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Chemistry of silicon–sulfur compounds Part 64*. Crystal and molecular structure of (tri-tert-butoxysilanethiolato)bis(triphenylphosphine)copper(I) $(t\text{-}C_4H_9O)_3SiSCu[P(C_6H_5)_3]_2$

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Abstract

(Tri-tert-butoxysilanethiolato)bis(triphenylphosphine)-copper(I), which was obtained by reaction of triphenylphosphine with $[(t\text{-}BuO)_3SiSCu]_4$ in benzene, forms colourless plates, with the following crystal data $a=12.772(1)$, $b=18.475(2)$, $c=10.259(1)$ Å, $\alpha=93.38(1)$, $\beta=106.302(7)$, $\gamma=90.128(9)°$, space group $P\bar{1}$ and $Z=2$ The structure was refined to an R (R_w) value of 0.0382 (0.0280). The crystal consists of monometallic molecules in which the copper atom is three-fold coordinated to one sulfur and two phosphorus atoms in an essentially trigonal planar arrangement. The relevant bond distances and angles are: Cu–P 2.292(1), 2.273(1), Cu–S 2 250(1), S–Si 2.074(1) Å; P–Cu–P 123.7(0)°, P–Cu–S 110 2(0), 126.0(0), Cu–S–Si 103 7(1)°.

Neutral copper thiolate complexes ligated additionally by phosphine ligands are well known [2–6]. Due to the tendency of thiolate sulfur to bridge metal centres they all were found to be oligomeric in the solid state. These compounds vary within the Cu/P ratio: 2:1 as in $(t\text{-}BuSCu)_4(PPh_3)_2$ [2], 1:1 as in $(C_5H_{11}SCu)_2[(Ph_2P)_2CH_2]_2$ [3] and $(PhSCu)_4(PPh_3)_4$ [4], 1:1.33 as in $(PhSCu)_3(PPh_3)_4$ [5] and 1:2 as in $(PhSCu)_2(PPh_3)_4$ [6].

In 1971 Reichle [7] reported that polymeric PhSCu reacts with triphenylphosphine yielding $PhSCu(PPh_3)_2$. Osmometric data for this compound in chlorobenzene solution indicated that either it is monomeric or, if dimeric, it is in a dissociative equilibrium:

$$(Ph_3P)_2Cu(SPh)_2Cu(PPh_3)_2 \Longleftrightarrow (Ph_3P)_2Cu(SPh)_2Cu(PPh_3)_2 + PPh_3$$

In 1983 Dance *et al.* [6] showed this compound to be in fact dimeric in the solid state. Therefore, a question concerning the possible existence of neutral, monomeric, phosphine ligated copper thiolates remained still elusive. Our continued interest in the chemistry of silicon–sulfur compounds resulted in the successful application of the tri-tert-butoxysilanethiol $(t\text{-}C_4H_9O)_3SiSH$, as a source of a new type thiolate ligand with an SH function at the silicon instead of at the carbon atom. We reported the syntheses and structures of several neutral, molecular and homoleptic metal silanethiolate complexes [8]. In a recent paper [9] we also described the synthesis of three heteroleptic copper(I) silanethiolates, $(t\text{-}C_4H_9O)_3SiSCu(PPh_3)_2$ (**1**) $(t\text{-}C_4H_9O)_3SiSCu(phen)$ (**2**) and $[(t\text{-}C_4H_9O)_3SiSCu]_2$-(bipy), obtained by the reaction of cyclo-tetrakis[tri-tert-butoxysilanethiolatocopper(I)] with triphenylphosphine, 1,10-phenanthroline and 2,2′-bipyridine, respectively.

Subsequent X-ray structure determination of **2** [10] revealed a monometallic molecule — the first example of a monomeric neutral copper complex with a thiolate ligand.

The triphenylphosphine adduct **1** has the same copper/ligator ratio as complex **2**. Moreover, on the basis of its ^1H NMR spectrum (non-equivalency of methyl hydrogens), we already suggested for **1** a monomeric structure, at least in solution [9]. Our assumption was confirmed by an X-ray single crystal structure determination.

The complex $(t\text{-}C_4H_9O)_3SiSCu(PPh_3)_2$ (**1**) crystallizes from hexane/ethanol (7:5 vol./vol.) as colourless plates triclinically in the space group $P\bar{1}$; $a=12.772(1)$, $b=18.475(2)$, $c=10.259(1)$ Å, $\alpha=93.38(1)$, $\beta=106.302(7)$, $\gamma=90.128(9)°$; $V=2318.9$ Å^3, $Z=2$. Structure solution and refinement (Siemens SHELXTL PLUS) were based on 4614 reflections with $F_o \geqslant 3\sigma(F_o)$ (Mo Kα, 0.71073 Å, 6088 total reflections collected) to give final residuals of 0.038 and 0.028 for R and R_w, respectively. Figure 1 gives a view of the complex with the atom labelling scheme; selected bond lengths and angles are given in the caption. Compound **1** consists of discrete monomeric tri-tert-butoxysilanethiolato-bis(triphenylphosphine)copper(I) units separated by van

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*Part 63 is ref 1

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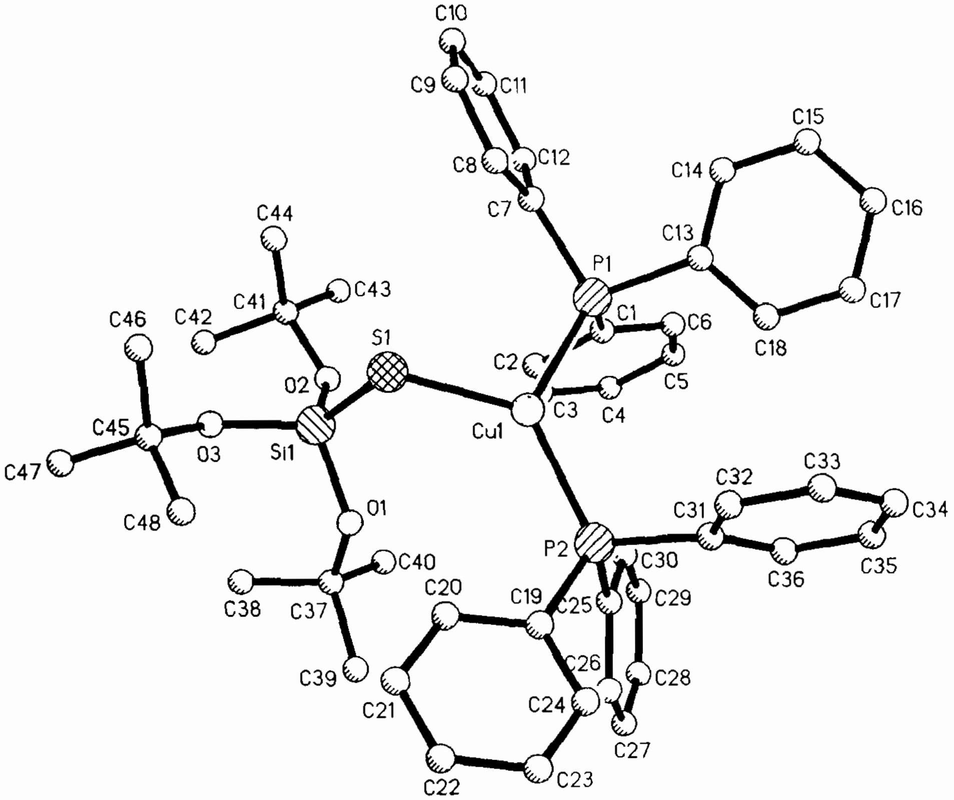

Fig 1. Molecular structure of $(t\text{-}C_4H_9O)_3SiSCu(PPh_3)_2$ (**1**) with atom labelling scheme (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cu(1)–S(1), 2.250(1); Cu(1)–P(1), 2.292(1), Cu(1)–P(2), 2.273(1); S(1)–Si(1), 2.074(1); P(1)–Cu(1)–P(2), 123.7(0); P(1)–Cu(1)–S(1), 110.2(0); P(2)–Cu(1)–S(1), 126.0(0), Cu(1)–S(1)–Si(1), 103.7(1), P–C, range 1.818–1.838, Si–O, range 1.626–1.636

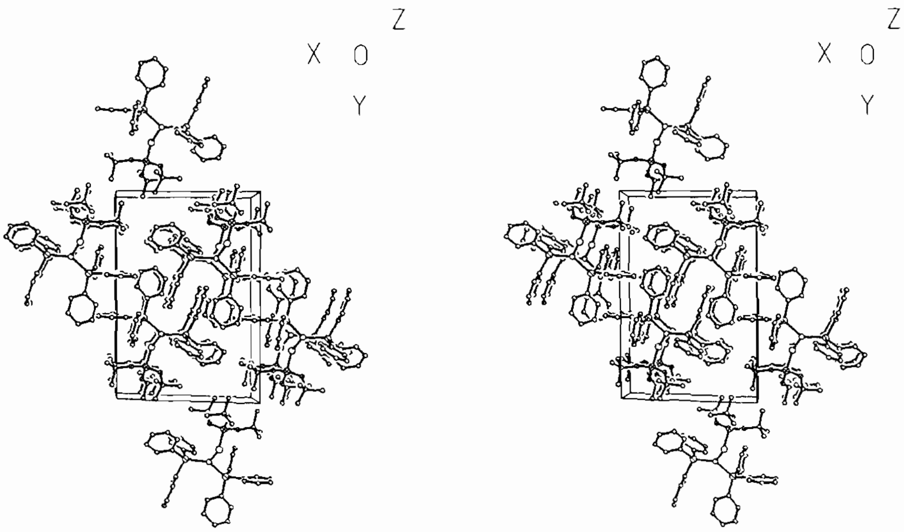

Fig. 2. Stereopair of the unit cell of $(t\text{-}C_4H_9O)_3SiSCu(PPh_3)_2$ (**1**).

der Waals distances. Figure 2 presents a stereodrawing of the molecular packing of **1**.

The copper coordination in **1** is essentially trigonal planar, but the corresponding angles deviate from the idealized value of 120°. The molecule is similar to that of **2** [10], although in **2** the deviations of the central bond angles, due to the imposed bite of the N–Cu–N angle, are markedly greater.

Triphenylphosphine ligands in **1** adopt eclipsed conformations and form approximately three-bladed chiral

TABLE 1. $Cu(PPh_3)_2X$ core structures

	Cu–P (Å)	Cu–X (Å)	P–Cu–P (°)	P–Cu–X (°)
Cl[a, b, d]	2.272(2) 2.260(2)	2.208(2)	125.48(7)	113.76(7) 120.74(6)
Br[a, c, d]	2.282(3) 2.263(2)	2.346(2)	126.0(1)	112.8(1) 121.0(1)
I[b]	2.273(2)	2.524(2)	126.9(1)	116.61(5)
$(t\text{-}C_4H_9O)_3SiS$[d]	2.292(1) 2.273(1)	2.250(1)	123.7(1)	110.2(1) 126.0(1)

[a] Hemibenzene solvate. [b] Ref 11 [c] Ref. 12 [d] This work.

propellers. The spatial requirement of one ligand, larger than that of the planar phenanthroline in **2**, results in a different spacefilling around the copper atom. Hence, the bulky silanethiolate substituent in **2** covers the Cu atom with preference on one side leaving the other one more or less open. In contrast, the region around copper in **1** is almost completely filled. Any significant contacts to other molecules of **1** and thus oligomerization seem to be improbable.

Although the structure of the tri-tert-butoxysilanethiolate ligand in **1** is similar to that found in **2**, the Cu–S bond length of 2.250 Å in **1** is 0.11 Å larger than that in **2**. Thus, this distance is within the lower limit of the Cu–S bond length for three-fold coordinated copper(I) found in other triphenylphosphine ligated oligomeric copper(I) thiolates (compare, for example, 2.245–2.263 Å in $(t\text{-}BuSCu)_4(PPh_3)_2$ [2] and 2.277–2.313 Å in $(PhSCu)_4(PPh_3)_4$ [4]; in the latter sulfur is at least triply bonded).

Due to its unique monomeric structure **1** can only hardly be compared with oligomeric phosphine ligated copper(I) thiolates but the complex fits nicely into the class of monomeric copper(I) phosphine complexes of formula $Cu(PPh_3)_2X$. This is illustrated in Table 1 where the relevant data for **1** and three halogenobis(triphenylphosphine)copper(I) complexes are compiled. Despite significant differences between simple halides and bulky silanethiolate ligands the core structures for all four complexes are similar.

Supplementary material

Atomic coordinates, displacement factor coefficients, full lists of bond lengths and angles and lists of F_o/F_c values have been deposited as Supplementary Data, No. CSD 57261. Copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen, Germany.

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