

Coordination Chemistry of Silanedithiolato Ligands Derived from Cyclotrisilathiane: Synthesis and Structures of Complexes of Iron(II), Cobalt(II), Palladium(II), Copper(I), and Silver(I)

Takashi Komuro,[†] Tsukasa Matsuo,[‡] Hiroyuki Kawaguchi,^{*‡} and Kazuyuki Tatsumi[†]

Research Center for Materials Science and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan, and Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

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The coordination chemistry of chelating silanedithiolato ligands has been investigated on Fe(II), Co(II), Pd(II), Cu(I), and Ag(I). Treatment of $M(\text{OAc})_2$ ($M = \text{Fe}, \text{Co}, \text{Pd}$) with cyclotrisilathiane (SSiMe_2)₃ in the presence of Lewis bases resulted in formation of $\text{Fe}(\text{S}_2\text{SiMe}_2)(\text{PMDETA})$ (**1**), $\text{Fe}(\text{S}_2\text{SiMe}_2)(\text{Me}_3\text{TACN})$ (**2**), $\text{Co}(\text{S}_2\text{SiMe}_2)(\text{PMDETA})$ (**3**), and $\text{Pd}(\text{S}_2\text{SiMe}_2)(\text{PEt}_3)_2$ (**4**) ($\text{PMDETA} = N,N,N',N',N'$ -pentamethyldiethylenetriamine; $\text{Me}_3\text{TACN} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane). The analogous reactions of $M(\text{OAc})$ ($M = \text{Cu}, \text{Ag}$) in the presence of PEt_3 gave rise to the dinuclear complexes $M_2\{(\text{SSiMe}_2)_2\text{S}\}(\text{PEt}_3)_3$ [$M = \text{Cu}$ (**5**), Ag (**6**)]. Complexes were characterized in solution by ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR and in the solid state by single-crystal X-ray diffraction. Mononuclear complexes **1–3** have a four-membered MS_2Si ring, and these five-coordinate complexes adopt trigonal-bipyramidal (for the PMDETA adducts) or square-pyramidal (for the Me_3TACN adduct) geometries. In dimer **6**, the $(\text{SSiMe}_2)_2\text{S}^{2-}$ silanedithiolato ligand bridges two metal centers, one of which is three-coordinate and the other four-coordinate. The chelating effect of silanedithiolato ligands leads to an increase in the stability of silylated thiolato complexes.

Introduction

Although transition-metal compounds involving silanethiolato ligands are relatively rare compared to alkylthiolato and arylthiolato complexes,^{1–4} recent studies have shown they

serve as potential precursors to mixed-metal sulfido clusters.^{5–7} These cluster-forming reactions are driven by the formation of energetically favorable Si–X bonds ($X = \text{halide}, \text{oxygen}, \text{etc.}$) and the delivery of the M–S^- moiety to transition-metal centers. This synthetic method is very attractive in exploring heterometallic clusters. However, due to the high lability of the silicon–sulfur bond, the silanethiolato complexes are known to undergo facile hydrolysis

* Author to whom correspondence should be addressed. E-mail: hkawa@ims.ac.jp. Fax: +81-564-55-5245.

[†] Nagoya University.

[‡] Institute for Molecular Science.

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and/or thermal degradation, which would restrict the use of silanethiolato complexes in cluster chemistry. To fully realize the potential of silanethiolato complexes in developing a methodology for the synthesis of heterometallic clusters, the stabilization of silanethiolato complexes is required.

In this context, we previously reported the synthesis and structures of a series of triphenylsilanethiolato complexes $M(\text{SSiPh}_3)_2(\text{TMEDA})$ ($M = \text{Mn, Fe, Co, Ni}$; $\text{TMEDA} = N,N,N',N'$ -tetramethylethylenediamine), $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$ ($\text{L} = \text{CH}_3\text{CN, 4-}^t\text{BuC}_5\text{H}_4\text{N, PET}_3$), and $\text{Cu}_4(\text{SSiPh}_3)_4$.⁸ The use of the bulky triphenylsilanethiolato ligand offers the advantage that a range of transition-metal derivatives can be isolated, while the use of this bulky ligand does pose a significant limitation with regard to metal sulfido clusters that can be targeted. For example, treatment of $\text{Fe}(\text{SSiPh}_3)_2(\text{CH}_3\text{CN})_2$ with $(\text{NEt}_4)_2[\text{FeCl}_4]$ resulted in formation of $(\text{NEt}_4)_2[\text{Fe}_2(\text{SSiPh}_3)_2\text{Cl}_4]$, where the ligand transfer was preferred to silicon–sulfur bond cleavage.

Herein, we have chosen to stabilize silanethiolato complexes by the chelating effect of the ligands. The chelating effect in coordination chemistry has most pronounced kinetic and thermodynamic consequences. This strategy could suppress the undesired degradation process of silanethiolato complexes via aggregation and/or ligand redistribution, while we found that chelating silanedithiolato complexes readily reacted with metal halides and acetates under mild conditions to produce mixed-metal sulfido clusters.^{9,10} Here, we describe the detailed synthesis and structures of chelating silanedithiolato complexes of iron(II), cobalt(II), palladium(II), copper(I), and silver(I). In this paper, our aim is to demonstrate the versatility of silanedithiolates to act as chelating ligands toward a variety of metals from across the periodic table. Portions of this work were communicated in preliminary reports.^{9,10}

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line techniques. Solvents were dried and distilled over an appropriate drying agent under an atmosphere of dinitrogen. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL Lambda-500 spectrometer (operating frequencies 500.00, 125.65, 202.35, and 99.25 MHz, respectively). Chemical shifts are reported in parts per million.

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Infrared samples were recorded as Nujol mulls or a neat oil between KBr plates using a JASCO FT/IR-410 spectrometer. For UV–vis spectra, a JASCO V-560 spectrometer was used. Elemental analyses were measured using Yanaco MT-6 and MSU-32 microanalyzers. Magnetic susceptibility measurements were carried out at room temperature (296 K) using the Evans detector (Sherwood Scientific MSB-AUTO) and corrected for underlying diamagnetism. $\text{Fe}(\text{OAc})_2$ ¹¹ and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN)¹² were prepared according to published methods. The other metal acetates were purchased [$\text{Cu}(\text{OAc})$ from Tokyo Chemical Industry, $\text{Co}(\text{OAc})_2$, $\text{Pd}(\text{OAc})_2$, and $\text{Ag}(\text{OAc})$ from Kishida Chemical Co.] and dried under vacuum prior to use. N,N,N',N',N'' -Pentamethyldiethylenetriamine (PMDETA) was distilled from CaH_2 .

Synthesis of Hexamethylcyclotrisilathiane [$(\text{Me}_2\text{SiS})_3$]. Sodium chips (4.27 g, 186 mmol), elemental sulfur (S_8) (2.98 g, 11.6 mmol), and naphthalene (1.11 g, 8.66 mmol) were placed in a flask and suspended in 100 mL of THF. After exposure to silent-sonic waves for 15 min, the mixture was refluxed overnight to produce a white solid. The white slurry was cooled to 0 °C, and Me_2SiCl_2 (11.5 mL, 94.8 mmol) was added dropwise with stirring. The mixture was slowly warmed to room temperature and stirred for 10 h. The yellow-white mixture was settled to separate a large amount of the precipitate. The supernatant was then filtered through Celite, and the solid was washed with THF (10 mL \times 2). The washings and the filtrate were combined, and the solvent was removed under vacuum. The brown residue was extracted with hexane (11 mL) and centrifuged. Concentration in vacuo followed by distillation yielded the title compound (6.66 g, 79%) as a light yellow liquid. ^1H NMR (CDCl_3): δ 0.70 (s, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.0 (s, with ^{29}Si satellites, $^1J_{\text{SiC}} = 60$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.4 (s). IR (neat): 2958 (w), 2898 (w), 1400 (w), 1251 (s, δ_{SiC}), 820 (s, ν_{SiC}), 785 (s), 672 (s), 520 (s), 476 (w), 449 (m) cm^{-1} .

Preparation of $\text{Fe}(\text{S}_2\text{SiMe}_2)(\text{PMDETA})$ (1). Treatment of $\text{Fe}(\text{OAc})_2$ (0.09 g, 0.52 mmol) with PMDETA (0.20 mL, 0.96 mmol) in THF (10 mL) at 60 °C gave a pale yellow solution. To the solution was added dropwise $(\text{Me}_2\text{SiS})_3$ (0.40 mL, 0.56 mmol; 1.41 M hexane solution) at –90 °C. The reaction mixture was warmed slowly to –10 °C for 50 min and concentrated in vacuo. Addition of hexane to the dark brown solution afforded a brown-white solid. The crude product was extracted with THF (7 mL), and hexane was layered. Over 10 days, colorless crystals and a black solid were formed. The resulting mixture was washed with hexane. Colorless blocks of **1** (0.075 g, 41%) were separated manually. ^1H NMR (CDCl_3): δ 127.2 ($\Delta\nu_{1/2} = 2300$ Hz, br), 99.3 ($\Delta\nu_{1/2} = 4000$ Hz, br), 74.8 ($\Delta\nu_{1/2} = 1700$ Hz, br), 11.0 ($\Delta\nu_{1/2} = 150$ Hz, br). IR (Nujol): 1303 (m), 1286 (m), 1229 (m, δ_{SiC}), 1173 (w), 1104 (m), 1061 (m), 1048 (m), 1031 (m), 1017 (m), 979 (m), 937 (m), 916 (w), 826 (s, ν_{SiC}), 794 (s), 749 (m), 664 (s), 522 (s), 478 (w), 458 (m) cm^{-1} . $\mu_{\text{eff}}(296 \text{ K}) = 5.2 \mu_{\text{B}}/\text{Fe}$. Anal. Calcd for $\text{C}_{11}\text{H}_{29}\text{FeN}_3\text{S}_2\text{Si}$: C, 37.59; H, 8.32; N, 11.96. Found: C, 37.24; H, 8.13; N, 12.02.

Preparation of $\text{Fe}(\text{S}_2\text{SiMe}_2)(\text{Me}_3\text{TACN})$ (2). $\text{Fe}(\text{OAc})_2$ (0.32 g, 1.8 mmol) was dissolved in 15 mL of hot (60 °C) THF with Me_3TACN (1.8 mL, 2.2 mmol; 1.22 M THF solution) to give a clear colorless solution. The solution was cooled to –80 °C and treated with $(\text{Me}_2\text{SiS})_3$ (1.3 mL, 1.8 mmol; 1.41 M hexane solution). Upon stirring, the reaction mixture was warmed slowly to room

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temperature. The resulting dark purple solution was concentrated and cooled to $-30\text{ }^{\circ}\text{C}$. After decantation and washing with Et_2O ($5\text{ mL} \times 2$), a colorless powder of **2** (0.47 g, 73%) was afforded. Colorless prisms suitable for X-ray analysis were obtained by slow diffusion of hexane into the THF solution of **2**. $^1\text{H NMR}$ (CDCl_3): δ 122.1 ($\Delta\nu_{1/2} = 1600\text{ Hz}$, br), 103.7 ($\Delta\nu_{1/2} = 270\text{ Hz}$, br), 87.7 ($\Delta\nu_{1/2} = 2500\text{ Hz}$, br), 66.0 ($\Delta\nu_{1/2} = 1300\text{ Hz}$, br), 53.8 ($\Delta\nu_{1/2} = 630\text{ Hz}$, br), 44.4 ($\Delta\nu_{1/2} = 1500\text{ Hz}$, br), 0.85 (s). IR (Nujol): 1498 (m), 1297 (m), 1285 (m), 1236 (m, δ_{SiC}), 1226 (m, δ_{SiC}), 1208 (w), 1149 (m), 1122 (w), 1078 (m), 1063 (s), 1011 (s), 986 (m), 894 (w), 829 (s, ν_{SiC}), 788 (s), 748 (m), 667 (s), 577 (w), 524 (s), 461 (m), 434 (m) cm^{-1} . μ_{eff} (296 K) = $5.2\ \mu_{\text{B}}/\text{Fe}$. Anal. Calcd for $\text{C}_{11}\text{H}_{27}\text{FeN}_3\text{S}_2\text{Si}$: C, 37.81; H, 7.79; N, 12.03; S, 18.35. Found: C, 37.86; H, 7.90; N, 11.71; S, 18.58.

Preparation of $\text{Co}(\text{S}_2\text{SiMe}_2)(\text{PMDETA})$ (3**).** The mixture of $\text{Co}(\text{OAc})_2$ (0.166 g, 0.94 mmol) and PMDETA (0.40 mL, 1.9 mmol) in THF (10 mL) was dissolved at $60\text{ }^{\circ}\text{C}$ to give a deep purple solution. A hexane solution of $(\text{Me}_2\text{SiS})_3$ (0.80 mL, 0.98 mmol; 1.22 M hexane solution) was added dropwise to the solution at $-85\text{ }^{\circ}\text{C}$. The mixture immediately turned a deep blue solution and was allowed to warm slowly to room temperature with stirring. After additional stirring for 30 min at room temperature, the solution was evaporated to dryness. The residue was washed with hexane (10 mL) to yield a crude purple-blue solid. The resulting solid was extracted with THF (6 mL) and centrifuged to remove an insoluble solid. Slow addition of hexane (10 mL) to the concentrated supernatant afforded a blue lilac crystalline powder of **3** (0.29 g, 87%). Deep blue blocks suitable for X-ray analysis were obtained by slow diffusion of hexane into the THF solution of **3**. $^1\text{H NMR}$ (CDCl_3): δ 141.8 ($\Delta\nu_{1/2} = 3000\text{ Hz}$, br), 98.7 ($\Delta\nu_{1/2} = 820\text{ Hz}$, br), 36.7 ($\Delta\nu_{1/2} = 250\text{ Hz}$, br), 15.1 ($\Delta\nu_{1/2} = 110\text{ Hz}$, br). IR (Nujol): 1302 (m), 1285 (m), 1249 (w), 1230 (s, δ_{SiC}), 1176 (w), 1155 (w), 1107 (m), 1060 (m), 1048 (m), 1027 (s), 1011 (m), 982 (m), 936 (m), 906 (w), 828 (s, ν_{SiC}), 791 (s), 753 (s), 663 (s), 607 (w), 576 (w), 526 (s), 480 (w), 463 (m) cm^{-1} . UV-vis (λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$), THF): 241sh (3400), 277 (2100), 346 (780), 563 (92), 648 (58). μ_{eff} (296 K) = $4.5\ \mu_{\text{B}}/\text{Co}$. Anal. Calcd for $\text{C}_{11}\text{H}_{29}\text{CoN}_3\text{S}_2\text{Si}$: C, 37.27; H, 8.24; N, 11.85; S, 18.09. Found: C, 37.06; H, 8.16; N, 11.79; S, 17.75.

Preparation of $\text{Pd}(\text{S}_2\text{SiMe}_2)(\text{PET}_3)_2$ (4**).** Treatment of $\text{Pd}(\text{OAc})_2$ (0.70 g, 3.1 mmol) with PET_3 (4.8 mL, 6.9 mmol; 1.44 M toluene solution) in toluene (25 mL) gave a yellow homogeneous solution. When $(\text{Me}_2\text{SiS})_3$ (3.3 mL, 3.1 mmol; 0.94 M hexane solution) was added, the color of the solution changed from yellow to red-orange. The reaction mixture was stirred for 2 h at room temperature. To remove an insoluble solid, the resulting yellow reaction mixture was centrifuged. The supernatant was concentrated under vacuum. After hexane (15 mL) was added, the solution was cooled to $-30\text{ }^{\circ}\text{C}$. Compound **4** was obtained as yellow microcrystals in 88% yield (1.28 g). Yellow prisms suitable for X-ray analysis were obtained by recrystallization from concentrated Et_2O solution at $-30\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (CDCl_3): δ 1.87 (dq, 12H, PCH_2CH_3 , $^2J_{\text{PH}} = 8.7\text{ Hz}$, $^3J_{\text{HH}} = 7.6\text{ Hz}$), 1.13 (dt, 18H, PCH_2CH_3 , $^3J_{\text{PH}} = 17\text{ Hz}$, $^3J_{\text{HH}} = 7.6\text{ Hz}$), 0.57 (s, 6H, SiMe_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 20.5 (s). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 36.1 (t, $^3J_{\text{SiP}} = 2\text{ Hz}$). IR (Nujol): 1413 (m), 1235 (m, δ_{SiC}), 1227 (m, δ_{SiC}), 1045 (s, PET_3), 1034 (s, PET_3), 830 (m, ν_{SiC}), 782 (m), 764 (s, PET_3), 737 (m), 720 (m), 696 (w), 674 (s), 632 (w, PET_3), 522 (w), 477 (w) cm^{-1} . UV-vis (λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$), THF): 253 (13000), 263 (13000), 301 (14000), 379sh (410), 414 (360). Anal. Calcd for $\text{C}_{14}\text{H}_{36}\text{P}_2\text{PdS}_2\text{Si}$: C, 36.16; H, 7.80; S, 13.79. Found: C, 36.07; H, 7.70; S, 13.88.

Preparation of $\text{Cu}_2\{(\text{SSiMe}_2)_2\text{S}\}(\text{PET}_3)_3$ (5**).** Addition of $(\text{Me}_2\text{SiS})_3$ (2.3 mL, 3.4 mmol; 1.48 M hexane solution) to a mixture

of $\text{Cu}(\text{OAc})$ (0.69 g, 5.6 mmol) and PET_3 (7.8 mL, 11 mmol; 1.44 M toluene solution) in Et_2O (20 mL) at room temperature gave a yellow solution. After the resulting solution was stirred for 3 h at room temperature, the solvent was removed in vacuo. Recrystallization from hexane at $-30\text{ }^{\circ}\text{C}$ afforded **5** as colorless crystals (1.44 g, 74%). Colorless prisms suitable for X-ray analysis were obtained by recrystallization from concentrated hexane solution at $-30\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (C_6D_6): δ 1.36 (dq, 18H, PCH_2CH_3 , $^2J_{\text{PH}} = 4.6\text{ Hz}$, $^3J_{\text{HH}} = 7.7\text{ Hz}$), 1.03 (dt, 27H, PCH_2CH_3 , $^3J_{\text{PH}} = 15\text{ Hz}$, $^3J_{\text{HH}} = 7.7\text{ Hz}$), 0.96 (s, 12H, SiMe_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -14.6 (br, $\Delta\nu_{1/2} = 48\text{ Hz}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): δ 16.0 (s). IR (Nujol): 2728 (w), 1426 (m), 1413 (m), 1238 (s, δ_{SiC}), 1038 (s), 828 (s, ν_{SiC}), 767 (s), 711 (m), 664 (m), 626 (w), 534 (s), 505 (w), 456 (m) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{57}\text{Cu}_2\text{P}_3\text{S}_3\text{Si}_2$: C, 38.07; H, 8.28; S, 13.86. Found: C, 37.69; H, 8.42; S, 13.15.

Preparation of $\text{Ag}_2\{(\text{SSiMe}_2)_2\text{S}\}(\text{PET}_3)_3$ (6**).** A mixture of $\text{Ag}(\text{OAc})$ (0.46 g, 2.8 mmol) and PET_3 (5.5 mL, 7.9 mmol; 1.44 M toluene solution) in Et_2O (15 mL) was treated with $(\text{Me}_2\text{SiS})_3$ (1.5 mL, 1.9 mmol; 1.29 M hexane solution). After being stirred for 1 h at room temperature, the resulting colorless solution was evaporated to dryness. The residue was dissolved with hexane (8 mL), and the solution was cooled to $-30\text{ }^{\circ}\text{C}$. Colorless prisms of **6** were isolated in 75% yield (0.82 g). $^1\text{H NMR}$ (C_6D_6): δ 1.25 (dq, 18H, PCH_2CH_3 , $^2J_{\text{PH}} = 4.9\text{ Hz}$, $^3J_{\text{HH}} = 7.7\text{ Hz}$), 1.04 (s, 12H, SiMe_2), 0.97 (dt, 27H, PCH_2CH_3 , $^3J_{\text{PH}} = 16\text{ Hz}$, $^3J_{\text{HH}} = 7.7\text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -3.9 (s). $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6): δ 21.1 (s). IR (Nujol): 2733 (w), 1415 (m), 1237 (s, δ_{SiC}), 1038 (s, PET_3), 826 (s, ν_{SiC}), 765 (s, PET_3), 714 (m), 666 (s), 625 (w, PET_3), 538 (s), 509 (m), 456 (m) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{57}\text{Ag}_2\text{P}_3\text{S}_3\text{Si}_2$: C, 33.76; H, 7.34; S, 12.29. Found: C, 33.28; H, 7.42; S, 12.07.

X-ray Crystallography. Crystallographic data are summarized in Table 1. X-ray-quality single crystals were obtained from THF/hexane for **1** and **2** as colorless crystals and **3** as deep blue crystals and from hexane for **6** as colorless crystals. Crystals were immersed in mineral oil on a nylon loop and transferred to a Rigaku Mercury CCD diffractometer (for **1–3**) or a Rigaku Saturn CCD diffractometer (for **6**) equipped with a Rigaku GNNP low-temperature device. Data were collected under a cold nitrogen stream using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71070\text{ \AA}$). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) program. Corrections for Lorentz-polarization effects and absorption were performed.

Calculations were performed with the CrystalStructure (Rigaku) software package. The structures of **2** and **3** were solved by direct methods, and the other structures were solved by the Patterson method, where the metal atoms and some heavy atoms were located unequivocally. The remaining heavy atoms were found in subsequent Fourier maps, and the structures were refined on F^2 by the full-matrix least-squares method. In the case of **1** and **3**, two methylene carbons of the PMDETA ligand for one molecule in the asymmetric unit were disordered with occupancy factors of 50:50. For **6**, a disorder involving the P(3) phosphine ligand across a virtual mirror plane passing through Ag(1), Ag(2), P(1), and P(2) was refined, resulting in occupancy factors of 55:45. Anisotropic refinement was applied to all non-hydrogen atoms except for the disordered atoms. The disordered atoms were isotropically refined, and no hydrogen atoms on the disordered atoms were included. All hydrogen atoms were put at calculated positions with C–H distances of 0.97 \AA . In the case of **6**, systematic absences were consistent with $P2_1$ (No. 4) and $P2_1/m$ (No. 11) space groups. The choice of the acentric space group was confirmed by the successful refinement of the model. The Flack parameter refined to 0.00(3),

Table 1. Crystallographic Data for **1–3** and **6**

	1	2	3	6
empirical formula	C ₁₁ H ₂₉ N ₃ S ₂ SiFe	C ₁₁ H ₂₇ N ₃ S ₂ SiFe	C ₁₁ H ₂₉ N ₃ S ₂ SiCo	C ₂₂ H ₅₇ P ₃ S ₃ Si ₂ Ag ₂
fw	351.42	349.41	354.51	782.70
T/K	173	173	173	173
cryst size/mm	0.25 × 0.20 × 0.20	0.12 × 0.08 × 0.05	0.20 × 0.10 × 0.10	0.14 × 0.11 × 0.07
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ (No. 4)
<i>a</i> /Å	21.647(7)	7.325(6)	21.442(8)	10.188(3)
<i>b</i> /Å	10.975(3)	12.835(10)	11.447(4)	11.726(4)
<i>c</i> /Å	16.612(5)	18.42(2)	15.952(6)	16.051(5)
β/deg	109.530(4)	90.940(13)	108.964(4)	106.969(6)
<i>V</i> /Å ³	3719.4(19)	1731.6(24)	3702.8(23)	1834.2(10)
<i>Z</i>	8	4	8	2
<i>D</i> _c /g cm ⁻³	1.255	1.340	1.272	1.417
μ(Mo Kα)/cm ⁻¹	10.89	11.69	12.07	14.42
no. of reflns collected	29224	13700	29497	14295
no. of unique reflns	8340	3875	8476	4310
no. of refined params	377	190	377	295
GOF on <i>F</i> ²	1.00	1.00	1.00	1.07
R1 ^a [<i>I</i> > 2σ(<i>I</i>)]	0.046	0.065	0.040	0.042
wR2 ^b (all data)	0.105	0.199	0.097	0.097

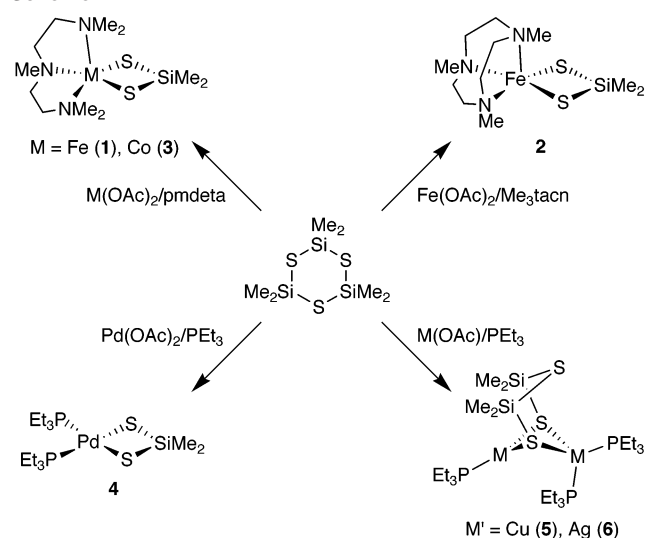
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

indicating that the correct absolute structure was used. Additional crystallographic data are given in the Supporting Information.

Results and Discussion

Synthesis of Silanedithiolato Complexes. The readily accessible cyclotrisilathiane (SSiMe₂)₃ has been chosen as a starting material for the synthesis of chelating silanedithiolato complexes in this paper. This heterocyclic compound was prepared according to the literature procedure reported by Boudjouk for the selenium analogue.¹³ Treatment of sulfur with 2 equiv of sodium in THF containing naphthalene under reflux followed by addition of Me₂SiCl₂ provided a light yellow liquid of cyclotrisilathiane in 79% yield after vacuum distillation. Compared to (Me₃Si)₂S that is widely used as a sulfur-transfer reagent,¹⁴ cyclotrisilathiane has received scant attention in syntheses of organometallic and coordination complexes. Rauchfuss reported that the related titanium complex (C₅H₄Me)₂Ti(S₂SiMe₂) was prepared by treating cyclotrisilathiane with Li₂S followed by (C₅H₄Me)₂TiCl₂.³ Replacing the dimethylsilyl group of cyclotrisilathiane with the metal fragment seems to be useful for the synthesis of silanedithiolato complexes. We found the formation of Me₂Si(OAc)₂ in the reactions of (SSiMe₂)₃ with metal acetates according to NMR spectroscopy and GC/MS analysis, while Corrigan and Yu reported that trimethylsilanethiolato complexes were prepared by the reactions of the metal acetates with (Me₃Si)₂S.^{1k,2,5b} Therefore, we chose to examine the combination of cyclotrisilathiane and metal acetates to provide a system for study.

The successful synthesis of silanedithiolato complexes is summarized in Scheme 1. Treatment of cyclotrisilathiane with the metal acetates M(OAc)_{*n*} (M = Fe, Co, Pd, *n* = 2; M = Cu, Ag, *n* = 1) in the presence of appropriate Lewis bases (PMDETA, Me₃TACN, and PEt₃) afforded silanedi-

Scheme 1

thiolato complexes Fe(S₂SiMe₂)(L) (L = PMDETA (**1**), Me₃TACN (**2**)), Co(S₂SiMe₂)(PMDETA) (**3**), Pd(S₂SiMe₂)-(PEt₃)₂ (**4**), and M₂{(SSiMe₂)₂S}(PEt₃)₃ (M = Cu (**5**), Ag (**6**)). Yields ranged from a low of 41% for **1** to 88% for **4** (the yield for **2** was 73%, for **3** 87%, for **5** 74%, and for **6** 75%). In these reactions, an excess of cyclotrisilathiane was required. When the amount of cyclotrisilathiane was decreased, yields of the desired products were lowered. On the other hand, exogenous ligands are found to play a crucial role in isolating silanethiolato complexes. For instance, the analogous reactions using the diamine ligand *N,N,N',N'*-tetramethylethylenediamine as the exogenous ligand resulted in formation of uncharacterized products.

We found that if all components of the reaction were combined before the metal acetate completely formed a Lewis base adduct, the yield of the desired product was highly irreproducible. We speculate that the silanedithiolato complex generated in the reaction mixture competes with cyclotrisilathiane as a sulfur-transfer reagent for the remaining metal acetate, resulting in the formation of undesired

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metal sulfido clusters. Exogenous ligands could prevent the resulting silanethiolato complexes from undergoing aggregation and/or ligand redistribution. This is supported by the observation that the Me₃TACN adduct **2** is isolated in higher yield than the PMDETA adduct **1** due to the robustness of the (Me₃TACN)Fe fragment. Irreproducible yields are avoided if the metal acetate is treated with triamines or PET₃ until it dissolves, and then a hexane solution of cyclotrisilathiane is added. This strategy has also been employed in the synthesis of copper(I) trimethylsilanechalcogenolato complexes Cu(ESiMe₃)(PR₃)₃ (E = S, Se, Te; R = Et, ⁱPr) by the Corrigan group.² When Lewis base adducts of metal acetates are generated beforehand in this manner, the yields of silanedithiolato complexes **1–6** are reproducible.

The triamine adducts **1–3** dissolve in THF and CH₂Cl₂, while the phosphine adducts **4–6** are very soluble in toluene and Et₂O. These silanedithiolato complexes are air- and moisture-sensitive, but are thermally stable. For instance, they do not show any signs of decomposition in CDCl₃ and C₆D₆ at room temperature over 2 days in the absence of air, according to their ¹H NMR spectra. The stability of these chelating silanedithiolato complexes contrasts with the thermosensitivity of the trimethylsilanethiolato complexes Cu(SSiMe₃)(PR₃)₃ (R = Et, ⁿPr), which are unstable in solution above 0 °C, resulting in formation of copper sulfido polynuclear compounds.^{2,5b} All these compounds **1–6** are characterized by analytical, spectroscopic, and crystallographic methods.

Magnetic moment measurements in a solid at room temperature yielded a value of 5.2 μ_B for **1** and **2**, which is typical for high-spin d⁶ iron(II) and somewhat greater than the spin-only value (4.90 μ_B) for four unpaired electrons. Complex **3** exhibits a magnetic moment of 4.5 μ_B, consistent with high-spin trigonal-bipyramidal cobalt(II) complexes (the spin-only d⁷ value is 3.89 μ_B).¹⁵ The dark, intense blue color of **3** is also characteristic of high-spin cobalt(II) complexes. The ¹H NMR spectra of these complexes consist of a series of paramagnetically shifted resonances. Unfortunately, it is difficult to assign the spectra due to extreme broadness leading to unreliable integration and missing peaks. Knowledge of the spectra, however, is useful in compound identification.

On the other hand, the NMR spectra of diamagnetic complexes **4–6** are structurally informative. In their ¹H NMR spectra, the relative intensity of the proton signals of silanedithiolate and triethylphosphine is consistent with their formulations. Although two metal centers are inequivalent in each crystal structure of **5** and **6** (vide infra), the methyl proton signal of the silanedithiolato ligand appears as a sharp singlet at room temperature. Thus, their structures are fluxional in solution via dynamic processes involving a rapid ring inversion of the M₂(SSiMe₂)₂S core (M = Cu and Ag) and a fast exchange of phosphine ligands between two metal centers. The ³¹P{¹H} NMR spectrum of **4** exhibits a sharp resonance at 20.5 ppm, while the signal at –14.6 ppm (Δν_{1/2}

= 48 Hz) for **5** is somewhat broad. Broadening of the signal is caused presumably by ^{63/65}Cu–³¹P quadrupole relaxation, as generally observed for phosphine complexes of copper(I) with low symmetry.¹⁶ For **6**, the ³¹P{¹H} NMR signal appears as a sharp singlet at –3.9 ppm, and the coupling between ^{107/109}Ag and ³¹P nuclei was not clearly seen due to the rapid exchange of the phosphine ligand in solution on the NMR time scale. The silanedithiolato complexes **4–6** are also characterized by the ²⁹Si{¹H} NMR spectra. The ²⁹Si{¹H} NMR signal of **4** is observed at 36.1 ppm as a triplet with a ³J_{SiP} coupling constant of 2 Hz and is shifted to a lower field than the singlets of **5** (16.0 ppm) and **6** (21.1 ppm). For comparison, the ²⁹Si{¹H} NMR signals of (SSiMe₂)₃ and (SSiMe₂)₂ are observed at 21.4 and 16.7 ppm, respectively.¹⁷

Crystal Structures of Silandithiolato Complexes. X-ray structure determinations have been carried out for **1–3** and **6**. Details of data collection and processing and structure solution are given in Table 1 and the Experimental Section. The structures of **4** and **5** have been reported in the preliminary communications and are not repeated in detail here.^{9,10}

M(S₂SiMe₂)(PMDETA) (M = Fe (1**), Co (**3**)).** Molecules of **1** and **3** crystallized in the *P*₂*1*/*c* space group with two independent molecules (A and B for **1** and C and D for **3**) per asymmetric unit. In each compound **1** and **3**, the largest difference between two independent molecules occurs in the configurations of the PMDETA ligands. For **1**, the FeN₂C₂ rings of the PMDETA ligand adopt a δ, λ configuration for one molecule (A). The other molecule (B) exhibits a disorder in methylene carbons of an FeN₂C₂ ring, and thus the disordered molecule contains the δ, δ and δ, λ configurations of the PMDETA ligand at 50% occupancy for each. In the case of **3**, the CoN₂C₂ rings of the PMDETA ligand adopt a λ, λ configuration for one molecule (C), while the other molecule (D) exhibits a disorder analogous to that described for **1**. The centrosymmetric space group of **1** and **3** requires the presence of a racemic mixture of complexes in the crystal. For conciseness, molecular structures of the δ, λ isomer (molecule A) for **1** and of the λ, λ isomer (molecule C) for **3** are shown in Figures 1 and 2, respectively. Selected bond distances and angles of **1** and **3** are listed in the first and third columns of Table 2.

The coordination geometry about the metal center is distorted trigonal pyramidal. The dimethylsilanedithiolato ligand is bound to the metal center in a bidentate fashion, and the triamine PMDETA ligand occupies the face with the central amine [N(2)] located at one axial position of the trigonal pyramid. Deviation from idealized trigonal-bipyramid geometry is indicated by the fact that the axial S(1)–M–N(2) angles are 165.39(6)° and 170.24(8)° for **1** and 176.13(6)° and 173.72(7)° for **3**. The axial M–S and M–N distances are longer than the corresponding distances in the equatorial plane. The four-membered MS₂Si rings diversely deviate from planarity, with dihedral angles of 1.9°

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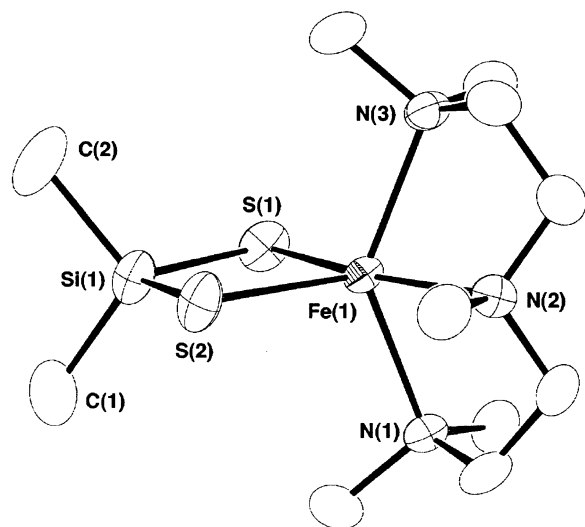


Figure 1. Molecular structure of one of the two crystallographically independent molecules of **1** at the 50% probability level. Hydrogen atoms are omitted for clarity.

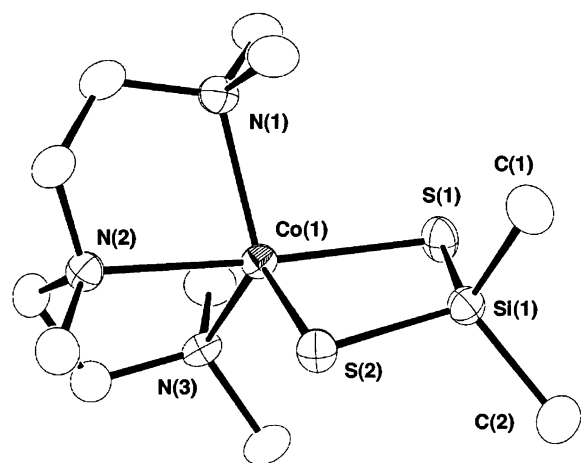


Figure 2. Molecular structure of one of the two crystallographically independent molecules of **3** at the 50% probability level. Hydrogen atoms are omitted for clarity.

and 7.2° for **1** and 10.4° and 0.9° for **3** between MS_2 and SiS_2 planes. The $\text{M}-\text{S}$ distances of **1** ($2.37\text{--}2.45 \text{ \AA}$) and **3** ($2.34\text{--}2.42 \text{ \AA}$) are at the long end of $\text{M}-\text{S}$ distances in the reported terminal alkylthiolato(arylthiolato) complexes of iron(II) ($2.25\text{--}2.34 \text{ \AA}$)¹⁸ and cobalt(II) ($2.19\text{--}2.33 \text{ \AA}$)¹⁹ respectively. The acute $\text{M}-\text{S}-\text{Si}$ angles (average 82.0° for **1** and 82.5° for **3**) are typical of small ring systems, while the silicon atoms are bound in a tetrahedral manner to two sulfur atoms. The $\text{S}-\text{Si}$ distances of **1** and **3** average 2.123 and 2.111 \AA , respectively, which are comparable to those

found in previously reported silathiane compounds.²⁰ The $\text{M}-\text{N}$ distances range from $2.197(2)$ to $2.277(3) \text{ \AA}$ for **1** and from $2.131(3)$ to $2.281(2) \text{ \AA}$ for **3**, which are characteristic of high-spin iron(II)²¹ and cobalt(II),²² respectively.

Fe(S₂SiMe₂)(Me₃TACN) (2). Complex **2** crystallized in the $P2_1/c$ space group as a racemic mixture of enantiomers containing the $\lambda, \lambda, \lambda$ and δ, δ, δ configurations of the three FeN_2C_2 five-membered rings in the metal-bound Me_3TACN ligand. A view of the molecular structure of **2** is shown in Figure 3, and selected bond distances and angles are listed in the second column of Table 2. The nature of the triamines has a dramatic effect on the resulting geometry of the complex. One difference between **1** and **2** is that the Me_3TACN complex **2** adopts a more square-pyramidal structure with the metal atom lying 0.26 \AA out of the basal coordination plane (N_2S_2) in the direction of the apical ligand [$\text{N}(1)$]. This distortion can be attributed to the coordination constraints of the cyclic tridentate Me_3TACN ligand, the $\text{N}-\text{Fe}-\text{N}$ angles of which are in the range $78.2(2)\text{--}80.2(2)^\circ$ to accommodate the five-membered chelate rings enforced by the tridentate Me_3TACN macrocycle. By virtue of this distortion, the cyclic Me_3TACN ligand has a lower steric demand than the acyclic PMDETA ligand, and the average $\text{Fe}-\text{S}$ distance of 2.391 \AA is somewhat shorter compared to that of **1** (2.406 \AA). The four-membered FeS_2Si ring is puckered with a dihedral angle of 11.7° between FeS_2 and SiS_2 planes. The angles within the FeS_2Si ring of **2** and the $\text{S}-\text{Si}$ distances are similar to those found in **1**. The basal $\text{Fe}-\text{N}$ bonds approximately trans to sulfur [$2.279(5)$ and $2.287(5) \text{ \AA}$] are elongated relative to the apical $\text{Fe}-\text{N}(1)$ bond [$2.193(5) \text{ \AA}$]. The average $\text{Fe}-\text{N}$ distance of 2.253 \AA is slightly longer than that of **1** (2.232 \AA). This could be ascribed to the conformational constraints imposed by the cyclic framework of the Me_3TACN ligand.

Ag₂{(SSiMe₂)₂S}(PET₃)₃ (6). The X-ray crystal structure of **6** is presented in Figure 4, which is analogous to that of the copper congener **5**.¹⁰ Table 3 summarized selected bond distances and angles for **6**. The structure of **6** consists of an intriguing $(\text{SSiMe}_2)_2\text{S}^{2-}$ silanedithiolato ligand which chelates two silver metals, resulting in a bicyclic $\text{Ag}_2\text{S}_3\text{Si}_2$ geometry. The Ag_2S_2 quadrilateral is folded, so that the dihedral angle between the two AgS_2 triangular faces is

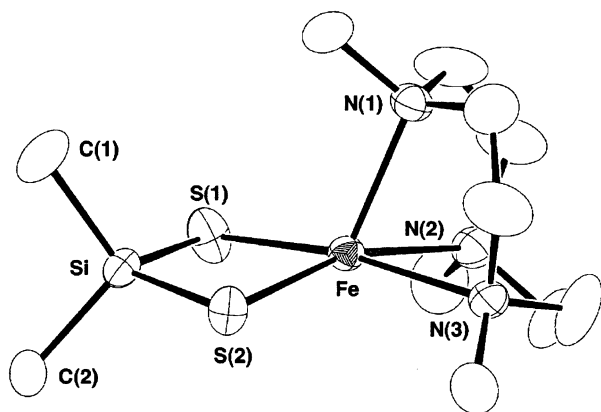
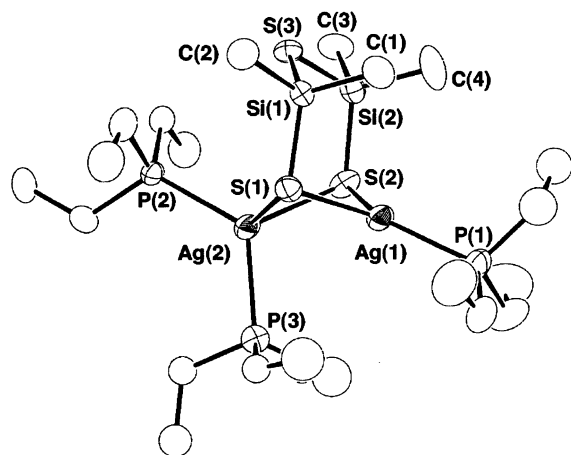
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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1–3**

	1 ^a		2		3 ^a
M(1)–S(1)	2.434(1)	[2.445(1)]	2.371(2)	2.420(1)	[2.409(1)]
M(1)–S(2)	2.372(1)	[2.371(1)]	2.410(2)	2.354(1)	[2.337(1)]
M(1)–N(1)	2.207(2)	[2.197(2)]	2.193(5)	2.181(2)	[2.162(3)]
M(1)–N(2)	2.276(2)	[2.277(3)]	2.279(5)	2.277(2)	[2.281(3)]
M(1)–N(3)	2.214(2)	[2.218(3)]	2.287(5)	2.145(2)	[2.131(2)]
Si(1)–S(1)	2.126(1)	[2.119(1)]	2.100(3)	2.115(1)	[2.111(1)]
Si(1)–S(2)	2.120(1)	[2.127(1)]	2.126(3)	2.112(1)	[2.107(1)]
Si(1)–C(1)	1.866(4)	[1.875(4)]	1.869(7)	1.883(3)	[1.872(4)]
Si(1)–C(2)	1.877(3)	[1.875(3)]	1.880(6)	1.876(3)	[1.872(4)]
S(1)–M(1)–S(2)	90.12(4)	[89.30(3)]	89.87(10)	89.10(3)	[89.98(3)]
S(1)–M(1)–N(1)	95.87(6)	[96.77(7)]	108.8(1)	97.26(7)	[95.51(7)]
S(1)–M(1)–N(2)	165.39(6)	[170.24(8)]	95.5(2)	176.13(6)	[173.72(7)]
S(1)–M(1)–N(3)	95.79(7)	[96.16(8)]	168.21(13)	99.65(7)	[99.08(7)]
S(2)–M(1)–N(1)	106.91(7)	[118.28(6)]	113.5(1)	119.96(7)	[123.45(8)]
S(2)–M(1)–N(2)	104.47(6)	[100.39(8)]	163.41(13)	94.20(7)	[95.74(8)]
S(2)–M(1)–N(3)	113.95(6)	[114.10(8)]	93.58(13)	119.46(6)	[111.22(7)]
N(1)–M(1)–N(2)	79.45(8)	[79.73(10)]	79.6(2)	79.34(9)	[79.19(10)]
N(1)–M(1)–N(3)	137.34(9)	[115.98(10)]	80.2(2)	118.03(9)	[123.16(10)]
N(2)–M(1)–N(3)	79.07(8)	[78.91(10)]	78.2(2)	80.48(9)	[81.27(9)]
S(1)–Si(1)–S(2)	106.47(5)	[105.74(5)]	106.08(11)	104.80(5)	[105.43(5)]
M(1)–S(1)–Si(1)	80.89(4)	[81.48(5)]	82.24(6)	81.80(5)	[81.37(5)]
M(1)–S(2)–Si(1)	82.49(4)	[83.10(4)]	80.80(9)	83.48(4)	[83.21(4)]

^a Values in brackets refer to molecule B for **1** and to molecule D for **3**.

**Figure 3.** Molecular structure of **2** at the 50% probability level. Hydrogen atoms are omitted for clarity.**Figure 4.** Molecular structure of **6** at the 50% probability level. One set of the disordered atoms of the PEt₃ ligands is shown. Hydrogen atoms are omitted for clarity.

126.0°. The two silver metals are separated by 3.082(1) Å. The Ag₂S₂ core is further coordinated to three phosphine ligands. The Ag(1) atom is trigonally coordinated, while the

Table 3. Selected Bond Distances (Å) and Angles (deg) for **6**

Ag(1)–S(1)	2.534(1)	Ag(1)–S(2)	2.568(1)
Ag(2)–S(1)	2.698(2)	Ag(2)–S(2)	2.675(2)
Ag(1)–P(1)	2.383(2)	Ag(2)–P(2)	2.445(1)
Ag(2)–P(3)	2.464(3)	S(1)–Si(1)	2.086(2)
S(2)–Si(2)	2.090(2)	S(3)–Si(1)	2.169(2)
S(3)–Si(2)	2.160(2)	Si(1)–C(1)	1.848(5)
Si(1)–C(2)	1.874(5)	Si(2)–C(3)	1.870(5)
Si(2)–C(4)	1.873(5)	Ag(1)–Ag(2)	3.089(1)
S(1)–Ag(1)–S(2)	100.70(5)	S(1)–Ag(1)–P(1)	133.92(6)
S(2)–Ag(1)–P(1)	125.39(6)	S(1)–Ag(2)–S(2)	93.94(4)
S(1)–Ag(2)–P(2)	111.06(4)	S(1)–Ag(2)–P(3)	107.39(8)
S(2)–Ag(2)–P(2)	112.13(4)	S(2)–Ag(2)–P(3)	101.60(8)
P(2)–Ag(2)–P(3)	125.78(8)	Ag(1)–S(1)–Ag(2)	72.30(4)
Ag(1)–S(2)–Ag(2)	72.18(3)	Ag(1)–S(1)–Si(1)	97.37(7)
Ag(2)–S(1)–Si(1)	109.11(6)	Ag(1)–S(2)–Si(2)	96.65(7)
Ag(2)–S(2)–Si(2)	109.30(6)	S(1)–Si(1)–S(3)	115.00(7)
S(2)–Si(2)–S(3)	115.10(8)	Si(1)–S(3)–Si(2)	109.46(7)

Ag(2) atom, bearing two phosphine ligands, has a tetrahedral geometry. These different coordination geometries reflect the steric crowding imposed by the methyl groups on the silicon atoms. One six-membered Ag₂S₂Si₂ ring containing the trigonal-planar Ag(1) center adopts a chair conformation, in which two axial methyl substituents [C(1) and C(4)] on the silicon atoms might prevent the Ag(1) metal from accommodating further ligands. Thus, the S(3) atom is oriented toward the tetrahedral Ag(2) center. It is noteworthy that the thioether-like S(3)–Si bonds [2.170(2) and 2.157(3) Å] are elongated relative to the thiolato S(1)–Si(1) and S(2)–Si(2) bonds [2.088(2) and 2.089(2) Å]. A similar elongation is seen in **5** ($\Delta r_{S-Si} \approx 0.06$ Å),¹⁰ which can be attributed to the hyperconjugative interaction between the occupied p orbital of the S(thiolato) and the vacant antibonding σ^* [Si–S(thioether-like)] orbital. The angles at the S atoms are large compared to those found in the four-membered rings of **1–3**. As expected on the basis of different coordination numbers, the Ag(1)–S [average 2.548 Å] and Ag(1)–P [2.388(2) Å] distances are substantially shorter than the corresponding distances at the Ag(2) center [Ag(2)–S,

2.690 Å; Ag(2)–P, 2.461 Å]. These Ag–S and Ag–P distances are typical of those of trigonal and tetrahedral silver compounds.²³

Summary. The synthesis of various transition-metal complexes with chelating silanedithiolato ligands was easily accomplished by treatment of metal acetates with cyclotrisilathiane (SSiMe_2)₃ in the presence of Lewis bases as exogenous ligands, and cyclotrisilathiane serves as a practical entry point into the coordination chemistry of silanedithiolato ligands. The synthetic route employed here is attractive in that two types of silanedithiolato ligands, $\text{S}_2\text{SiMe}_2^{2-}$ and $(\text{SSiMe}_2)_2\text{S}^{2-}$, are produced. In addition of Lewis bases as exogenous ligands, the chelating effect of silanedithiolato ligands could block a troublesome degradation process of the silanethiolato complex via aggregation and/or ligand

redistribution. This leads to a remarkable increase in the stability of silanethiolato complexes. On the other hand, we found that these silanedithiolato complexes reacted with various metal chlorides and acetates under mild conditions.^{9,10} For example, we previously reported that the reactions of **5** with $(\text{C}_5\text{H}_5)\text{TiCl}_3$ and $\text{TiCl}_4(\text{thf})_2$ afforded the copper–titanium sulfido clusters $(\text{C}_5\text{H}_5)_2\text{Ti}_2\text{Cu}_6\text{S}_6(\text{PEt}_3)_6$ and $\text{ClTiCu}_3\text{S}_3(\text{PEt}_3)_4$, respectively.¹⁰ The mixed-metal sulfido cluster synthesis based on complexes described here is the subject of ongoing work.

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Supporting Information Available: Listing of X-ray crystallographic files in CIF format for complexes of **1–3** and **6**. This material is available free charge via the Internet at <http://pubs.acs.org>.

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