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Copper(I) Complexes with Thioether-Functionalized Silylamido Ligands

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The thioether-functionalized aminosilanes $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SR})_2$ ($\text{R}=\text{Ph}$, Me) were lithiated with *n*-BuLi and subsequently allowed to react with CuCl in the presence of PMe_3 . In the case of $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SPh})_2$, the dinuclear complex $[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2-\text{SPh})_2\}(\text{PMe}_3)_2]$ was isolated. In $[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2-\text{SPh})_2\}(\text{PMe}_3)_2]$ the copper atoms adopt a distorted trigonal-

planar coordination (Cu–N: 191.2(2) pm, Cu–P: 216.3(1) pm, Cu–S: 244.4(1) pm). The reaction of $\text{Li}_2\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})_2$ with CuCl in the presence of PMe_3 led to rearrangement processes from which the ionic cluster compound $[\text{Cu}(\text{PMe}_3)_4][\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{S})(\text{N}-\text{C}_6\text{H}_4-2-\text{S}-\text{Me})_2\}(\text{PMe}_3)_2]$ was isolated in low yield.

Introduction

Di- and trifunctional silylamides of the type $\text{R}_2\text{Si}(\text{NR}')_2^{2-}$ and $\text{RSi}(\text{NR}')_3^{3-}$ are suitable ligands for a variety of transition metals. Particularly, research on compounds of Ti, Zr, Hf, V and Nb has played an outstanding role in the development of silylamide coordination chemistry.^[1] However, some groups of transition metals, i.e. coinage metals, have found less attention. Probably this originates from the difficult handling of the Cu, Ag and Au derivatives due to their limited thermal stability and their air and moisture sensitivity. Moreover, particularly the monovalent coinage metals often form a variety of polynuclear complexes, which makes the isolation and unambiguous characterization of specific products challenging. Recently, we reported on the octanuclear complexes $[\text{Cu}_8\{(\text{R}_2\text{Si}(\text{NPh})_2)_4\}]$ ($\text{R}=\text{Me}, \text{Ph}$)^[2] and the decanuclear compounds $[\text{Li}(\text{THF})_4]_2[\text{Cu}_{10}\{(\text{RSi}(\text{NPh})_3)_4\}]$ ($\text{R}=\text{Me}, \text{Ph}, \text{vinyl}$)^[3] During the course of these investigations we were interested to improve the coordination capabilities of silylamide ligands by introduction of pendant donor groups. Side-arm functionalized silylamide ligands were applied as early as 2004 by Pasarelli for the synthesis of catalytically active Zr complexes.^[4] In the last years we focused on thioether functionalized silylamides $\text{R}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SR}')_2^{2-}$ which allowed

for the synthesis of Ti, Ag,^[5] Au,^[6] Ni^[7] and Mo complexes^[8] with novel structural motifs. Here we report on the application of the silylamide ligands $\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SPh})_2^{2-}$ and $\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})_2^{2-}$ in the synthesis of the Cu(I) complexes $[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SPh})_2\}(\text{PMe}_3)_2]$ and $[\text{Cu}(\text{PMe}_3)_4][\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{S})(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})_2\}(\text{PMe}_3)_2]$.

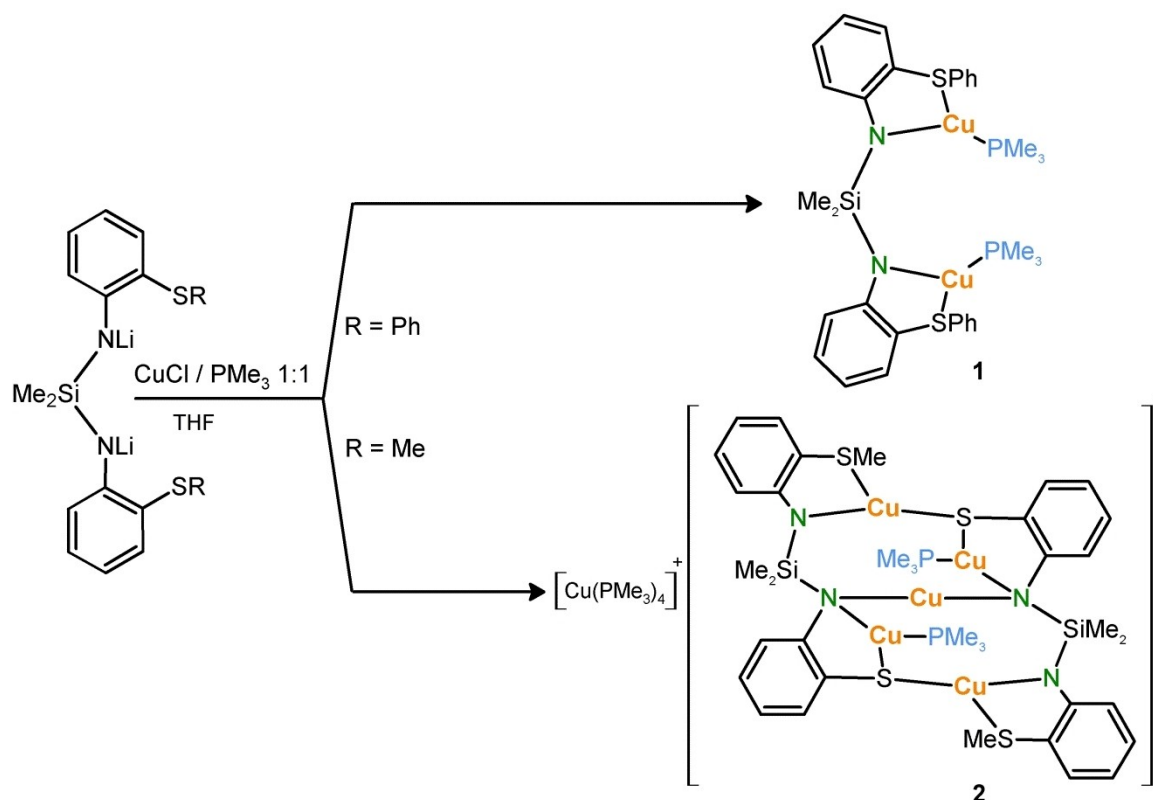
Results and discussion

The synthesis of the copper complexes is briefly depicted in Scheme 1. Treatment of a solution of CuCl and PMe_3 (molar ratio 1:1) in THF at -70°C with a solution of $\text{Li}_2[\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SPh})_2]$ in THF led to the formation of an intensively yellow colored reaction mixture. After stirring at room temperature THF was removed under reduced pressure and the solid residue was extracted with toluene. Yellow crystals of compound **1** were obtained in 62% isolated yield by slow diffusion of *n*-hexane into the toluene solution. Compound **1** is soluble in THF, diethyl ether and toluene. In *n*-hexane and benzene the solubility is much lower. Compound **1** is remarkably air-sensitive. On contact with air the yellow crystals are immediately decomposed to give a black residue. Contrary to the synthesis of compound **1**, the analogous reaction of $\text{Li}_2[\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-\text{SMe})_2]$ with CuCl in the presence of PMe_3 led to the conversion of one thioether group into a thiolate function and the complex $[\text{Cu}(\text{PMe}_3)_4][\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{S})(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})_2\}(\text{PMe}_3)_2]$ (**2**) was isolated in low yield. In literature, cleavage of S–C thioether bonds has been reported in many instances, particularly in the case of cobalt complexes with thioether-containing hexadentate pyrazine amide ligands.^[9] It is obvious that Cu(I) plays a crucial role in the formation of **2** as the corresponding Ag(I) and Au(I) complexes do not show comparable behavior.^[6] Probably, the C–S bond activation is induced by oxidative addition. However, this mechanistic detail requires further investigations. Compound **2** forms pale yellow crystals which are reasonably soluble in THF and toluene and less soluble in diethyl ether, benzene and aliphatic hydrocarbons. On contact with air compound **2** rapidly turns black.

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Scheme 1. Synthesis of the Cu(I) complexes **1** and **2**.

The $^1\text{H-NMR}$ spectrum of compound **1** (in THF- D_8) displays the signals of the $\text{Me}_2\text{Si}(\text{N-C}_6\text{H}_4\text{-SPh})_2$ moiety and the PMe_3 ligands in the appropriate intensity ratio. The $^{29}\text{Si-NMR}$ signal consists of a singlet at $\delta = -15.1$ ppm, which is close to the chemical shifts of $\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2$ (-10.2 ppm), $[\text{Ag}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ (-14.7 ppm) and $[\text{Au}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ (-11.2 ppm).^[6] The $^{31}\text{P-NMR}$ spectrum consists of a broad singlet signal at $\delta = -43.0$ ppm. In comparison to the analogous derivatives $[\text{Ag}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ (-35.7 ppm) and $[\text{Au}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ (-10.7 ppm) the ^{31}P resonance is shifted upfield. The $^1\text{H-NMR}$ spectrum of compound **2** displays the signals of the $\text{Me}_2\text{Si}(\text{N-C}_6\text{H}_4\text{-SPh})_2$ units and the PMe_3 ligands in the appropriate intensity ratio according to the formula $[\text{Cu}(\text{PMe}_3)_4][\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N-C}_6\text{H}_4\text{-2-S})\}(\text{N-C}_6\text{H}_4\text{-2-SMe})_2(\text{PMe}_3)_2]$. The $^{31}\text{P-NMR}$ spectrum clearly indicates the presence of the $[\text{Cu}(\text{PMe}_3)_4]^+$ cation by a broad quartet signal at -40.5 ppm with a $|^1J_{\text{P,Cu}}|$ spin coupling constant of approx. 790 Hz, which is consistent with the data reported for the $[\text{Cu}(\text{PMe}_3)_4]^+$ ion in the previous literature.^[10] The cluster anion gives rise to a singlet signal at $\delta = -43.3$ ppm. The $^{63}\text{Cu-NMR}$ spectrum consists of a quintet signal centered at $\delta = 279$ ppm (vs. $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ in MeCN; $\delta_{\text{Cu}} = 0$ ppm),^[11] $|^1J_{\text{P,Cu}}| = 763$ Hz. As to be expected, the signals of the copper atoms of the cluster anion are not detectable due to the ^{63}Cu quadrupole moment and the low symmetric environment of the copper atoms. The

^{29}Si shift of **2** is -17.7 ppm and therefore close to the value observed for compound **1**.

Crystal structures

In order to get deeper insight into the molecular structures of compounds **1** and **2**, single crystal X-ray analyses were carried out. Details of the crystallographic data and the data collection are summarized in Table 1. Compound **1** (Figure 1) crystallizes in the monoclinic space group $C 2/c$. The crystal structure consists of discrete molecules $[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ and disordered toluene molecules without any unusually short intermolecular contacts. The $[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{NH-C}_6\text{H}_4\text{-2-SPh})_2\}(\text{PMe}_3)_2]$ unit possesses crystallographically imposed C_2 symmetry with the crystallographic C_2 axis passing through the silicon atom. The molecular structure of compound **1** consists of a $\text{Me}_2\text{Si}(\text{N-C}_6\text{H}_4\text{-2-SPh})_2$ fragment in which both the nitrogen atoms are attached to a $\text{Cu}(\text{PMe}_3)$ moiety. Additionally, the coordination sphere of the copper atoms is completed by the sulfur atom of the SPh group. This leads to a distorted trigonal planar coordination (sum of the angles around Cu: 357.8°). The Cu–N distance is 191.2(2) pm. Similar values have been observed in other copper(I) silylamide complexes like $[\text{Cu}_8\{\text{R}_2\text{Si}(\text{NPh})_2\}_4]$ ($\text{R} = \text{Me, Ph}$; 190.0–195.1 pm),^[2] $[\text{Cu}_{10}\{\text{RSi}(\text{NPh})_3\}_4]^{2-}$ ($\text{R} = \text{Me, Ph, Vinyl}$; 187.1–193.7 pm)^[3] and other polynuclear copper(I) amides, e.g. $[\text{CuNMe}_2]_4$ (188.5–

), depending on the coordination number, charge of the complex and co-ligands attached to copper.^[16] In contrast to the rather short Cu–P distance the Cu–S separation of 244.4(1) pm is relatively large. According to the data of the CSD database the Cu–S separations in mixed Cu(I) phosphane/thioether complexes are varying from 228.2–287.9 pm (60 entries, 106 data, median value: 236.2 pm, lower quantile: 233.1 pm, upper quantile: 242.1 pm). The relatively large Cu–S separation fits well to the observation of a nearly linear N–Cu–P arrangement (N–Cu–P: 156.3(1)°). Thus, the coordination around copper can be described as “2 + 1” with the thioether group acting as weakly coordinating additional ligand. However, in comparison with the silver and gold derivatives [Ag₂Me₂Si(N–C₆H₄–2–SPh)₂(PMe₃)₂] and [Au₂Me₂Si(N–C₆H₄–2–SPh)₂(PMe₃)₂] which display N–M–P angles of 167.6(1)–178.1(3)° the influence of the SPh coordination in **1** is markedly larger. A further remarkable difference between compound **1** and the analogous Ag and Au compounds [M₂Me₂Si(N–C₆H₄–2–SPh)₂(PMe₃)₂] (M = Ag, Au) concerns the conformation of the central SiN₂M₂ unit. In the case of the Ag and Au derivatives, the torsion angles N–Si–N–M are –0.5 and –73.5° for the silver compound and –2.9 and –68.3° for the gold compound. These conformations allow for weak Ag–Ag (339 pm) and Au–Au (335 pm) contacts. Contrary to this, the torsion angles N–Si–N–Cu are –115.8° with a distinctly larger separation of the copper atoms (606 pm). Thus, it is reasonable to assume that the different

conformations are mostly due to the presence (Ag and Au) or absence of metallophilic interactions (Cu).

A comparison of the structural parameters of the Me₂Si(N–C₆H₄–2–SPh)₂ unit in compound **1** with related compounds reveals no larger differences. The Si–N bond length of 173.2(2) pm fits well to the usually observed range, e.g. [M₂Me₂Si(N–C₆H₄–2–SPh)₂(PMe₃)₂] (M = Ag 171.2(4)–173.3(4) pm, M = Au 173(1)–175(1) pm),^[6] [NiMe₂Si(N–C₆H₄–2–SPh)₂] (170.9(1) pm).^[7] The N–Si–N angle (114.2(1)°) is the largest that has been observed so far in a series of complexes with thioether-functionalized silylamides [R₂Si(N–C₆H₄–2–SR')₂]^{2–}. Generally, it was observed that [R₂Si(N–C₆H₄–2–SR')₂]^{2–} ligands exhibit quite flexible SiN₂ units. In the parent aminosilane Me₂Si(NH–C₆H₄–2–SPh)₂, the N–Si–N angle is 110.5(1)° and a much smaller angle (89.6(1)°) was observed in [NiMe₂Si(N–C₆H₄–2–SPh)₂] where the Me₂Si(N–C₆H₄–2–SPh)₂^{2–} ligands adopts a κ-N,N',S,S' tetradentate chelating mode.^[7] The large N–S₁N angle observed in the copper complex **1** is most probably due to steric crowding.

The crystal structure of compound **2** (Figure 2) consists of well separated [Cu(PMe₃)₄]⁺ cations and [Cu₅{Me₂Si(N–C₆H₄–2–SMe)(N–C₆H₄–2–S)}₂][–] anions without unusual short intermolecular contacts. The copper atom of the [Cu(PMe₃)₄]⁺ cation resides on a crystallographic C₂ axis. The coordination around copper is nearly tetrahedral with Cu–P bond lengths in a range of 227.0(1)–228.4(1) pm and P–Cu–P angles between 105.7(1) and 115.0(1)°. Similar values have been observed in other crystal structures containing the [Cu(PMe₃)₄]⁺ cation. The CSD data-

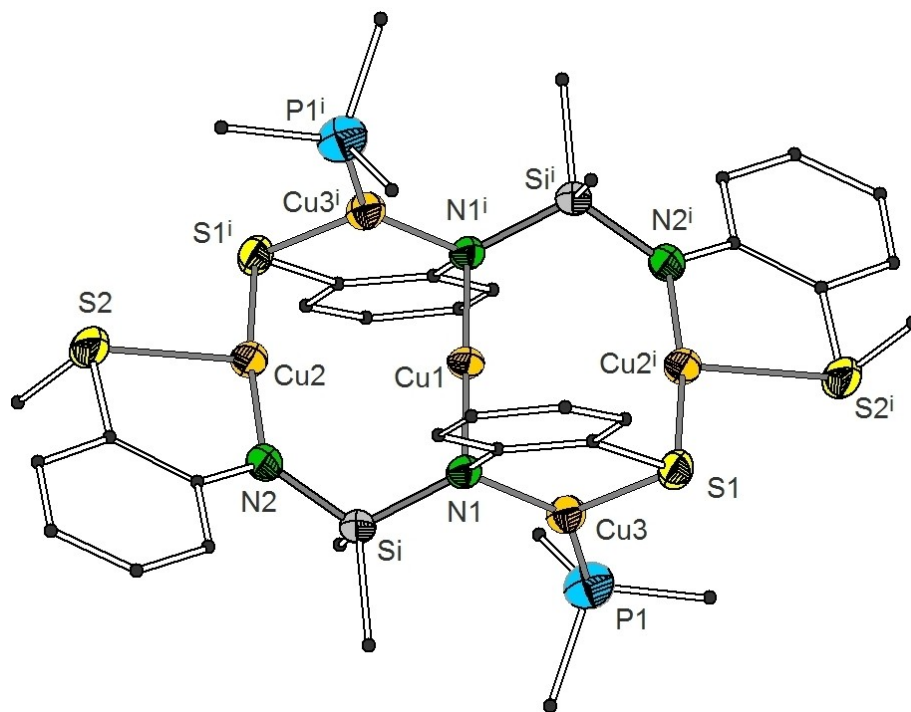


Figure 2. Molecular structure of compound **2** in the crystal. Thermal ellipsoids for Cu, Si, S, P and N with 50% probability (for clarity C atoms are drawn as spheres with arbitrary radius and H atoms are omitted). Selected bond lengths/pm and angles/°: Cu(1)–N(1) 191.2(2), Cu(2)–N(2) 192.1(2), Cu(2)–S(2) 248.3(1), Cu(2)–S(1)ⁱ 219.0(1), Cu(3)–N(1) 201.7(2), Cu(3)–S(1) 228.4(1), Cu(3)–P(1) 217.2(1), Si–N(1) 175.0(2), Si–N(2) 172.0(2), N(1)–Cu(1)–N(1)ⁱ 180.0, N(2)–Cu(2)–S(1)ⁱ 167.8(1), N(2)–Cu(2)–S(2) 86.1(1), S(2)–Cu(2)–S(1)ⁱ 105.1(1), N(1)–Cu(3)–P(1) 141.7(1), N(1)–Cu(3)–S(1) 91.0(1), P(1)–Cu(3)–S(1) 127.0(1), N(1)–Si–N(2) 113.9(1).

base comprises 25 entries with $[\text{Cu}(\text{PMe}_3)_4]^+$ cations. The Cu–P separations are ranging from 223.2 to 230.8 pm with a median value of 226.8 pm (113 data). The $[\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})(\text{N}-\text{C}_6\text{H}_4-2-\text{S})\}_2]^-$ anion is formally composed of five Cu^+ cations and two $\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})(\text{N}-\text{C}_6\text{H}_4-2-\text{S})\}^{3-}$ ligands. The $[\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})(\text{N}-\text{C}_6\text{H}_4-2-\text{S})\}_2]^-$ anion exhibits crystallographically imposed $\bar{1}$ symmetry with the copper atom Cu1 residing on the center of inversion. Cu1 is linearly coordinated by two amide nitrogen atoms (N1 and N1¹) of two adjoining $\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})(\text{N}-\text{C}_6\text{H}_4-2-\text{S})\}^{3-}$ ligands (Cu–N: 191.2(2) pm). In the case of Cu2, the silylamide unit is coordinated by the amide nitrogen atom (Cu–N: 192.1(2) pm) and the sulfur atom S2 of the thioether group (Cu–S: 248.3(1) pm). Additionally, Cu2 is linked to the sulfur atom S1¹ of the neighboring silylamide ligand (Cu–S: 219.0(1) pm). The coordination mode of Cu2 is best described as “2+1” coordination based on a nearly linear N2–Cu–S1¹(thiolate) unit (N–Cu–S: 167.8(1)°) with a strong Cu–S(thiolate) bond and a weakly interacting SMe group. In the case of Cu3, the amide nitrogen N1 (Cu–N: 201.7(2) pm) and the thiolate sulfur atom S1 (Cu–S: 228.4(1) pm) are attached in a chelating manner. Additionally, Cu3 is linked to a PMe_3 group (Cu–P: 217.2(1) pm). This leads to an essentially planar coordination around Cu3 with a rather small N–Cu–S angle (91.0(1)°) as part of the NC_2SCu five-membered chelate ring and two larger N–Cu–P (141.7(1)°) and S–Cu–P angles (127.0(1)°). The sum of the bond angles around Cu3 is 359.7°.

Conclusions

The dianionic silylamide $\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2\text{SPh})_2^{2-}$ is a suitable ligand for the formation of dinuclear Cu(I) complexes. Like in the case of related Ag(I) and Au(I) complexes, the presence of PMe_3 ligands improves the thermal stability of the products. The main structural difference between the formally analogous complexes $[\text{M}_2(\text{PMe}_3)_2\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2\text{SPh})_2]$ (M=Cu, Ag, Au) arises from a conformational change of the $\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2\text{SPh})_2$ unit which shifts the Cu atoms to a large spatial separation. In the Ag and Au derivatives, the metal atoms are approaching much closer due to metallophilic interactions. The accidental formation of the tetranuclear Cu(I) compound **2** clearly reveals that the presence of thiolate functionalities extends the coordination capabilities of silylamide ligands. However, for future systematic investigations on this type of hybrid silylamide-thiolate ligands, a straightforward synthesis route will be required.

Experimental

General

All operations were performed under an argon atmosphere using standard Schlenk techniques. THF and toluene were distilled from sodium/benzophenone, *n*-pentane and *n*-hexane from lithium alanate and THF- D_8 from a sodium/potassium alloy under argon. The aminosilanes $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SR})_2$ (R=Ph, Me) were prepared

according to previously reported methods.^[5,6] Solution ^1H , ^{13}C , ^{29}Si , ^{31}P , and ^{63}Cu NMR spectra were recorded on a VARIAN Inova 500 (500 MHz) spectrometer. COSY and HSQC experiments were carried out for the unambiguous assignment of the ^1H and ^{13}C NMR signals. The ^{63}Cu NMR shifts are referenced vs. $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ in MeCN ($\delta_{\text{Cu}}=0$ ppm).^[11] The IR spectra were measured with a BRUKER Tensor 27 spectrometer equipped with a diamond ATR unit. Due to the low thermal stability and the enhanced air and moisture sensitivity of the compounds **1** and **2**, elemental analyses were not suitable. The copper content was determined photometrically as $[\text{Cu}(\text{NH}_3)_4]^{2+}$.^[17]

General procedure for the synthesis of the copper complexes **1** and **2**

A suspension of 0.5 g CuCl (5.0 mmol) in 5 ml of THF is treated with the appropriate amount of PMe_3 (0.53 ml, 5.0 mmol) and stirred for 2 h at 60 °C. After cooling down to –70 °C a solution of 2.5 mmol $\text{Li}_2[\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-\text{SR})_2]$ (R=Ph, compound **1**; Me, compound **2**) prepared from $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-\text{SR})_2$ and *n*-BuLi in 10 ml of THF is added. The reaction mixture is slowly warmed up to room temperature and stirred for two hours. Afterwards THF is removed in vacuo and the residue is treated with 15 ml of toluene. The insoluble material is then removed by filtration and the filtrate is layered with *n*-hexane. Within several days the products were precipitated in the form of bright yellow (compounds **1**) and pale yellow crystals (compound **2**).

$[\text{Cu}_2\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SPh})_2\}(\text{PMe}_3)_2]$ (**1**)

Yield: 1.14 g (62%), $\text{C}_{32}\text{H}_{42}\text{Cu}_2\text{N}_2\text{P}_2\text{S}_2$; $M=735.96$ g/mol

Analysis: Cu 16.8% (17.3 calc.)

IR: 3061(w), 3039(w), 3028(w), 2970(w), 2959(w), 2935(w), 2906(w), 2887(w), 2809(w), 2575(w), 1576(s), 1532(w), 1497(w), 1474(m), 1450(s), 1429(s), 1382(w), 1313(s), 1285(m), 1276(w), 1262(s), 1239(s), 1182(w), 1162(m), 1125(w), 1081(w), 1071(w), 1048(w), 1025(m), 955(s), 946(m), 925(s), 919(s), 841(w), 822(s), 781(s), 742(s), 733(s), 690(s), 676(w), 662(s), 614(m), 549(w), 501(m), 464(s), 437(m), 408(w), 368(m), 357(m), 335(s), 306(m), 289(m), 270(m).

^1H -NMR (THF- D_8): δ 0.36 (s + d, $|^2J_{\text{H,Si}}|=6.2$ Hz, 6H; SiCH_3), 1.04 (d, $|^2J_{\text{H,P}}|=6.9$ Hz, 6H; PCH_3), 6.11 (m, 2H; 4-CH), 6.82 (m, 2H; 5-CH), 7.07 (m, 2H; *p*-CH), 7.16 (m, 4H; *m*-CH), 7.19 (m, 4H; *o*-CH), 7.23 (m, 2H; 3-CH), 7.33 (m, 2H; 6-CH).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (THF- D_8): δ 4.5 (s; SiCH_3), 15.4 (d, $|^1J_{\text{C,P}}|=23.4$ Hz; PCH_3), 112.4 (s; 4-CH), 118.3 (s; phenylene-CS), 121.9 (s; 6-CH), 126.0 (s; *p*-CH), 127.9 (s; *m*-CH), 129.5 (s; *o*-CH), 131.2 (s; 5-CH), 137.0 (s; 3-CH), 138.3 (s; phenyl-CS), 163.9 (s; CN).

$^{29}\text{Si}\{^1\text{H}\}$ -NMR (THF- D_8): δ –15.1 (s).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (THF- D_8): δ –43.0 (s br).

$[\text{Cu}(\text{PMe}_3)_4][\text{Cu}_5\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-\text{S})(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})\}_2(\text{PMe}_3)_2]$ (**2**)

Yield: 0.17 g (9%) $\text{C}_{48}\text{H}_{88}\text{Cu}_6\text{N}_4\text{P}_6\text{S}_4\text{Si}_2$; $M=1472.81$ g/mol.

Analysis: Cu 26.2% (25.9 calc.)

IR: 3036(w), 2962(m), 2929(w), 2916(w), 2899(m), 2807(w), 1572(s), 1532(w), 1453(s), 1446(s), 1422(s), 1320(s), 1301(m), 1283(s), 1267(m), 1235(s), 1208(s), 1153(m), 1124(m), 1056(w), 1034(m), 934(s), 902(s), 854(w), 839(w), 807(s), 786(s), 744(s), 725(s), 700(w), 670(m), 652(m), 615(w), 608(w), 578(w), 547(w), 512(w), 471(w).

455(m), 426(w), 411(w), 362(w), 352(m), 329(m), 300(w), 284(m), 266(m).

$^1\text{H-NMR}$ (THF- D_6): δ 0.03 (s br, 12H; SiCH_3), 1.05 (d, $|^2J_{\text{H,P}}| = 6.4$ Hz, 18H; PCH_3 , anion), 1.26 (s br, 36H; PCH_3 , cation), 2.40 (s, 6H; SCH_3), 6.06 (m, 2H; 4-CH N-phenylene-S), 6.37 (m, 2H; 4-CH N-phenylene-SMe), 6.58 (m, 2H; 5-CH N-phenylene-S), 6.76 (m, 2H; 5-CH N-phenylene-SMe), 6.77 (m, 2H; 6-CH N-phenylene-SMe), 7.28 (m, 2H; 3-CH N-phenylene-SMe), 7.53 (m, 2H; 3-CH N-phenylene-S), 7.79 (m, 2H; 6-CH N-phenylene-S).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (THF- D_6): δ 2.5 (s; SiCH_3), 16.9 (d, $|^1J_{\text{C,P}}| = 21.3$ Hz; PCH_3 , anion), 17.5 (s br; PCH_3 , cation), 21.2 (s; SCH_3), 111.1 (s; 4-CH N-phenylene-S), 117.2 (s; 4-CH N-phenylene-SMe), 120.7 (s; 6-CH N-phenylene-SMe), 123.0 (s; CS N-phenylene-SMe), 123.6 (s; 5-CH N-phenylene-S), 123.9 (s; 6-CH N-phenylene-S), 129.2 (s; 5-CH N-phenylene-SMe), 132.9 (s; 3-CH N-phenylene-S), 135.1 (s; 3-CH N-phenylene-SMe), 160.5 (s; CN N-phenylene-SMe).

$^{29}\text{Si}\{^1\text{H}\}$ -NMR (THF- D_6): δ -17.7 (s).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (THF- D_6): δ -40.5 (quartet; $|^1J_{\text{P,Cu}}| = 790$ Hz; $[\text{Cu}(\text{PMe}_3)_4]^+$), -43.3 (s; PMe_3 , anion).

$^{63}\text{Cu}\{^1\text{H}\}$ -NMR (THF- D_8): δ 279 (quintet; $|^1J_{\text{P,Cu}}| = 763$ Hz; $[\text{Cu}(\text{PMe}_3)_4]^+$).

CCDC 2120057 and 2120058 contain the supplementary crystallographic data for compounds 1 and 2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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