Crystal and Molecular Structures of the Sulfurization and Selenation Products of Bis[bis(trimethylsilyl)amino]germanium(II). Crystal Structure of (Triphenylphosphine)gold(I) Bis(trimethylsilyl)amide

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Treatment of bis[bis(trimethylsilyl)amino]germanium(II) with elemental sulfur or selenium affords high yields of the corresponding monosulfide $[(Me_3Si)_2N]_2GeS$ and selenide $[(Me_3Si)_2N]_2GeSe$, respectively. The crystalline products have now been shown to be cyclic dimers with $(GeS/Se)_2$ four-membered rings by X-ray single crystal structure analysis. The crystal structure of (triphenylphosphine)gold(I) bis(trimethylsilyl)amide (Ph_3P)Au-N(SiMe_3)_2 has also been determined. The molecule is a monomer with a tricoordinate nitrogen atom in a planar configuration [Si_2NAu]. The compound does not undergo insertion of the bis[bis(trimethylsilyl)amino]germylene.

Introduction

Bis[bis(trimethylsilyl)*amino*]germanium(II) was first prepared by Lappert *et al.* as one of the early examples of a stable carbene analogue with twocoordinate germanium(II) centres [1, 2]. Like the related bis[bis(trimethylsilyl)*methyl*]germanium(II) molecule [3], compound 1 is known to undergo many redox and insertion reactions, including oxidation by all four of the elemental chalcogens (X = O, S, Se, Te) [4]. The products have the formula $\{[(Me_3Si)_2N]_2GeX\}_n$, but the number *n* has been specified only for X = O and X = Te. These compounds have been shown [4, 5] to be cyclic dimers with four-membered rings (GeO)₂ and (GeTe)₂, respectively.

In the course of our recent studies of insertion reactions of germanium(II) compounds into functional gold(I) complexes [6 - 11] we also investigated the reactivity of (triphenylphosphine)gold(I) bis(trimethylsilyl)amide [12] towards [(Me₃Si)₂-N]₂Ge. An insertion of the germanium(II) compound into the Au-N bond could lead to a germylgold(I) species with an extremely crowded germyl substituent. Our experiments have shown, however, that the two reagents give no addition product whatsoever within the stability range of the starting materials. Even after extended periods of time at reaction temperatures up to 60 °C the two components are recovered unchanged.

In order to obtain direct information about the steric crowding of the gold(I) complex we determined its crystal structure. We also reinvestigated the sulfurization and selenation of compound 1 in order to clarify the degree of association of the oxidation products.

Results and Discussion

Colourless (triphenylphosphine)gold(I) bis(trimethylsilyl)amide (1) [1, 2] and low-melting yellow bis[bis(trimethylsilyl)amino]germanium(II) [12] were readily prepared as crystalline solids following the literature methods. The analytical and



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Fig 1. Molecular structure of compound **1** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au-P 2.2281(8), Au-N 2.026(3), N-Si1 1.713(3), N-Si2 1.708(3); P-Au-N 176.44(8), Si1-N-Si2 125.76(16), Si1-N-Au 110.39(14), Si2-N-Au 119.57(15).

spectroscopic data of the products were in agreement with literature readings where available, and a few complementary measurements have been carried out (Experimental Part).

Attempts to react equimolar quantities of the two components in various solvents at temperatures up to 60 °C were all unsuccessful. The two compounds were left unchanged as demonstrated by NMR spectroscopy. No insertion of the germylene into the Au-N bond occurred. At higher temperatures decomposition ensued.

The failure of these experiments probably has to be ascribed to both excessive steric hindrance by the bulky bis(trimethylsilyl)amino groups at the gold and germanium atoms and thermodynamic stabilisation of the germylene due to π -interactions between the free electron pairs of the nitrogen atoms and the electron deficient germanium centre.

In order to delineate the geometrical details of the gold(I) component **1** the crystal and molecular structure was determined by single crystal Xray diffraction. Such a study of a compound with a Au-N-Si linkage was also desirable in the context of recent structural work on the analogous gold(I) siloxides [13] and silthiolates [14] with Au-O-Si and Au-S-Si linkages, respectively.

Crystals of $(Ph_3P)AuN(SiMe_3)_2$ (1), are triclinic, space group $P\bar{I}$, with two molecules in the unit cell. The structure of the individual molecules, between which there are no conspicuously short contacts,



Fig 2. Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1-N1 1.8463(4), Ge1-N2 1.845(4), Ge1-S1 2.2257(13), Ge1-S2 2.2275(13), Ge2-N3 1.836(4), Ge2-N4 1.841(4); Ge2-S1 2.2479(13), Ge2-S4 2.2267(14), N1-Si11 1.771(4), N1-Si12 1.771(4), N2-Si21 1.762(4), N2-Si22 1.756(4), N3-Si31 1.767(4), N3-Si32 1.758(4), N4-Si41 1.772(4), N4-Si42 1.767(4); N1-Ge1-N2 110.92(17), N1-Ge1-S1 109.72(12), N1-Ge1-S2 115.65(13), N2-Ge1-S1 115.70(13), N2-Ge1-S2 109.91(13), S1-Ge1-S2 94.15(5), N3-Ge2-N4 110.31(17), N3-Ge2-S1 111.09(12), N3-Ge2-S2 111.34(12), N4-Ge2-S2 116.40(13), S1-Ge2-S2 93.57(5), Ge1-S1-Ge2 85.85(4), Ge1-S2-Ge2 86.32(5).

is shown in Fig. 1. The large ligands are clearly protecting the gold atom against an approach of other molecules of **1** and of other reactants.

The gold atoms are in the expected linear coordination by a phosphorus and a nitrogen atom [P-Au-N 176.44(8)°]. The Au-N distance [Au-N 2.026(3) Å] is similar to the data of related imide compounds, *e. g.* the phthalimide with the same Ph₃P ligand [Au-N 2.040(4) and 2.028(4) Å for the solvent-free crystal or the CHCl₃ solvate, respectively] [15]. The sum of the angles at the nitrogen atom amounts to only 355.72°, indicating a significant deviation from planarity.

The environment of the germanium atom in the germylene was probed by single crystal X-ray diffraction studies of the corresponding sulfide and selenide. These derivatives are available through direct sulfurization and selenation in tetrahydrofuran as described in the literature [4]. White colourless crystals were obtained in high yields. The crystals of the two compounds are not isomorphous, and they



Fig 3. Molecular structure of compound **3** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1-N1 1.8516(19), Ge1-Se 2.3678(4), Ge2-N2 1.857(2); Ge2-Se 2.3766(4), N1-Si1 1.767(2), N1-Si2 1.759(2), N2-Si3 1.766(2), N2-Si4 1.771(2); N1-Ge1-N1' 111.21(13), N1-Ge1-Se 110.91(6), N1-Ge1-Se' 114.24(6), Se-Ge1-Se' 94.44(2), N2-Ge2-N2' 114.25(13), N2-Ge2-Se 108.26(7), N2-Ge2-Se' 115.29(6), Se-Ge2-Se' 93.98(2), Ge1-Se-Ge2 85.793(16).

are also not isomorphous with the related oxide and telluride [4, 5].

Crystals of the sulfide 2 from pentane are monoclinic, space group $P2_1/c$, with Z = 4 molecules in the unit cell. There is no solvent in the crvstals. The individual molecules represent dimers of the original germylene sulfide units. These dimers have no crystallographically imposed symmetry, but the positions of the core atoms $Ge_2S_2N_4$ obey quite closely the symmetry requirements of point group D_{2h} (Fig. 2). The four disilylamino groups are substituents of a four-membered ring $(GeS)_2$, which is virtually planar [sum of the internal angles $359.89(5)^{\circ}$], but deviates very significantly from the geometry of a square. The angles at the germanium atoms [Ge2 93.57(5), Ge1 94.15(5)°] are larger than 90° , while the angles at the sulfur atoms $[S1 85.85(4), S2 86.32(5)^{\circ}]$ are smaller.

By contrast with the findings for **2**, the selenide **3** crystallizes from *n*-pentane in the monoclinic space group C2/c with Z = 4 molecules and four molecules of solvent C_5H_{12} in the unit cell. Like with **2**, the individual molecules are dimers of the germylene selenide units, but these dimers obey crystallographic C_2 symmetry with the twofold axis passing through

the two germanium atoms and the central carbon atom of the pentane solvent molecule. This solvent molecule has the all-trans conformation of an extended hydrocarbon chain, while the $Ge_2Se_2N_4$ core of the dimeric bis(amino)germanium sulfide has two inequivalent germanium atoms bridging equivalent selenium atoms. The four-membered ring (GeSe)₂ is planar with a sum of internal angles of 360.00(2)°, and with angles of 93.98(2)° at Ge2, 94.44(2)° at Ge1, and 85.79(2)° at Se.

Similar to the situation in the gold complex 1, and in many other metal disilylamides, the configuration at the nitrogen atoms in molecules 2 and 3 is close to planar. This configuration leads to a maximum shielding of the $(GeS)_2$ and $(GeSe)_2$ cores of molecules 2 and 3, respectively.

A comparison of the data for $[(Me_3Si)_2N]_4Ge_2E_2$ with E = O, S, Se, Te shows great similarities. The basic structure follows the same principle in all cases, except for a gradual widening of the fourmembered ring following the growth of the covalent radius of the chalcogen atoms: Ge-O 1.805(9) Å (average), Ge-S 2.238(1) Å, Ge-Se 2.372(1) Å, Ge-Te 2.595(2) Å.

All Ge₂E₂ rings are planar, with deviations from the square geometry smallest for E = O [average Ge-O-Ge 87.5(4)°, O-Ge-O 92.5(4)°] and larger and almost uniform for E = S, Se, Te [average Ge-Te-Ge 85.58(6)°, Te-Ge-Te 94.38(6)°]. The homologous series thus shows virtually no structural anomalies.

Experimental Part

All experiments were carried out routinely in an inert atmosphere of dry pure nitrogen. Standard equipment was used throughout.

(Triphenylphosphine)gold(I) bis(trimethylsilyl)amide (1) [12]

To a slurry of (Ph₃P)AuCl (0.69 g, 1.39 mmol) [16] in tetrahydrofuran (8 ml) was added dropwise with stirring 1.39 ml of a 1.0 m solution of $(Me_3Si)_2NLi$ in tetrahydrofuran at 20 °C. After 1 h the solvent was removed *in vacuo*. Extraction of the residue with pentane (15 ml) and evaporation of the solvent from the extract left a crystalline colourless solid (0.47 g, 54.6% yield). ¹H NMR (C₆D₆): 0.57, s, 18H, Me; 6.92-7.45, m, 15H, Ph. ¹³C{¹H}: 6.82, s, Me; 128.6, s, C_i; 131.2, d, *J*(PC) 2.4, C_p; 131.3, d, *J*(PC) 9.5, C_m; 134.2, d, *J*(PC) 13.0, C₀. ³¹P{¹H}: 34.7, s. – C₂₄H₃₃AuNPSi₂ (619.63): Calcd C 46.51, H 5.53, N 2.26. Found C 46.32, H 5.37, N 2.12%.

	1	2	$\boldsymbol{3}\cdot C_5H_{12}$
Crystal data			
Formula M_r Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) V (Å) ρ_{calc} (g·cm ⁻³) Z Z	C ₂₄ H ₃₃ AuNPSi ₂ 619.63 triclinic <i>P</i> Ī 8.560(1) 12.357(1) 13.606(2) 71.27(1) 79.89(1) 74.56(1) 1307.4(3) 1.574 2	$\begin{array}{c} C_{24}H_{72}Ge_2N_4S_2Si_8\\ 850.88\\ monoclinic\\ P2_1/c\\ 9.074(2)\\ 41.117(10)\\ 12.508(3)\\ 90\\ 106.61(1)\\ 90\\ 4472.0(18)\\ 1.264\\ 4\\ 1809 \end{array}$	$\begin{array}{c} C_{29}H_{84}Ge_2N_4Se_2Si_8\\ 1016.82\\ monoclinic\\ C2/c\\ 16.288(1)\\ 27.595(4)\\ 11.604(1)\\ 90\\ 106.09(1)\\ 90\\ 5011.3(9)\\ 1.348\\ 4\\ 2120\end{array}$
F(000) $\mu(Mo K_{\alpha}) (cm^{-1})$	612 57.90	1808	2120 28.67
Data collection	01100	10170	
T (°C) hkl Range $\sin(\theta/\lambda)_{max}$ (Å ⁻¹) Measured reflections Unique reflections Absorption correction T_{min}/T_{max}	-120 $-10 \rightarrow 19, 0 \rightarrow 15, -16 \rightarrow 17$ 0.64 5965 $5690 [R_{int} = 0.0112]$ Psi-scans 0.444/0.999	-110 $-11 \rightarrow 10, 0 \rightarrow 50, 0 \rightarrow 15$ 0.62 9139 $8748 [R_{int} = 0.0368]$ Psi-scans 0.813/0.999	-120 $-20 \rightarrow 20, 0 \rightarrow 35, -14 \rightarrow 3$ 0.64 7279 $5470 [R_{int} = 0.0192]$ Psi-scans 0.600/0.999
Refinement			
Refined parameters Final $R1^{[a]}$ [I >2 σ (I)] Final $wR2^{[b]}$ [I >2 σ (I)] (shift/error) _{max} $\rho_{fin}(max/min)$ (eÅ ⁻³)	262 0.0489 0.1316 < 0.001 1.597/-2.241	361 0.0553 0.1082 < 0.001 0.925/-1.030	205 0.0228 0.0574 < 0.001 1.419/-1.214

Table 1. Crystal data, data collection, and structure refinement for compounds 1, 2, and 3.

^[a] $R = \Sigma (||F_o| - |F_c||)/\Sigma |F_o|; {}^{[b]} wR2 = \{ [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2] \}^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3; a = 0.0396$ (1), 0.0369 (2), 0.0353 (3); b = 0.87 (1), 16.33 (2), 7.13 (3).

Treatment of complex **1** (0.42 g, 1.07 mmol) [12] with $[Me_3Si)_2N]_2Ge$ (0.66g, 1.07 mmol) [3] in pentane (20 ml) at -50 °C, +20 °C or in boiling hexane (60 °C) left the components unchanged as shown after work-up by NMR spectroscopy.

Bis[bis(trimethylsilyl)amino]germanium sulfide (2) *and selenide* (3)

A mixture of $[(Me_3Si)_2N]_2$ Ge (2.08 g, 5.29 mmol) [3] and sulfur (0.17 g, 5.29 mmol) was suspended in tetrahydrofuran (15 ml) and heated to reflux for 24 h. The resulting reaction mixture was filtered at 20 °C and the solvent removed *in vacuo*. Recrystallization from pentane at -30 °C gave colourless crystals (1.35 g, 60% yield). ¹H NMR (C₆D₆): 0.50, s. ¹³C{¹H}: 7.03, s. ²⁹Si{¹H}: 5.79, s. C₂₄H₇₂Ge₂N₄S₂Si₈ (850.87): Calcd C 33.90, H 8.50, N 6.60, S 7.50. Found C 32.66, H 8.49, N 6.15, S 8.04%. The selenide **3** was prepared similarly from 1.98 g (5.04 mmol) of the germylene and 0.40 g (5.04 mmol) of grey selenium (2.32 g, 90.5% yield). ¹H NMR (C₆D₆): 0.50, s. ¹³C{¹H}: 6.96, s. ²⁹Si{¹H}: 5.50, s. The crystals contain 1 mole equivalent of pentane. C₂₉H₈₄Ge₂N₄Se₂Si₈ (1016.82): Calcd C 34.26, H 8.33, N 5.51: Found C 33.37, H 7.91, N 5.57%.

Crystal structure determinations: Specimens of suitable quality and size of compounds **1**, **2**, and **3** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo-K_{α} radiation, λ (Mo-K_{α}) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied and intensity data were corrected for absorption

effects. The structures were solved by direct methods (SHELXS-97) and completed by full-matrix-least squares techniques against F² (SHELXL-97). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions (U_{iso(fix)} = $1.5 \times U_{eq}$ of the attached C atom). Further information

on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS 141598 - 141600.

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