[6] Yield: 59 %. UV/Vis (CH_2Cl_2) $\lambda_{max} = 361, 618, 679$ nm; FAB MS: m/z 725.5 $[M-Cl]^+$, calcd for $C_{34}H_{42}N_{10}SeMn$: m/z 725.2.

[7] Yield: 41 %. UV/Vis (CH_2Cl_2) $\lambda_{max} = 344, 381, 656, 694$ nm; atmospheric pressure CI-MS: m/z 1066.5 $[M+H]^+$, 1030.5 $[M-Cl]^+$; calcd $C_{56}H_{69}N_{10}O_2MnCuCl$: m/z 1066.4, calcd $C_{56}H_{68}N_{10}O_2MnCu$: m/z 1030.4; elemental analysis calcd for $C_{56}H_{71}N_{10}O_3MnCuCl$ (**1**+H_2O): C 61.98, H 6.50, N 12.91; found: C 62.01, H 6.27, N 13.12.

[8] Crystal data for **1**, $C_{59}H_{73}Cl_3CuMnN_{11}O_2$: triclinic, space group $P\bar{1}$, $a = 13.009(3)$, $b = 14.273(4)$, $c = 17.856(6)$ Å, $\alpha = 104.66(2)$, $\beta = 104.964(16)$, $\gamma = 104.781(14)°$, $V = 2910.9(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.358$ Mg m^{-3}, final $R1$ value of 0.0581 and wR_2 value of 0.1363 were based on 13690 independent reflections ($I > 2\sigma(I)$) out of 27297 reflections collected and 678 variable parameters. The data collection were performed at 153 K on a Bruker SMART-1000 CCD area detector, by using graphite monochromated Mo_K radiation ($\lambda = 0.71073$ Å), by the ϕ and ω-scan mode, within the limits $1.57 < \theta < 28.84°$. The linear absorption coefficient μ is 0.770 mm^{-1}. An integration absorption correction was applied. Minimum and maximum transmission factors were 0.8337 and 0.9801, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-97), expanded by using Fourier techniques (SHELXS-97), and refined by full-matrix least-squares on F^2. The non-hydrogen atoms were refined anisotropically except those on the disordered C33 methyl group. Hydrogen atoms were included in idealized positions, except those on the disorder carbon atoms, but not refined. The program Squeeze (A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C-34) was used to take out 84 electrons which correspond to the dichloromethane molecule. This solvent was refined as a diffuse contribution without specific atom positions, but the density and absorption coefficient reflect the full formula. All calculations were performed using the Bruker SHELXTL crystallographic software package. CCDC-190473 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Cu and Ag Silanethiolato Complexes

Copper and Silver Complexes Containing the $S(SiMe_2S)_2{}^{2-}$ Ligand: Efficient Entries into Heterometallic Sulfido Clusters

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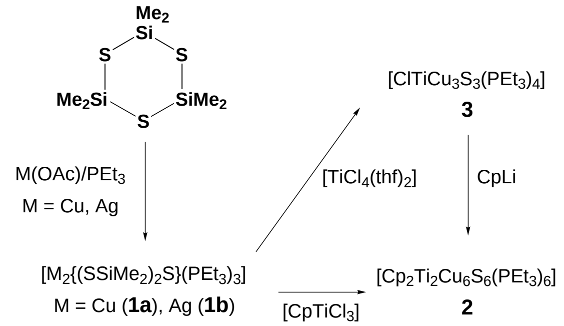
Hiroyuki Kawaguchi, and Kazuyuki Tatsumi*

The development of synthetic routes to mixed-metal sulfido clusters is a critical prerequisite to study these important materials.[1] It is well known that $(Me_3Si)_2S$ is a good sulfur-transfer reagent, and can replace a halide, alkoxide, acetate, or oxide with a sulfido ligand through the formation of energetically favorable Si–Cl or Si–O bonds.[2] Therefore, the corresponding $M{-}SSiMe_3$ species have the potential to be synthetic precursors of sulfido clusters.[3,4] However, because of the high lability of Si–S bond, there is a tendency to restrict the use of silanethiolato complexes. Thus, the stabilization of these complexes is required if they are to be used in the development of cluster syntheses. Cyclotrisilathiane has received less attention than $(Me_3Si)_2S$ for use in preparations of sulfido clusters.[5] In exploring of the utility of this reagent, we discovered the formation of thermally stable copper and silver complexes containing the intriguing $S(SiMe_2S)_2{}^{2-}$ ligand. Herein we report the synthesis of these complexes, and their reactions with titanium–chloride complexes.

Treatment of Cu(OAc) with cyclotrisilathiane in the presence of PEt_3 at room temperature generated $[Cu_2\{(SSiMe_2)_2S\}(PEt_3)_3]$ (**1a**) as colorless crystals in 74 % yield (Scheme 1). The silver congener **1b** was obtained as colorless



Scheme 1. Synthesis of **1** and reactions with titanium chloride complexes to give **2** and **3**.

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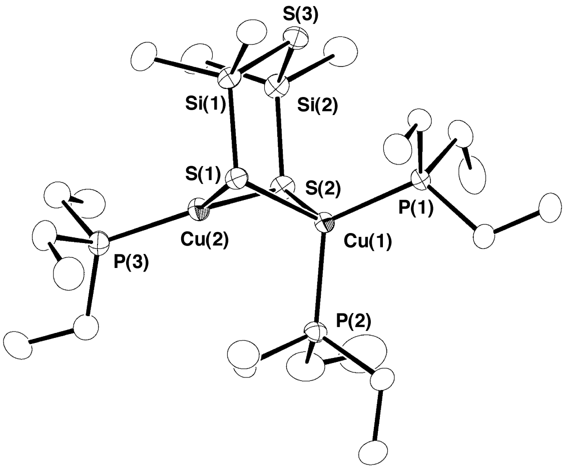

Figure 1. Molecular structure of **1a**. Selected interatomic distances [Å] and angles [°]: Cu(1)-Cu(2) 2.715(1), Cu(1)-S(1) 2.440(1), Cu(1)-S(2) 2.480(1), Cu(2)-S(1) 2.339(1), Cu(2)-S(2) 2.305(1), Cu(1)-P(1) 2.258(1), Cu(1)-P(2) 2.266(1), Cu(2)-P(3) 2.209(1), S(1)-Si(1) 2.099(1), S(2)-Si(2) 2.102(1), S(3)-Si(1) 2.161(1), S(3)-Si(2) 2.163(1); S(1)-Cu(1)-S(2) 97.45(4), S(1)-Cu(2)-S(2) 105.56(3), Cu(1)-S(1)-Cu(2) 69.21(3), Cu(1)-S(2)-Cu(2) 69.05(2), P(1)-Cu(1)-P(2) 118.46(3).

crystals in 75% yield from the analogous reaction. The X-ray study revealed that **1a** is a bicyclic structure (Figure 1).[6] The silanedithiolato ligand bridges two Cu atoms, one of which is three-coordinate and the other four-coordinate. Because of these different coordination geometries, the average Cu(1)–S bond length (2.460 Å) is elongated relative to the average Cu(2)–S bond length (2.322 Å). The S(3) atom is oriented toward the tetrahedral Cu(1) center to avoid steric crowding. The Cu_2S_2 quadrilateral is folded, the dihedral angle between the two CuS_2 planes is 127.4°, and the two Cu atoms are separated by 2.715(1) Å. The thioether-like S(3)–Si(1) and S(3)–Si(2) bonds are about 0.06 Å longer than the thiolato S(1)–Si(1) and S(2)–Si(2) bonds, which may be attributed to the hyperconjugative interaction between the occupied p orbital of the S_{thiolato} atom and the vacant antibonding σ^* (Si–$S_{\text{thioether-like}}$) orbital. Although the solid-state molecular structure of **1a** is unsymmetrical, the resonance signal from the methyl protons of the silanedithiolato ligand appears as a sharp singlet in the ^{1}H NMR spectrum at room temperature, which indicates that the structure is fluxional in solution by means of dynamic processes involving a rapid ring inversion of the $Cu_2(SSiMe_2)_2S$ core and a fast exchange of the PEt_3 ligands between two Cu centers. In the $^{29}Si\{^1H\}$ NMR spectrum, the resonance signal arising from the $S(SiMe_2S)_2{}^{2-}$ ligand shifts upfield considerably, relative to the starting silyl sulfide ($\delta = 21.4$ ppm).

The stability of **1a** deserves comment. The related complex $[Cu(SSiMe_3)(PEt_3)_3]$ is unstable in solution above 0 °C resulting in formation of sulfidocopper clusters.[3a] In contrast, **1a** did not show any signs of decomposition in C_6D_6 at room temperature over two days when monitored by ^{1}H NMR spectroscopy. However, **1a** reacts with metal halides under mild conditions to afford mixed-metal clusters in high yields. For example, the addition of 0.5 equivalents of $[CpTiCl_3]$ to **1a** in toluene at −50 °C gave a dark red solution, from which we isolated $[Cp_2Ti_2Cu_6S_6(PEt_3)_6]$ (**2**) as dark red crystals after suitable workup (Scheme 1). Analogously, the reaction of **1a** with 0.5 equivalents of $[TiCl_4(thf)_2]$ afforded $[ClTiCu_3S_3(PEt_3)_4]$ (**3**) as yellow crystals. Both compounds are diamagnetic, and the elemental analyses were in agreement with the structures elucidated by X-ray crystallography.

In the molecular structure of **2**, the centrosymmetric octanuclear core is a distorted Ti_2Cu_6 cube with a μ_4-S^{2-} ligand occupying the position above the center of each of the six faces (Figure 2).[6] Two Cp and six PEt_3 ligands also coordinate to the titanium and the copper sites, respectively. All Cu atoms assume a tetrahedral geometry. Alternatively, the core structure can be viewed as a $[Cu_6S_6(PEt_3)_6]^{6-}$ prismane, which is capped at each of the two Cu_3S_3 hexagonal chairs by $[CpTi^{3+}]$ units. The cluster core of **2** is structurally analogous to the dodecahedral skeletons found in $[Co_8S_6(SPh)_8]^{4-}$,[7] $[Fe_8S_6I_8]^{3-}$,[8] and $[Fe_6S_6X_6\{M(CO)_3\}_2]^{n-}$ (X = Cl, Br, I; M = Mo, W; $n = 3$, 4).[9] The Cu–S bond lengths and the Cu–Cu distances fall within the ranges that are typical for sulfido-bridged copper(I) clusters.[10] The average Cu–Ti distance of 2.869 Å suggests the existence of a dative bond between the d^{10} Cu atom and the d^0 Ti atom.[11]

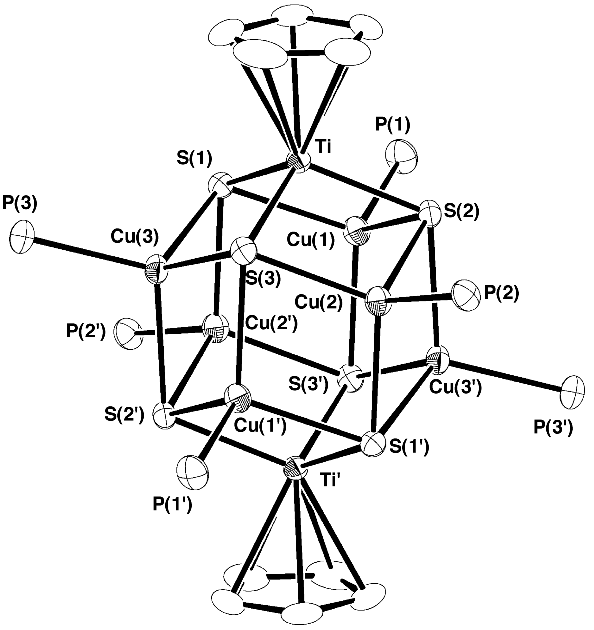

Figure 2. Molecular structure of **2**; ethyl groups of phosphane ligands have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cu-Cu 2.743(1)–2.769(1), Cu-Ti 2.865(1)–2.876(2), Cu-S 2.328(1)–2.442(2), Ti-S 2.310(2)–2.314(2), Cu-P 2.253(2)–2.260(2); S-Ti-S 104.74(5)–105.06(5), S-Cu-S 102.49(7)–110.13(5).

The molecular structure of **3** (Figure 3) consists of a tetranuclear $TiCu_3S_3$ core analogous to half of the octanuclear core found in **2**, and a crystallographic mirror plane passes through the molecule.[6] One Cl atom bound to a Ti center remains after completion of the cluster forming reaction. There are two different copper coordination environments in **3**. As expected, the Cu–Ti distances, and the Cu–S, and Cu–P bond lengths of the Cu(1) and Cu(1′) atoms in the trigonal-

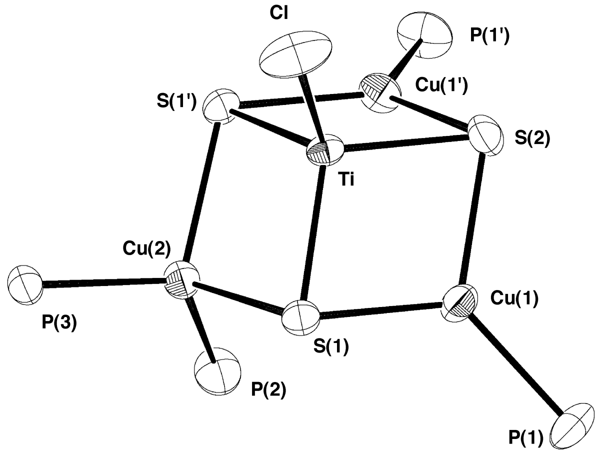

Figure 3. Molecular structure of **3**; ethyl groups of phosphane ligands have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cu(1)-Ti 2.702(1), Cu(2)-Ti 2.863(2), Cu(1)-S(1) 2.243(1), Cu(1)-S(2) 2.256(1), Cu(2)-S(1) 2.360(1), Ti-S(1) 2.252(1), Ti-S(2) 2.263(2), Cu(1)-P(1) 2.202(1), Cu(2)-P(2) 2.248(2), Cu(2)-P(3) 2.266(2), Ti-Cl 2.288(2); S(1)-Cu(1)-S(2) 106.59(6), S(1)-Cu(2)-S(1') 99.83(6), S(1)-Ti-S(2) 106.05(5), S(1)-Ti-S(1') 106.64(7), P(1)-Cu(1)-S(1) 126.65(5), P(1)-Cu(1)-S(2) 126.51(6), P(2)-Cu(2)-P(3) 121.11(7).

planar coordination environments are shorter than the corresponding distances of the tetrahedrally coordinated Cu(2) atom. Although **3** is stable in solution, addition of one equivalent of CpLi to solution of **3** in THF resulted in the formation of **2** concomitant with a small amount of unidentified copper compounds. This result implies that the steric and electronic properties of the ligand bound to the Ti atom are related to the observed cluster sizes and shapes.

In conclusion, we have described new dimetallic silanedithiolato complexes of copper and silver that are stable in solution at room temperature and react readily with titanium–chloride complexes under mild conditions to afford mixed-metal sulfido clusters. We are extending our work to prepare other silanethiolato complexes by using cyclotrisilathiane, and to study their potential utility in the synthesis of ternary clusters .

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques, all solvents were dried, and deoxygenated before use.

1a: A solution of $(Me_2SiS)_3$ (0.92 g, 3.4 mmol) in hexane (2.3 mL) was added to a solution of Cu(OAc) (0.69 g, 5.6 mmol) and PEt_3 (7.8 mL, 11 mmol: 1.41 M toluene solution) in Et_2O (20 mL), which gave a yellow solution. After the mixture had been stirred for 3 h at room temperature, the solvent was removed in vacuo. Recrystallization from hexane afforded **1a** as colorless crystals (1.44 g, 74%). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.36$ (dq, 18H; PCH_2CH_3), 1.03 (dt, 27H; PCH_2CH_3), 0.96 ppm (s, 12H; $SiMe_2$); $^{31}P\{^1H\}$ NMR (202.35 MHz, C_6D_6): $\delta = -14.6$ ppm (br, $\Delta\nu_{1/2} = 48$ Hz); $^{29}Si\{^1H\}$ NMR (99.25 MHz, C_6D_6): $\delta = 16.0$ ppm (s); elemental analysis calcd (%) for $C_{22}H_{57}Cu_2P_3S_3Si_2$: C 38.07, H 8.28, S 13.86; found: C 37.69, H 8.42, S 13.15. **1b**: ^{1}H NMR (C_6D_6): $\delta = 1.21$ (dq, 18H; PCH_2CH_3), 1.06 (s, 12H; $SiMe_2$), 0.97 ppm (dt, 27H; PCH_2CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -5.2$ ppm (br, $\Delta\nu_{1/2} = 110$ Hz); elemental analysis calcd (%) for $C_{22}H_{57}Ag_2P_3S_3Si_2$: C 33.76, H 7.34, S 12.29; found: C 33.28, H 7.42, S 12.07.

2: A solution of $[CpTiCl_3]$ (0.10 g, 0.46 mmol) in toluene (10 mL) was added to a solution of **1a** (0.64 g, 0.92 mmol) in toluene (10 mL) at −50 °C. The resulting dark red mixture was stirred overnight at room temperature. This solution was concentrated to a small volume, then hexane was added. Cooling the solution to −30 °C gave a brown polycrystalline solid of **2** (0.29 g, 84% based on Ti). ^{1}H NMR ($CDCl_3$): $\delta = 5.96$ (s, 10H; C_5H_5), 1.54 (dq, 36H; PCH_2CH_3), 1.08 ppm (dt, 54H; PCH_2CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.7$ ppm (br, $\Delta\nu_{1/2} = 94$ Hz); elemental analysis calcd (%) for $C_{46}H_{100}Cu_6P_6S_6Ti_2$: C 36.62, H 6.68, S 12.75; found: C 36.56, H 6.72, S, 12.81.

3: A solution of **1a** (0.42 g, 0.60 mmol) in toluene (4.5 mL) was added to a solution of $[TiCl_4(thf)_2]$ (0.10 g, 0.30 mmol) in toluene (15 mL) at −50 °C. Workup similar to that used for **2** yielded **3** as a yellow powder (0.21 g, 83% based on Ti). ^{1}H NMR ($CDCl_3$): $\delta = 1.56$ (m, 24H; PCH_2CH_3), 1.09 ppm (dt, 36H; PCH_2CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -3.1$ ppm (br, $\Delta\nu_{1/2} = 1100$ Hz); elemental analysis calcd (%) for $C_{24}H_{60}ClCu_3P_4S_3Ti$: C 34.20, H 7.18, S 11.41; found: C 34.10, H 7.17, S 10.95.

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[6] Crystal data for **1a**: $C_{22}H_{57}S_3P_3Si_2Cu_2$ ($M_r = 694.06$); $P2_1/c$ (no. 14), $a = 15.985(5)$, $b = 11.309(3)$, $c = 19.712(5)$ Å, $\beta = 96.792(4)°$, $V = 3538.5(17)$ Å^3, $\rho_{calcd} = 1.303$ g cm^{-3}, $Z = 4$, $\mu = 15.93$ cm^{-1}, 27340 measured, 7840 unique, 346 variables, GOF = 1.05, $R1 = 0.035$ ($I > 2\sigma(I)$), $wR_2 = 0.088$ (all unique reflections). For **2**: $C_{46}H_{100}S_6P_6Ti_2Cu_6 \cdot C_6H_{14}$ ($M_r = 1594.75$); $P2_1/n$ (no. 14), $a = 12.450(7)$, $b = 14.061(8)$, $c = 20.683(12)$ Å, $\beta = 92.557(7)°$, $V = 3617.1(35)$ Å^3, $\rho_{calcd} = 1.464$ g cm^{-3}, $Z = 2$, $\mu = 22.74$ cm^{-1}, 28735 measured, 8211 unique, 327 variables, GOF = 1.00, $R1 = 0.047$, $wR_2 = 0.120$. For **3**: $C_{24}H_{60}S_3P_4ClTiCu_3$ ($M_r = 842.80$); $Pnma$ (no. 62), $a = 20.772(8)$, $b = 16.653(6)$, $c = 11.356(4)$ Å, $V = 3928.1(25)$ Å^3, $d_{calc} = 1.425$ g cm^{-3}, $Z = 4$, $\mu = 22.02$ cm^{-1}, 31867 measured, 4651 unique, 199 variables, GOF = 1.03, $R1 = 0.043$, $wR_2 = 0.122$. Diffraction data of **1a, 2**, and **3** were collected at −100 °C on a Rigaku Mercury CCD diffractometer ($Mo_{K\alpha}$ radiation). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the CrystalStructure software package. All non-hydrogen atoms

were refined anisotropically, and hydrogen atoms were located at calculated positions. Ethyl groups of the phosphane ligands in **2** and **3** were partly disordered, and their carbon atoms were refined isotropically. CCDC-194040 (**1a**), CCDC-194041 (**2**) and CCDC-194042 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

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