1.578(14)
Ag(2)–O(2′)	2.259(11)	Si(1)–O(3)	1.665(15)
Ag(2)–O(2)	2.290(13)	Si(2)–O(2)	1.564(11)
Ag(2)–O(1)	2.376(12)	Si(2)–O(3)	1.639(12)
O(2)–Ag(2′)	2.259(11)		
O(1)–Ag(1)–P(2)	133.7(4)	Si(1)–O(1)–Ag(1)	132.4(12)
O(1)–Ag(1)–O(2′)	87.3(4)	Si(1)–O(1)–Ag(2)	113.0(6)
P(2)–Ag(1)–O(2′)	135.8(3)	Ag(1)–O(1)–Ag(2)	98.3(5)
O(2′)–Ag(2)–P(1)	115.9(4)	Si(2)–O(2)–Ag(2′)	126.6(7)
O(2′)–Ag(2)–O(2)	94.6(3)	Si(2)–O(2)–Ag(2)	117.4(7)
P(1)–Ag(2)–O(2)	141.8(3)	Ag(2′)–O(2)–Ag(2)	85.4(3)
O(2′)–Ag(2)–O(1)	80.3(4)	Si(2)–O(2)–Ag(1′)	129.6(5)
P(1)–Ag(2)–O(1)	114.2(5)	Ag(2′)–O(2)–Ag(1′)	94.2(4)
O(2)–Ag(2)–O(1)	92.3(6)	Ag(2)–O(2)–Ag(1′)	91.0(5)
O(1)–Si(1)–O(3)	112.2(8)	Si(2)–O(3)–Si(1)	134.8(10)
O(2)–Si(2)–O(3)	112.1(6)		

Primed atoms are related to unprimed atoms (at *x*, *y*, *z*) by −*x*, 1.0 − *y*, 1.0 − *z*.

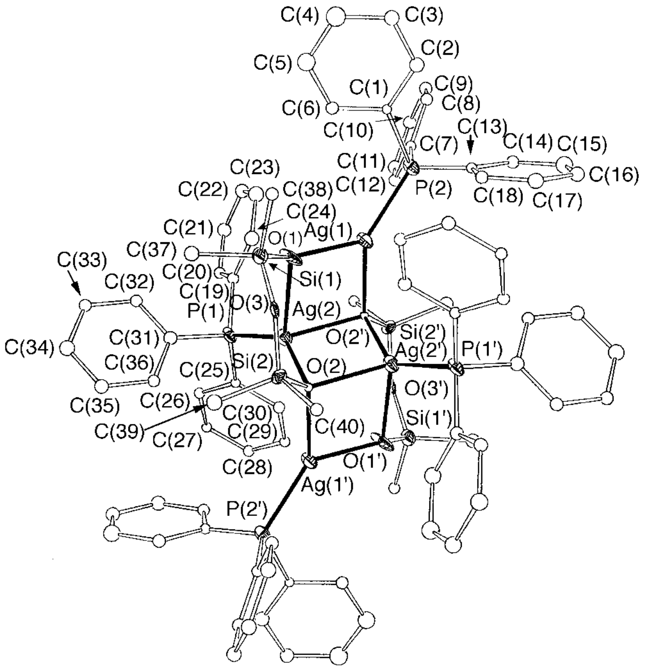

Fig. 3 The asymmetric unit of compound **2** showing the labelling scheme used in the text and tables. Details as in Fig. 1

silver environments, namely trigonal $PO_2Ag(1)$ and tetrahedral $PO_3Ag(2)$.

Each siloxide ligand provides two distinct oxygen atoms to the molecular core. At each extreme the oxygen [O(1)] bonded to Si(1) is bridging two silver atoms, while in the centre of the unit the oxygen [O(2)] bonded to Si(2) bridges three silver atoms. Silver–oxygen bond lengths (Table 2) involving O(2) are generally consistent [2.259(11)–2.297(11) Å] while those involving O(1) are noticeably different [Ag(1)–O(1) 2.025(12), Ag(2)–O(1) 2.376(12) Å]. A phosphorus bonded to each silver completes their co-ordination sphere. The Ag–P bonds are shorter than expected [2.247(5), 2.265(7) Å], other bond lengths for triphenylphosphine adducts of silver halides such as $[AgX(PPh_3)]_4$ (X = Cl or I) being considerably longer at 2.372–2.466 Å.[25] Similarly, silicon–oxygen bonds where oxygen is part of the Ag_4O_4 unit are considerably shorter [Si(1)–O(1) 1.578(14), Si(2)–O(2) 1.564(11) Å] than those in the Si–O–Si part of the ligand [Si(1)–O(3) 1.66(2), Si(2)–O(3) 1.639(12) Å].

The structure of compound **2** is similar to that determined for the 'step' type silver iodide–triphenylphosphine adduct $[AgI(PPh_3)]_4$,[25] where the core is made up of an Ag_4I_4 unit and each silver is further co-ordinated by a triphenylphosphine to give three- and four-co-ordinate silver atoms. For comparison, a number of copper(II) siloxide structures have been determined *e.g.* $[Cu(OSiPh_2OSiPh_2O)_2\{\mu\text{-Li(py)}_2\}_2]$ (py = pyridine)[26] and $[Cu\{OSi(OCMe_3)_3\}_2(py)_2]$,[27] although these structures contain chelating and terminal siloxide ligands with respect to copper, rather than bridging ligands as in **2**. The only structurally characterised gold siloxides are $Au(OSiMe_3)(PPh_2Me)$[28] and $Au(OSiMe_3)(PMe_3)$,[29] though $Au(OSiPh_3)(PPh_3)$ has also been synthesized.[29]

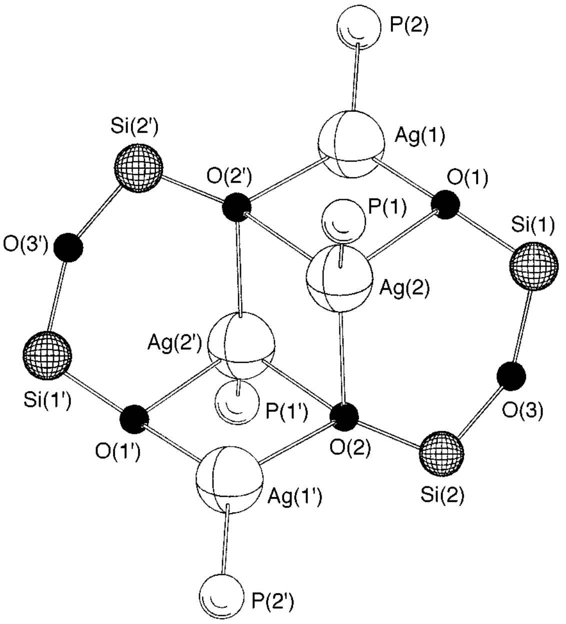

Fig. 4 The structural core of compound **2**. Methyl groups and phenyl rings have been omitted for clarity. Primed atoms are related to unprimed atoms (at *x*, *y*, *z*) by −*x*, 1 − *y*, 1 − *z*

Spectroscopically, three methyl resonances from the siloxide ligand were observed in both the ^1H and ^{13}C NMR spectra at room temperature, indicating non-equivalent methyl groups in the solution structure. Integrals determined from ^1H NMR spectra suggest methyl groups in approximately a 1 : 1 : 2 ratio. Silicon-29 variable-temperature NMR experiments revealed two distinct silicon environments at −80, −40 and 20 °C and this is in accordance with the determined solid-state structure. At room temperature these resonances are observed at δ −8.1 and −18.9 and are comparable with those observed when the disiloxide ligand is bound to tin (δ −17.0 to −19.9).[30] A number of minor resonances were also detected at room temperature possibly representative of solution decomposition products. Room-temperature ^{31}P NMR spectroscopy revealed a slightly broadened singlet which resolved on cooling to −80 °C into a pair of doublets consistent with a single phosphorus directly bound to silver. The two phosphorus environments must be sufficiently similar as to be indistinguishable, although the spectrum appeared slightly broader than expected. Spin–spin coupling values $[^1J(^{109}Ag–^{31}P) = 694,\ ^1J(^{107}Ag–^{31}P) = 602$ Hz] were slightly lower than those reported for $[AgX(PR_3)]_4$ [R = 2,4,6-$(MeO)_3C_6H_2$; X = Cl, Br or I; $^1J(^{109}Ag–^{31}P) = 745–821$ Hz].[31] Attempts to record silver NMR spectra for this compound failed to yield any observable resonances.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), EX400 (^{29}Si, ^{31}P NMR), Perkin-Elmer 599B (IR). For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates and all NMR data were recorded on saturated solutions in $CDCl_3$.

Table 3 Crystal data and structure refinement for compounds **1** and **2***

	1	**2**
Empirical formula	$C_{36}H_{48}Ag_4N_4$	$C_{61}H_{70}Ag_2O_5P_2Si_2$
M	242.07	1217.03
a/Å	12.110(3)	13.160(4)
b/Å	12.301(4)	13.345(4)
c/Å	13.182(4)	17.445(4)
α/°	88.60(2)	88.36(2)
β/°	86.84(2)	80.81(2)
γ/°	65.40(2)	67.88(2)
U/Å^3	1782.7(9)	2800.1(14)
D_c/Mg m^{-3}	1.804	1.443
μ/mm^{-1}	2.195	0.850
F(000)	960	1316
Crystal size/mm	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.8
θ range for data collection/°	2.35 to 22.00	2.09 to 23.70
hkl ranges	0–13, −12 to 14, −15 to 15	−13 to 0, −15 to 0, −18 to 18
Reflections collected	4646	4970
Independent reflections (R_{int})	4391 (0.0392)	4952 (0.0337)
Data, restraints, parameters	3481, 0, 374	4952, 0, 229
Goodness of fit on F^2	1.041	1.046
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0484, 0.1075	0.0914, 0.2612
(all data)	0.1256, 0.1587	0.1605, 0.3011
Largest difference peak and hole/e Å^{-3}	1.195 and −0.803	1.307 and −1.332
Weighting scheme, w	$1/[\sigma(F_o^2) + (0.0730P)^2 + 3.2034P]$	$1/[\sigma(F_o^2) + (0.2152P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.0004(2)	0.0011(12)

* Details in common: 170(2) K; λ(Mo-Kα) 0.709 30 Å; triclinic, space group $P\bar{1}$ (no. 2); $Z = 2$; full-matrix least-squares refinement on F^2; extinction expression $F_c^* = kF_c(1 + 0.001F_c^2I^3/\sin 2\theta)^{-\frac{1}{4}}$.

Syntheses

[2-(Dimethylaminomethyl)phenyl]silver(I) 1. A solution of *n*-butyllithium (51.2 mmol) in diethyl ether (15 cm^3) was added dropwise to a solution of *N*,*N*-dimethylbenzylamine (7.0 g, 51.8 mmol) in diethyl ether (50 cm^3). The reactant mixture was stirred for 72 h under nitrogen resulting in a thick lemon precipitate. The mixture was cooled to −77 °C using a solid CO_2–acetone bath. Silver bromide (9.7 g, 51.7 mmol) was added slowly to the constantly stirred reaction mixture. The reagents were stirred at this temperature for several hours and then allowed to warm to room temperature overnight. While cold the mixture appeared grey, although on warming a brown precipitate was evident. the precipitate was allowed to settle and the supernatant liquid removed using a cannula. The precipitate was then washed successively with diethyl ether (40 cm^3) and pentane (20 cm^3) and the product extracted with toluene (3 × 100 cm^3). Toluene was immediately removed from the combined extracts to yield a red solid (yield 1.8 g, 14%). A small amount of the toluene extract was refrigerated to yield crystals that were suitable for X-ray crystallography [Found (Calc. for $C_9H_{12}AgN$): C, 44.6 (44.7); H, 5.02 (5.00); N, 5.72 (5.79)%]. IR (Nujol mull, cm^{-1}): 745 (sh), 752 (sh), 804w, 841 (sh), 1009 (sh), 1038w, 1098w, 1154w, 1169w, 1260w, 1306w, 1352w, 1401w and 1568w. ^{1}H NMR ($CDCl_3$): δ 7.34–7.29 (m, 4 H, $C_6\mathit{H}_4CH_2NMe_2$), 3.42 (s, 2 H, CH_2) and 2.24 (s, 6 H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 129.1 ($\mathit{C}_6H_4CH_2NMe_2$), 128.2 ($\mathit{C}_6H_4CH_2NMe_2$), 127.0 ($\mathit{C}_6H_4CH_2NMe_2$), 65.8 (CH_2) and 45.4 (NMe_2).

{[Ag(PPh$_3$)]$_2$(μ_4-OMe$_2$SiOSiMe$_2$O)}$_2$ 2. [2-(Dimethylaminomethyl)phenyl]silver(I) **1** (0.10 g, 0.4 mmol) and triphenylphosphine (0.22 g, 0.8 mmol) were dissolved in freshly distilled toluene (30 cm^3). The glass joint of the flask was lightly greased with high vacuum dimethylsilicone grease. The stoppered flask was wrapped in foil and stored at −10 °C for several weeks, at which point small clear crystals began to form [Found (Calc. for $C_{40}H_{42}Ag_2O_3P_2Si_2$): C, 53.1 (53.1); H, 4.59 (4.68)%]. IR (Nujol mull, cm^{-1}): 411w, 505w (sh), 519w (sh), 693 (sh), 745, 774, 843w (br), 943m, 988 (br), 1028w, 1096w (sh), 1240w (sh) and 1435s (sh). ^{1}H NMR ($CDCl_3$): δ 7.50–7.14 (m, 45 H, PPh_3, $C_6\mathit{H}_5CH_3$), 2.35 (s, 12 H, $C_6H_5C\mathit{H}_3$), 0.17 (s, 3 H, $OSiMe_2$), 0.14 (s, 3 H, $OSiMe_2$) and 0.11–0.10 (m, 6 H, $OSiMe_2$). ^{13}C NMR ($CDCl_3$): δ 137.8 (s, $\mathit{C}_6H_5CH_3$), 134.1 (d, *J* 16.5, PPh_3), 132.1 (d, *J* 28.6, PPh_3), 130.1 (s, PPh_3), 129.0 (s, $\mathit{C}_6H_5CH_3$), 128.7 (d, *J* 10 Hz, PPh_3), 128.2 (s, $\mathit{C}_6H_5CH_3$), 125.3 (s, $\mathit{C}_6H_5CH_3$), 21.4 (s, $C_6H_5CH_3$), 0.92 (s, $OSiMe_2$), 0.87 (s, $OSiMe_2$) and 0.71 (s, $OSiMe_2$). ^{31}P NMR ($CDCl_3$–CH_2Cl_2): δ(22 °C) 8.7 (s); (−40 °C) 7.2 [d unresolved, $^1J(^{109}Ag–^{31}P) \approx 470$]; (−80 °C) 6.3 [dd, $^1J(^{107}Ag–^{31}P) = 602$, $^1J(^{109}Ag–^{31}P) = 694$ Hz]. ^{29}Si NMR [$CDCl_3$–CH_2Cl_2–Cr(acac)$_3$]: δ(21 °C) −8.1 (s) and −18.9 (s); (−40 °C) −8.0 (s) and −18.2 (s); (−80 °C) −7.1 (s) and −17.1 (s).

X-Ray crystallography

Details of the crystal data and data collection parameters for both structure determinations are given in Table 3. The diagrams of the asymmetric units of compounds **1** and **2** were produced using ORTEX.[32]

Compound 1. In the final least-squares cycles all atoms were allowed to vibrate anisotropically except for C(10), C(13), C(16), C(19) and C(24). Anisotropic refinement of these carbons resulted in unsatisfactory thermal parameters, so they were refined isotropically. Hydrogen atoms were included at calculated positions.

Compound 2. Data quality and residuals were impeded by two obstacles. First, the crystals were not of exceptionally high quality. Secondly, the crystals in the sample available for structural analysis were not of ideal size. Moreover, crystal mounting in a sealed capillary prior to transfer to the diffractometer was a particularly precarious task due to rapid solvent loss. Attempts to apply an empirical absorption correction (despite a low μ value) did not improve convergence. In the final least-squares cycles the Ag, P and Si atoms were allowed to vibrate anisotropically (anisotropic refinement of the other remaining atoms only served to yield unsatisfactory thermal parameters in some cases). Hydrogen atoms were included at calculated positions except in the case of the water molecules. Phenyl rings were treated as regular hexagons.

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