

## Synthesis and Reactions of Triphenylsilanethiolato Complexes of Manganese(II), Iron(II), Cobalt(II), and Nickel(II)

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Reactions of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  with 1 and 2 equiv of  $\text{Ph}_3\text{SiSH}$  in hexane afforded dinuclear silanethiolato complexes,  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-SSiPh}_3)]_2$  (**1**) and  $[\text{Fe}(\text{SSiPh}_3)(\mu\text{-SSiPh}_3)]_2$  (**2**), respectively. Various Lewis bases were readily added to **2**, generating mononuclear adducts,  $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$  [ $\text{L} = \text{CH}_3\text{CN}$  (**3a**),  $4\text{-}^i\text{BuC}_5\text{H}_4\text{N}$  (**3b**),  $\text{PEt}_3$  (**3c**),  $(\text{LL}) = \text{tmeda}$  (**3d**)]. From the analogous reactions of  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{M} = \text{Mn}, \text{Co}$ ) and  $[\text{Ni}(\text{NPh}_2)_2]_2$  with  $\text{Ph}_3\text{SiSH}$  in the presence of TMEDA, the corresponding silanethiolato complexes,  $\text{M}(\text{SSiPh}_3)_2(\text{tmeda})$  [ $\text{M} = \text{Mn}$  (**4**),  $\text{Co}$  (**5**),  $\text{Ni}$  (**6**)], were isolated. Treatment of **3a** with  $(\text{PPh}_4)_2[\text{MoS}_4]$  or  $(\text{NEt}_4)_2[\text{FeCl}_4]$  resulted in formation of a linear trinuclear  $\text{Fe-Mo-Fe}$  cluster  $(\text{PPh}_4)_2[\text{MoS}_4\{\text{Fe}(\text{SSiPh}_3)_2\}_2]$  (**7**) or a dinuclear complex  $(\text{NEt}_4)_2[\text{Fe}_2(\text{SSiPh}_3)_2\text{Cl}_4]$  (**8**). On the other hand, the reaction of **3a** with  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  gave a cyclic tetranuclear copper cluster  $\text{Cu}_4(\text{SSiPh}_3)_4$  (**9**), where silanethiolato ligands were transferred from iron to copper. Silicon–sulfur bond cleavage was found to occur when the cobalt complex **5** was treated with  $(\text{NBu}_4)\text{F}$  in THF, and a cobalt–sulfido cluster  $\text{Co}_6(\mu\text{-S})_8(\text{PPh}_3)_6$  (**10**) was isolated upon addition of  $\text{PPh}_3$  to the reaction system. The silanethiolato complexes reported here are expected to serve as convenient precursors for sulfido cluster synthesis.

### Introduction

Transition metal–sulfur clusters have attracted attention in light of their relevance to various active sites of metalloproteins, desulfurization catalysis, and inorganic functional materials.<sup>1</sup> An important and challenging subject in this chemistry is to develop rational methods to synthesize desirable sulfur cluster complexes of high nuclearity, by assembling suitable metal–sulfur fragments.<sup>2</sup> For this purpose, we have developed cluster-forming reactions of preformed mononuclear thiolato complexes via carbon–sulfur bond cleavage.<sup>3</sup> For instance,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{S}^i\text{Bu})_3$  was found to react with  $\text{FeCl}_3$ , resulting in isolation of the cubane-type cluster  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2\text{Fe}_2\text{S}_4\text{Cl}_2$ .<sup>3b</sup>

As an extension of our study on thiolato/sulfido complexes of transition metals, we have investigated the synthesis and reactions of silanethiolato complexes.<sup>4</sup> Compared with

complexes containing alkyl(aryl) thiolate ligands, the coordination chemistry of silanethiolates has yet to be explored.<sup>4–8</sup> However, the use of silanethiolates has the following two advantages in developing rational synthetic routes to transition metal–sulfido clusters. First, silicon–sulfur bonds are expected to be more labile and more readily cleaved under mild conditions than carbon–sulfur bonds. Second, the

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reactivity of silanethiolato ligands can be controlled by the steric and electronic properties of the substituents in the silyl group. The most intriguing example of such a study is the copper silanethiolato complex  $\text{Cu}(\text{SSiMe}_3)(\text{PPR}^n)_3$  prepared by Corrigan and co-workers, treatment of which with  $\text{Hg}(\text{OAc})_2(\text{PPR}^n)_2$  gave rise to the gigantic  $\text{Hg}/\text{Cu}/\text{S}$  cluster,  $\text{Hg}_{15}\text{Cu}_{20}\text{S}_{25}(\text{PPR}^n)_{18}$ .<sup>6b</sup> We herein describe the synthesis and structures of a series of triphenylsilanethiolato complexes of Mn(II), Fe(II), Co(II), and Ni(II). Also reported are our preliminary findings of the stability/reactivity of these triphenylsilanethiolato complexes.

## Experimental Section

**General.** All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon with standard Schlenk-line techniques. Solvents were dried and distilled over an appropriate drying agent under an atmosphere of dinitrogen. All commercially available reagents were used as received. The compounds  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$ )<sup>9</sup> and  $[\text{Ni}(\text{NPh}_2)_2]_2$ <sup>10</sup> were prepared according to published methods.

<sup>1</sup>H NMR spectra were recorded on a JEOL Lambda-500 spectrometer and referenced internally to residual proton-solvent. Chemical shifts are reported in ppm. Infrared spectra were recorded on Nujol mulls between KBr plates on a JASCO FT/IR-410 spectrometer. For UV–visible spectra, a JASCO V-560 spectrometer was used. Elemental analyses were measured with LECO-CHNS and Yanaco MT-6 and MSU-32 microanalyzers.

**Preparation of  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-SSiPh}_3)_2]$  (**1**).** To a solution of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  (0.36 g, 0.95 mmol) in hexane (5 mL) was added slowly a solution of  $\text{HSSiPh}_3$  (0.27 g, 0.92 mmol) in hexane (25 mL) at 0 °C. The color of the solution changed from pale green to brown, during which time a lemon-yellow solid precipitated. After several minutes of stirring at 0 °C, the solution was removed by decantation. Compound **1** was obtained as an air-sensitive lemon-yellow crystalline powder (0.35 g, 74%). IR (Nujol): 3067 (m), 3049 (m), 1588 (w), 1429 (s), 1258 (m), 1246 (s), 1185 (w), 1110 (s), 1029 (w), 998 (w), 954 (s), 865 (s), 832 (s), 800 (m), 755 (w), 738 (m), 709 (s), 697 (s), 680 (m), 619 (w), 517 (s), 496 (s), 433 (m)  $\text{cm}^{-1}$ .

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**Preparation of  $\text{Fe}(\text{SSiPh}_3)_2(\text{CH}_3\text{CN})_2$  (**3a**).** A solution of triphenylsilanethiol (1.70 g, 5.81 mmol) in hexane (85 mL) was added to a solution of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  (1.11 g, 2.94 mmol) in hexane (10 mL). The complex  $[\text{Fe}(\text{SSiPh}_3)(\mu\text{-SSiPh}_3)]_2$  (**2**) immediately precipitated as a yellow powder. After the mixture was stirred at room temperature for 5 min, the precipitate was isolated by decantation and dried in vacuo. The resulting solid was suspended in 60 mL of  $\text{CH}_3\text{CN}$ , giving colorless microcrystals of **3a** (1.63 g, 78%). Anal. Calcd for  $\text{C}_{40}\text{H}_{36}\text{FeN}_2\text{S}_2\text{Si}_2$ : C, 66.65; H, 5.03; N, 3.89; S, 8.90. Found: C, 66.41; H, 4.96; N, 3.95; S, 8.76. <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  10.38 ( $\Delta\nu_{1/2} = 190$  Hz, br, Ph), 8.31 ( $\Delta\nu_{1/2} = 29$  Hz, br, Ph), 6.34 ( $\Delta\nu_{1/2} = 22$  Hz, br, Ph), 1.98 (s,  $\text{CH}_3\text{CN}$ ). IR (Nujol): 2304 (m,  $\nu_{\text{NC}}$ ), 2276 (m,  $\nu_{\text{NC}}$ )  $\text{cm}^{-1}$ . UV–visible ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ),  $\text{CH}_3\text{CN}$ ): 322 (4500), 264 sh.

Compound **3a** (0.43 g, 0.60 mmol) was dissolved in THF (30 mL) and stirred at room temperature. The solution gradually darkened and a black powder precipitated, resulting in a colorless solution. After the solution was stirred overnight, THF (30 mL) was added, and the mixture was stirred for 3 more days. The solution was reduced to half volume, and centrifuged to separate a black solid and a colorless solution. The black solid was washed with THF (20 mL) and dried, affording black powder (0.09 g). Data for black powder: Anal. Found: C, 18.33; H, 2.40; S, 25.54. Fluorescent X-ray spectrum: Fe:S:Si = 1:1.1:0.1.

**$\text{Fe}(\text{SSiPh}_3)_2(4\text{-}^t\text{BuC}_5\text{H}_4\text{N})_2$  (**3b**).** A solution of triphenylsilanethiol (0.72 g, 2.5 mmol) in  $\text{Et}_2\text{O}$  (50 mL) was added to a mixture of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  (0.46 g, 1.22 mmol) and 4-*tert*-butylpyridine (0.73 mL, 5.0 mmol) in  $\text{Et}_2\text{O}$  (10 mL). The solution was stirred for 10 min, during which yellow microcrystals of **3b** precipitated. The product was isolated by decantation (0.88 g, 80% yield). Anal. Calcd for  $\text{C}_{54}\text{H}_{56}\text{FeN}_2\text{S}_2\text{Si}_2$ : C, 71.34; H, 6.21; N, 3.08; S, 7.05. Found: C, 71.41; H, 6.26; N, 3.12; S, 6.87. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  13.63 ( $\Delta\nu_{1/2} = 140$  Hz, br), 7.82 ( $\Delta\nu_{1/2} = 25$  Hz, br), 5.94 ( $\Delta\nu_{1/2} = 21$  Hz, br), 1.38 ( $\Delta\nu_{1/2} = 26$  Hz, br). IR (Nujol): 3062 (m), 3047 (m), 1615 (s), 1544 (w), 1499 (m), 1427 (s), 1274 (w), 1261 (w), 1228 (w), 1184 (w), 1104 (s), 1068 (m), 1022 (m), 998 (w), 842 (w), 831 (s), 746 (s), 738 (m), 705 (s), 683 (s), 622 (w), 560 (s), 508 (s), 502 (s), 494 (s), 467 (w), 438 (m), 428 (w), 418 (m)  $\text{cm}^{-1}$ . UV–visible ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ),  $\text{CH}_2\text{Cl}_2$ ): 394 (1500), 306 (4700), 254 sh.

**$\text{Fe}(\text{SSiPh}_3)_2(\text{PET}_3)_2$  (**3c**).** Reaction of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  (0.29 g, 0.76 mmol) and triphenylsilanethiol (0.43 g, 1.5 mmol) in the presence of  $\text{PET}_3$  (1.5 mL, 2.2 mmol, 20% toluene solution) in hexane (50 mL) yielded 0.58 g of **3c** as colorless crystals in 87%. Anal. Calcd for  $\text{C}_{48}\text{H}_{60}\text{FeP}_2\text{S}_2\text{Si}_2$ : C, 65.88; H, 6.91; S, 7.33. Found: C, 65.90; H, 6.99; S, 7.10. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  11.89 ( $\Delta\nu_{1/2} = 380$  Hz, br), 10.15 ( $\Delta\nu_{1/2} = 56$  Hz, br), 6.66 ( $\Delta\nu_{1/2} = 29$  Hz, br), 4.08 ( $\Delta\nu_{1/2} = 370$  Hz, br). IR (Nujol): 3065 (m), 3044 (m), 1585 (w), 1566 (w), 1427 (s), 1306 (w), 1259 (w), 1186 (w), 1106 (s), 1065 (w), 1038 (w), 1029 (w), 997 (w), 848 (w), 768 (w), 745 (m), 739 (m), 734 (m), 703 (s), 682 (s), 620 (w), 562 (s), 550 (s), 503 (s), 491 (s), 436 (w), 419 (w)  $\text{cm}^{-1}$ . UV–visible ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ), ether): 372 sh (1700), 305 sh (3100), 259 sh.

**$\text{Fe}(\text{SSiPh}_3)_2(\text{tmeda})$  (**3d**).** A mixture of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  (1.01 g, 2.67 mmol) and TMEDA (0.80 mL 5.3 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was treated as described for **3b** with triphenylsilanethiol (1.56 g, 5.3 mmol) in  $\text{Et}_2\text{O}$  (50 mL). Compound **3d** was isolated as colorless crystals (1.71 g, 85%). Anal. Calcd for  $\text{C}_{42}\text{H}_{46}\text{FeN}_2\text{S}_2\text{Si}_2$ : C, 66.82; H, 6.14; N, 3.71; S, 8.49. Found: C, 66.74; H, 6.03; N, 3.58; S, 8.22. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  20.53 ( $\Delta\nu_{1/2} = 180$  Hz, br, tmeda), 7.73 ( $\Delta\nu_{1/2} = 23$  Hz, br, Ph), 5.82 ( $\Delta\nu_{1/2} = 16$  Hz, br, Ph). IR (Nujol): 1426 (s), 1106 (s), 702 (s), 567 (s), 558 (s), 500 (s)  $\text{cm}^{-1}$ . UV–visible ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ),  $\text{CH}_2\text{Cl}_2$ ): 305 (5800), 260 sh.

**Mn(SSiPh<sub>3</sub>)<sub>2</sub>(tmeda) (4).** The same procedure as used for **3d** was followed. Reaction of Mn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.29 g, 0.77 mmol) and triphenylsilanethiol (0.43 g, 1.5 mmol) in the presence of TMEDA (0.22 mL, 1.5 mmol) in Et<sub>2</sub>O (25 mL) yielded 0.42 g of **4** as colorless crystals in 72%. Anal. Calcd for C<sub>42</sub>H<sub>46</sub>MnN<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>: C, 66.90; H, 6.15; N, 3.71; S, 8.50. Found: C, 66.84; H, 6.15; N, 3.73; S, 8.33. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.6 (Δν<sub>1/2</sub> = 240 Hz, br). IR (Nujol): 3065 (m), 3048 (m), 1584 (w), 1567 (w), 1429 (s), 1355 (w), 1287 (m), 1262 (w), 1193 (w), 1185 (w), 1167 (w), 1156 (w), 1125 (w), 1105 (s), 1063 (w), 1024 (m), 1007 (w), 997 (w), 950 (m), 793 (m), 743 (s), 736 (m), 702 (s), 683 (s), 622 (w), 565 (s), 503 (s), 489 (s), 436 (m), 428 (w) cm<sup>-1</sup>.

**Co(SSiPh<sub>3</sub>)<sub>2</sub>(tmeda) (5).** Addition of a Et<sub>2</sub>O (20 mL) solution of triphenylsilanethiol (0.43 g, 1.5 mmol) into a mixture of Co-[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.28 g, 0.74 mmol) and TMEDA (0.22 mL, 1.5 mmol) in Et<sub>2</sub>O (10 mL) followed by workup similar to **3d** afforded 0.39 g of **5** as blue crystals (70%). Anal. Calcd for C<sub>42</sub>H<sub>46</sub>CoN<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>: C, 66.54; H, 6.12; N, 3.70; S, 8.46. Found: C, 66.25; H, 6.05; N, 3.62; S, 8.05. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25 (Δν<sub>1/2</sub> = 20 Hz, br), 5.38 (Δν<sub>1/2</sub> = 85 Hz, br), 5.22 (Δν<sub>1/2</sub> = 16 Hz, br). IR (Nujol): 3062 (m), 1585 (w), 1566 (w), 1428 (s), 1305 (w), 1286 (m), 1262 (w), 1187 (w), 1102 (s), 1043 (w), 1025 (m), 998 (w), 950 (m), 798 (m), 747 (m), 739 (m), 699 (s), 684 (m), 622 (w), 563 (s), 507 (s), 495 (s), 467 (w), 431 (m), 418 (m) cm<sup>-1</sup>. UV-visible (λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>): 684 (750), 572 (180), 362 (3300), 312 (4700), 260 sh.

**Ni(SSiPh<sub>3</sub>)<sub>2</sub>(tmeda) (6).** To a suspension of [Ni(NPh<sub>2</sub>)<sub>2</sub>] (0.39 g, 0.49 mmol) in toluene (15 mL) containing TMEDA (0.30 mL, 2.0 mmol) was added triphenylsilanethiol (0.59 g, 2.0 mmol) in toluene (15 mL). The mixture immediately became a dark yellow homogeneous solution that was stirred for 10 min at room temperature. After the solution was centrifuged to remove a small amount of an insoluble solid, the supernatant was evaporated to dryness. The resulting residue was washed with Et<sub>2</sub>O/hexane (1:1) to give 0.31 g of **6** as a yellow powder in 41% yield. Anal. Calcd for C<sub>42</sub>H<sub>46</sub>N<sub>2</sub>NiS<sub>2</sub>Si<sub>2</sub>: C, 66.57; H, 6.12; N, 3.70; S, 8.46. Found: C, 65.92; H, 5.91; N, 3.69; S, 8.38. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.35 (Δν<sub>1/2</sub> = 98 Hz, br), 8.74 (Δν<sub>1/2</sub> = 20 Hz, br), 7.16 (Δν<sub>1/2</sub> = 16 Hz, br). IR (Nujol): 3064 (m), 1428 (s), 1106 (s), 1018 (w), 951 (w), 802 (w), 743 (m), 704 (s), 683 (m), 621 (w), 569 (s), 560 (s), 502 (s), 490 (s), 436 (w) cm<sup>-1</sup>. UV-visible (λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>): 543 (200), 433 (4900), 402 sh (2900), 378 sh (2100), 345 sh (1200), 264 sh.

**(PPh<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>{Fe(SSiPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (7).** Addition of (PPh<sub>4</sub>)<sub>2</sub>[MoS<sub>4</sub>] (0.28 g, 0.31 mmol) in CH<sub>3</sub>CN (25 mL) to a slurry of **3a** (0.45 g, 0.62 mmol) in CH<sub>3</sub>CN (10 mL) immediately gave a homogeneous dark red solution. The mixture was stirred for 20 h at room temperature and evaporated to dryness. The residue was washed with Et<sub>2</sub>O (15 mL) and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The solution was centrifuged to remove an insoluble material. The supernatant was concentrated, and Et<sub>2</sub>O was added. Cooling the solution to -25 °C gave black microcrystals of **7**·CH<sub>2</sub>Cl<sub>2</sub> (0.50 g, 71%). Anal. Calcd for C<sub>121</sub>H<sub>102</sub>Cl<sub>2</sub>Fe<sub>2</sub>MoP<sub>2</sub>S<sub>8</sub>Si<sub>4</sub>: C, 64.15; H, 4.54; S, 11.32. Found: C, 64.48; H, 4.70; S, 10.91. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 11.44 (Δν<sub>1/2</sub> = 370 Hz, br), 8.94 (Δν<sub>1/2</sub> = 71 Hz, br), 7.86 (Δν<sub>1/2</sub> = 23 Hz, br), 7.65 (Δν<sub>1/2</sub> = 53 Hz, br), 6.68 (Δν<sub>1/2</sub> = 38 Hz, br), 5.45 (s, CH<sub>2</sub>Cl<sub>2</sub>). IR (Nujol): 1584 (w), 1426 (s), 1183 (w), 1105 (s), 1027 (w), 996 (w), 741 (m), 723 (s), 699 (s), 689 (s), 681 (s), 621 (w), 553 (s), 526 (s), 501 (s), 468 (w), 459 (w), 423 (w), 413 (w, Mo-S) cm<sup>-1</sup>. UV-visible (λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>): 611 sh (1300), 499 (12000), 387 sh (13000), 349 sh (16000), 319 (19000), 262 sh.

**(NEt<sub>4</sub>)<sub>2</sub>[Fe<sub>2</sub>(SSiPh<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>] (8).** To a suspension of **3a** (0.37 g, 0.51 mmol) in CH<sub>3</sub>CN (10 mL) was added a solution of (NEt<sub>4</sub>)<sub>2</sub>

[FeCl<sub>4</sub>] (0.24 g, 0.52 mmol) in CH<sub>3</sub>CN (25 mL). The resulting homogeneous solution was stirred for 20 min at room temperature. The resulting brown solution was concentrated in vacuo, and then addition of Et<sub>2</sub>O (30 mL) to the solution caused the separation of a colorless powder. This material was isolated by decantation and dried in vacuo to give **8** in 91% yield (0.51 g). Anal. Calcd for C<sub>52</sub>H<sub>70</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>: C, 56.94; H, 6.43; N, 2.55; S, 5.85. Found: C, 56.76; H, 6.35; N, 2.72; S, 5.77. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 8.27 (Δν<sub>1/2</sub> = 24 Hz, br), 6.69 (Δν<sub>1/2</sub> = 31 Hz, br), 6.54 (Δν<sub>1/2</sub> = 220 Hz, br), 2.97 (Δν<sub>1/2</sub> = 25 Hz, br, CH<sub>3</sub>CH<sub>2</sub>N), 1.20 (Δν<sub>1/2</sub> = 20 Hz, br, CH<sub>3</sub>CH<sub>2</sub>N). IR (Nujol): 1579 (m), 1435 (s), 1306 (w), 1265 (w), 1099 (s), 1031 (w), 998 (w), 875 (w), 844 (w), 821 (w), 743 (m), 733 (s), 705 (s), 690 (s), 611 (m), 534 (s), 521 (m), 481 (m) cm<sup>-1</sup>. UV-visible (λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>3</sub>CN): 294 sh (5400), 250 sh.

**[Ph<sub>3</sub>SiSLi(thf)]<sub>4</sub>.** A solution of Ph<sub>3</sub>SiCl (10.0 g, 33.9 mmol) in THF (80 mL) was added to an excess of Li (2.30 g, 0.33 mol) in THF (40 mL) at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 12 h. The mixture was added to a suspension of sulfur (1.08 g, 33.7 mmol) in THF (20 mL) at -78 °C. The reaction mixture was stirred at room temperature for an additional 12 h. The yellow solution was evaporated to dryness. The residue was extracted with toluene (120 mL) and centrifuged to remove LiCl. The supernatant was concentrated under vacuum to afford yellow crystals of [Ph<sub>3</sub>SiSLi(thf)]<sub>4</sub> (8.21 g, 65%). According to the X-ray study, the lithium salt has a cubane geometry, where vertexes are occupied by sulfur atoms and lithium atoms in an alternative manner. Crystal data: tetragonal, space group P421c (No. 144), a = b = 15.665(8) Å, c = 17.182(9) Å, V = 4216(3) Å<sup>3</sup>, Z = 8, D<sub>c</sub> = 0.990 Mg/m<sup>-3</sup>, Mo Kα, μ = 2.07 cm<sup>-1</sup>, R(R<sub>w</sub>) = 0.085(0.087), GOF = 1.17. Anal. Calcd for C<sub>88</sub>H<sub>92</sub>O<sub>4</sub>Li<sub>4</sub>Si<sub>4</sub>S<sub>4</sub>: C, 71.32; H, 6.26; S, 8.65. Found: C, 70.91; H, 6.45; S, 9.07. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.1 (m, 36H, Ph), 7.2 (m, 24H, Ph), 1.86 (br, 16H, thf), 3.75 (br, 16H, thf). IR (Nujol): 3063 (m), 3045 (m), 1427 (s), 1260 (w), 1183 (w), 1104 (s), 1045 (m), 896 (w), 743 (m), 701 (s), 686 (m), 622 (w), 575 (s), 499 (s), 431 (w) cm<sup>-1</sup>.

**Cu<sub>4</sub>(SSiPh<sub>3</sub>)<sub>4</sub> (9). Method 1.** A solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) (0.27 g, 0.72 mmol) in CH<sub>3</sub>CN (15 mL) was added to a slurry of **3a** (0.26 g, 0.36 mmol) in CH<sub>3</sub>CN (10 mL). The solution was stirred at room temperature for 15 min, during which time a colorless crystalline solid precipitated. The resulting solid was isolated by decantation. Recrystallization from toluene yielded **9** as colorless crystals (0.21 g, 81%).

**Method 2.** Addition of a CH<sub>3</sub>CN (25 mL) solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) (1.18 g, 3.17 mmol) into [Ph<sub>3</sub>SiSLi(thf)]<sub>4</sub> (1.19 g, 0.80 mmol) in toluene (25 mL) followed by a workup analogous to method 1 produced 0.83 g of **9** in 73% yield. Anal. Calcd for C<sub>72</sub>H<sub>60</sub>Cu<sub>4</sub>S<sub>4</sub>Si<sub>4</sub>: C, 60.90; H, 4.26; S, 9.03. Found: C, 60.82; H, 4.21; S, 8.76. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.44 (m, 24H, Ph), 7.36 (m, 11H, Ph), 7.21 (m, 19H, Ph). IR (Nujol): 1586 (w), 1426 (s), 1302 (w), 1260 (w), 1186 (w), 1109 (s), 1029 (w), 997 (w), 850 (w), 738 (m), 708 (s), 696 (s), 681 (m), 620 (w), 542 (s), 533 (s), 501 (s), 490 (s), 429 (m) cm<sup>-1</sup>. UV-visible (λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), CH<sub>2</sub>Cl<sub>2</sub>): 284 sh (19000), 270 sh (21000).

**Reaction of Co(SSiPh<sub>3</sub>)<sub>2</sub>(tmeda) with (NBu<sub>4</sub>)F.** To a mixture of **5** (0.29 g, 0.38 mmol) in THF (20 mL) and PPh<sub>3</sub> (0.20 g, 0.76 mmol) in THF (10 mL) was added slowly (NBu<sub>4</sub>)F (0.75 mL, 1.0 M THF solution). The deep blue solution immediately turned black. After being stirred for 2 h, the solution was evaporated to dryness. The remaining oil was extracted with CH<sub>3</sub>CN and the solvent was removed. To the residue was added toluene and the mixture was centrifuged to remove insoluble materials. After evaporation, the resulting solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> (7 mL) and Et<sub>2</sub>O was

**Table 1.** Crystallographic Data for Compounds **1**, **3a–d**, **4–6**, **8**, and **9**

	<b>1</b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d·CH<sub>2</sub>Cl<sub>2</sub></b>
empirical formula	C <sub>48</sub> H <sub>66</sub> Fe <sub>2</sub> N <sub>2</sub> S <sub>2</sub> Si <sub>6</sub>	C <sub>40</sub> H <sub>36</sub> FeN <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>54</sub> H <sub>56</sub> FeN <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>48</sub> H <sub>64</sub> FeP <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>43</sub> H <sub>48</sub> Cl <sub>2</sub> FeN <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>
fw	1015.39	720.88	909.19	879.12	839.91
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>C</i> c (No. 9)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
<i>a</i> /Å	12.1281(7)	8.875(2)	12.713(1)	13.732(3)	14.243(9)
<i>b</i> /Å	16.2285(3)	22.64(1)	18.553(5)	13.906(5)	16.064(9)
<i>c</i> /Å	15.2438(5)	18.723(4)	10.814(2)	13.303(4)	10.451(4)
α/deg			92.85(2)	103.39(2)	92.06(4)
β/deg	114.055(2)	91.12(2)	98.68(1)	103.57(2)	100.20(3)
γ/deg			103.67(1)	88.09(2)	66.42(5)
<i>V</i> /Å <sup>3</sup>	2739.7(2)	3761.1(2)	2440.3(9)	2401.7(1)	2155.2(2)
<i>Z</i>	2	4	2	2	2
μ(Mo Kα)/cm <sup>-1</sup>	7.68	6.05	4.81	5.48	6.58
total data collected	6518	3325	7650	7157	7090
reflns with [ <i>I</i> > 3σ( <i>I</i> )]	3591	3142	6363	5021	6158
<i>R</i>	0.051	0.072	0.061	0.052	0.071
<i>R</i> <sub>w</sub>	0.075	0.093	0.084	0.077	0.120

	<b>4·CH<sub>2</sub>Cl<sub>2</sub></b>	<b>5·2CH<sub>2</sub>Cl<sub>2</sub></b>	<b>6·2CH<sub>2</sub>Cl<sub>2</sub></b>	<b>8</b>	<b>9</b>
empirical formula	C <sub>43</sub> H <sub>48</sub> Cl <sub>2</sub> MnN <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>44</sub> H <sub>50</sub> Cl <sub>4</sub> N <sub>2</sub> CoS <sub>2</sub> Si <sub>2</sub>	C <sub>44</sub> H <sub>50</sub> Cl <sub>4</sub> N <sub>2</sub> NiS <sub>2</sub> Si <sub>2</sub>	C <sub>52</sub> H <sub>70</sub> Cl <sub>4</sub> Fe <sub>2</sub> N <sub>2</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>72</sub> H <sub>60</sub> Cu <sub>4</sub> S <sub>4</sub> Si <sub>4</sub>
fw	839.00	927.93	927.70	1096.94	1420.09
cryst syst	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> 1̄ (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 1̄ (No. 2)	12.308(5)
<i>a</i> /Å	14.359(7)	35.8012(10)	35.806(6)	10.855(2)	12.308(5)
<i>b</i> /Å	16.100(8)	11.0545(6)	11.0410(8)	13.914(5)	13.154(2)
<i>c</i> /Å	10.616(5)	27.8316(8)	27.789(5)	9.983(3)	11.090(4)
α/deg	92.23(4)			94.42(4)	98.06(20)
β/deg	100.07(3)	122.6191(8)	122.860(7)	102.93(2)	109.63(2)
γ/deg	66.06(4)			108.65(2)	96.91(2)
<i>V</i> /Å <sup>3</sup>	2207.1(2)	9277.4(6)	9227.9(2)	1374.4(8)	1647.2(1)
<i>Z</i>	2	8	8	1	1
μ(Mo Kα)/cm <sup>-1</sup>	6.00	7.74	8.27	8.76	15.15
total data collected	5998	43436	4629	4188	6084
reflns with [ <i>I</i> > 3σ( <i>I</i> )]	3709	5052	4604	3128R	3990
<i>R</i>	0.097	0.056	0.061	0.062	0.036
<i>R</i> <sub>w</sub>	0.160	0.079	0.093	0.084	0.052

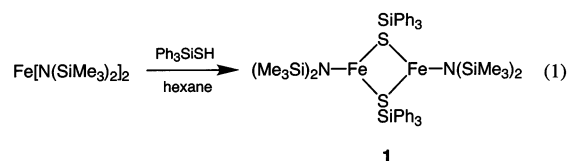
layered. Over 10 days, black crystals and a dark-brown paste were formed. The resulting mixture was washed with CH<sub>3</sub>CN and Et<sub>2</sub>O. Black prisms of Co<sub>6</sub>S<sub>8</sub>(PPh<sub>3</sub>)<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**10**·CH<sub>2</sub>Cl<sub>2</sub>, 13 mg, 9%) were separated manually. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.2–6.8 (m, 90H, Ph), 5.29 (s, 1H, CH<sub>2</sub>Cl<sub>2</sub>). IR (Nujol): 3052 (m), 1585 (w), 1569 (w), 1479 (m), 1432 (s), 1186 (w), 1090 (m), 1071 (w), 1028 (w), 998 (w), 741 (m), 691 (s), 618 (w), 524 (s), 508 (m), 496 (w), 435 (w) cm<sup>-1</sup>. UV–visible (λ<sub>max</sub>, nm, CH<sub>2</sub>Cl<sub>2</sub>): 492 sh, 432, 345, 266 sh.

**X-ray Crystal Structure Determination.** Crystallographic data are summarized in Table 1. Diffraction data were collected on Rigaku AFC7-MSC/ADSC Quantum1 CCD (for **1** at 193 K), R-Axis-4 (for **3a–d**, **4**, and **6** at 173 K), Mercury CCD (for **5** at 193 K), and AFC5S (for **9** at room temperature) diffractometers, using monochromated Mo K radiation. Crystals of **1**, **3a–d**, **4**, **5**, and **6** were coated in oil and cooled under a cold nitrogen stream, while those of **9** were mounted in glass capillaries and sealed under argon.

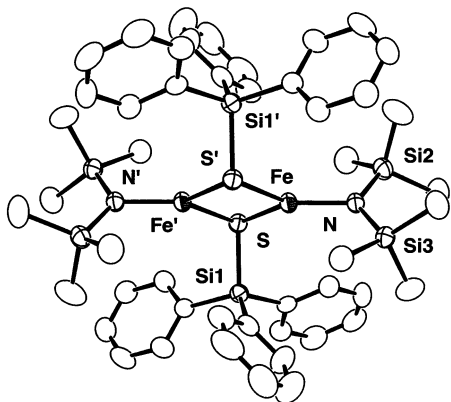
The structures were solved with use of direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on *F* by using the CrystalStructure package. Anisotropic refinement was applied to all non-hydrogen atoms, and all the hydrogen atoms were put at calculated positions. For **8**, the methylene carbons of the NEt<sub>4</sub><sup>+</sup> counteranions are disordered with the occupancy factors of 50:50. In the case of **3d**, **4**, **5**, and **6**, atoms of the crystal solvents (CH<sub>2</sub>Cl<sub>2</sub>) were disordered and isotropically refined, and no hydrogen atoms of CH<sub>2</sub>Cl<sub>2</sub> were included. Additional crystallographic data are given in the Supporting Information.

## Results and Discussion

**Reaction of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with Ph<sub>3</sub>SiSH.** Addition of 1 equiv of Ph<sub>3</sub>SiSH to a hexane solution of Fe[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> at room temperature caused an immediate color change from light green to brown, and a lemon-yellow solid of [Fe{N(SiMe<sub>3</sub>)<sub>2</sub>}(μ-SSiPh<sub>3</sub>)]<sub>2</sub> (**1**) precipitated. The amide–thiolato complex was isolated in 74% yield as an extremely air-sensitive lemon-yellow crystalline powder, which was insoluble in aliphatic hydrocarbon solvents. The IR spectrum of **1** exhibited characteristic bands arising from bis(trimethylsilyl)amide and triphenylsilanethiolato ligands, and its dimeric structure was revealed by X-ray structural analysis.



The X-ray derived molecular structure of **1** is illustrated in Figure 1, and selected bond distances and angles are given in Table 2. The two Fe(II) centers are bridged by two silanethiolato ligands, and a crystallographic inversion center resides in the center of the molecule. Being bound to one terminal amide ligand, each Fe atom assumes a trigonal planar geometry, where the sum of the angles at the Fe atom is 360.0°. The average Fe–S bond distance of 2.343 Å and



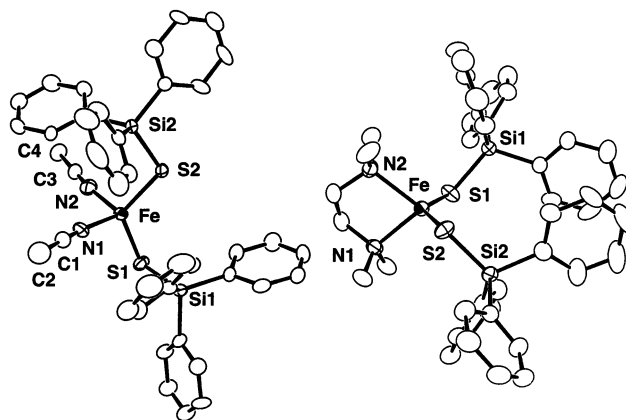
**Figure 1.** Structure of  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-SSiPh}_3)_2]$  (**1**) showing 50% probability ellipsoids.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) in  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}(\text{SSiPh}_3)_2]$  (**1**)

Fe–Fe'	2.979(1)	Fe–S	2.340(1)
Fe–S'	2.345(1)	Fe–N	1.892(3)
S–Si1	2.160(2)	N–Si2	1.714(4)
N–Si3	1.730(4)		
S–Fe–S'	101.04(4)	Fe–S–Fe'	78.96(4)
Fe–S–Si	107.76(6)	Fe'–S–Si	109.79(6)
N–Fe–S	126.7(1)	N–Fe–S'	132.24(12)
Fe–N–Si2	120.5(2)	Fe–N–Si3	114.8(2)
Si2–N–Si3	124.5(2)		

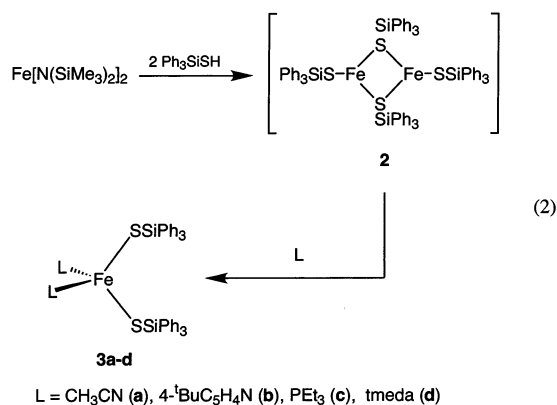
the Fe–N distance of 1.892(3) Å are both comparable to those of Fe(II) complexes with bridging thiolates,  $[\text{Fe}_2(\text{SC}_6\text{H}_2\text{-}2,4,6\text{-}^i\text{Bu}_3)_4]$  (Fe–S = 2.366 Å) and  $\text{Fe}_3(\text{SC}_6\text{H}_2\text{-}2,4,6\text{-}^i\text{Pr}_4)[\text{N}(\text{SiMe}_3)_2]_2$  (Fe–S = 2.343, 2.364 Å; Fe–N = 1.882 Å).<sup>11</sup> The amide nitrogen is also nearly planar as is evidenced by the sum of the angles (359.8°) at the nitrogen atom. The planarity at the amide nitrogen may be due to the steric bulk of the silyl substituents and/or Fe–N  $\pi$  bonding interactions. Each  $\text{FeNSi}_2$  plane is twisted from the  $\text{Fe}_2\text{S}_2$  plane, where the dihedral angle between the planes is 61.1°. The triphenylsilyl substituents on the thiolate sulfur atoms are oriented up and down from the  $\text{Fe}_2\text{S}_2$  plane. The *transoid* conformation of triphenylsilyl substituents and the twist of the  $\text{FeNSi}_2$  and  $\text{Fe}_2\text{S}_2$  planes are probably caused by the steric congestion among the silyl groups of  $\text{Ph}_3\text{SiS}$  and  $(\text{Me}_3\text{Si})_2\text{N}$  ligands. The Fe–Fe distance of 2.979(1) Å is significantly shorter than those of the related Fe(II) complexes,  $\text{Fe}_2(\text{SC}_6\text{H}_2\text{-}2,4,6\text{-}^i\text{Bu}_3)_4$  [3.554 Å] and  $\text{Fe}_3(\text{SC}_6\text{H}_2\text{-}2,4,6\text{-}^i\text{Pr}_3)_4[\text{N}(\text{SiMe}_3)_2]_2$  [3.243(1), 3.354(1) Å],<sup>11</sup> which suggests Fe–Fe bonding interactions in the structure of **1**. The acute Fe–S–Fe angle of 78.96(4)° supports this argument.

When  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  was reacted in hexane with 2 equiv of  $\text{Ph}_3\text{SiSH}$ , a large amount of a light yellow powder was formed. The IR spectrum of the product shows only the bands characteristic of the triphenylsilanethiolato ligand, and the Fe:S ratio was estimated to be 1:2 by the X-ray fluorescence microanalysis. We tentatively formulate the product as  $[\text{Fe}(\text{SSiPh}_3)(\mu\text{-SSiPh}_3)_2]$  (**2**). Attempts to grow crystals suitable for X-ray study have not been successful. However, complex **2** was found to react instantaneously with Lewis bases, and



**Figure 2.** Structures of  $\text{Fe}(\text{SSiPh}_3)_2(\text{CH}_3\text{CN})_2$  (**3a**, left) and  $\text{Fe}(\text{SSiPh}_3)_2(\text{tmeda})$  (**3d**, right) showing 50% probability ellipsoids.

giving four-coordinate Lewis base adducts,  $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$  [ $\text{L} = \text{CH}_3\text{CN}$  (**3a**),  $4\text{-}^i\text{BuC}_5\text{H}_4\text{N}$  (**3b**),  $\text{PEt}_3$  (**3c**);  $(\text{L})_2 = \text{tmeda}$  (**3d**)]. Complexes **3b–d** were also prepared by the reactions of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  with triphenylsilanethiol in  $\text{Et}_2\text{O}$  or hexane containing the corresponding Lewis bases. According to the X-ray structural analysis, these four Lewis base adducts are all monomeric, and their combustion analyses are consistent with the formulation. They were isolated in 70–90% yields as either colorless (**3a**, **3c**, **3d**) or yellow (**3b**) crystalline solids. Their broad NMR signals indicate that **3a–d** are paramagnetic. The IR spectrum of **3a** shows two  $\text{C}\equiv\text{N}$  stretching bands at 2304 and 2276  $\text{cm}^{-1}$ . These bands are slightly shifted to higher frequencies relative to that of free acetonitrile (2250  $\text{cm}^{-1}$ ), which has been observed for  $\eta^1$ -coordinated acetonitrile molecules.<sup>12</sup>



The crystal structures of all the base adducts, **3a–d**, were determined by X-ray analysis. They have a common slightly distorted tetrahedral geometry at Fe, which is coordinated by two silanethiolate sulfur atoms and two base atoms (N or P). Since their structures are very much alike, only those of **3a** and **3d** are shown in Figure 2. Selected geometrical parameters of **3a–d** are compared in Table 3. Although there is little difference in their Fe–S distances (2.29–2.32 Å), which are similar to those of the related thiolato complex  $\text{Fe}(\text{S-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(1\text{-methylimidazole})_2$  (av 2.316 Å),<sup>13</sup> the S–Fe–S angles vary notably from 122° to 136°. The small

(11) (a) Power, P. P.; Shoner, S. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 330–332. (b) MacDonnell, F. M.; Ruhlandt-Senge, K.; Ellison, J. J.; Holm, R. H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 1815–1822.

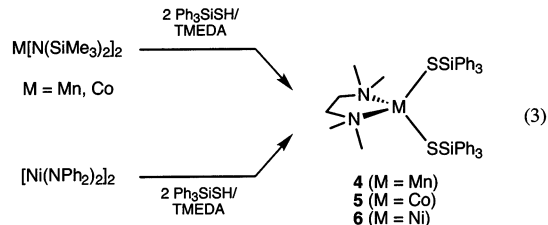
(12) Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. J. *Chem. Soc., Dalton Trans.* **2001**, 1723–1753.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) in  $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$  [ $\text{L} = \text{CH}_3\text{CN}$  (**3a**), 4-*t*-Bu- $\text{C}_5\text{H}_4\text{N}$  (**3b**),  $\text{PEt}_3$  (**3c**) and  $\text{M}(\text{SSiPh}_3)_2(\text{tmeda})$  [ $\text{M} = \text{Fe}$  (**3d**),  $\text{Mn}$  (**4**),  $\text{Co}$  (**5**),  $\text{Ni}$  (**6**)]

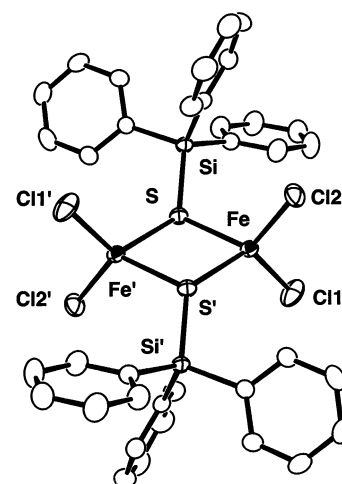
	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>4</b>	<b>5</b>	<b>6</b>
M–S1	2.322(2)	2.303(1)	2.311(2)	2.326(1)	2.381(3)	2.277(2)	2.271(2)
M–S2	2.294(2)	2.304(1)	2.304(2)	2.321(2)	2.390(3)	2.271(1)	2.276(2)
S1–Si1	2.106(2)	2.101(1)	2.104(2)	2.103(2)	2.107(5)	2.102(2)	2.100(2)
S2–Si2	2.109(2)	2.100(1)	2.110(2)	2.103(2)	2.095(4)	2.099(2)	2.110(2)
M–L	2.058(7)	2.116(3)	2.458(2)	2.191(4)	2.27(1)	2.118(4)	2.085(5)
	2.074(7)	2.115(3)	2.486(2)	2.218(4)	2.246(9)	2.141(5)	2.113(5)
M–S1–Si1	105.07(9)	119.31(6)	118.85(7)	111.53(7)	109.9(2)	111.61(7)	110.95(9)
M–S2–Si2	110.73(8)	117.42(6)	116.95(8)	109.30(7)	110.2(2)	113.37(8)	109.75(7)
S1–M–S2	122.50(7)	128.77(4)	135.21(6)	136.08(5)	139.0(1)	133.56(6)	140.82(7)
L–M–L	102.3(3)	91.3(1)	108.78(6)	82.9(2)	82.4(4)	87.0(2)	87.7(2)
S–M–L	110.2(2)	113.89(9)	105.17(7)	100.0(1)	104.7(3)	101.8(1)	110.2(2)
	110.6(2)	101.62(9)	96.58(6)	109.2(1)	108.4(3)	111.9(1)	98.4(2)
	102.9(2)	102.75(9)	101.56(6)	109.9(1)	108.4(3)	110.7(1)	99.4(2)
	106.0(2)	112.45(9)	107.80(7)	105.7(1)	99.4(3)	102.3(1)	108.3(2)

bite angle of  $82.9(8)^\circ$  for chelating TMEDA in **3d**, relative to the  $\text{L–Fe–L}$  angles in **3a–c**, is accompanied by the large  $\text{S–Fe–S}$  angle. It seems that steric repulsion between silanethiolate and L (or TMEDA) determines the  $\text{S–Fe–S}$  bond angle. In the case of **3c**, the long  $\text{Fe–P}$  bonds reduce steric congestion around Fe, thereby allowing the  $\text{S–Fe–S}$  angle to open up. Another distortion from the ideal tetrahedral geometry can be seen in the dihedral angle between the  $\text{FeS}_2$  plane and the plane defined by two base atoms (N or P) and Fe, which are  $88.8^\circ$  for **3a**,  $81.9^\circ$  for **3b**,  $85.1^\circ$  for **3c**, and  $84.6^\circ$  for **3d**.

**Synthesis of  $\text{M}(\text{SSiPh}_3)_2(\text{tmeda})$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ ).** A series of mononuclear iron(II) silanethiolato complexes,  $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$ , were synthesized in high yield by the reactions of  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  with triphenylsilanethiol in the presence of Lewis bases. These reactions proceeded smoothly, and the products were easily purified. On the other hand, the reactions of  $\text{FeCl}_2$  with  $[\text{Ph}_3\text{SiSLi}(\text{thf})_4]$  and Lewis bases were not straightforward and the yields of silanethiolato complexes were low. Since the protonolysis of the iron bisamide complex with silanethiol seems to be a superior route to the silanethiolato complexes, we applied this method to the preparation of other transition metal complexes of the type  $\text{M}(\text{SSiPh}_3)_2(\text{tmeda})$  [ $\text{M} = \text{Mn}$  (**4**),  $\text{Co}$  (**5**),  $\text{Ni}$  (**6**)]. Thus, treatment of  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{M} = \text{Mn}, \text{Co}$ ) in the presence of TMEDA followed by standard workup afforded **4** and **5** as colorless and blue crystals, respectively. From the analogous reaction of  $[\text{Ni}(\text{NPh}_2)_2]_2$  we isolated **6** as yellow crystals. The  $^1\text{H}$  NMR spectra of **4–6** in  $\text{CDCl}_3$  showed broad resonances, implying that these complexes are paramagnetic at room temperature. Their IR spectra are similar to that of **3d**, and the combustion analyses were all consistent with the common formulation  $\text{M}(\text{SSiPh}_3)_2(\text{tmeda})$ .



(13) Forde, C. E.; Lough, A. J.; Morris, R. H.; Ramachandran, R. *Inorg. Chem.* **1996**, *35*, 2747–2751.

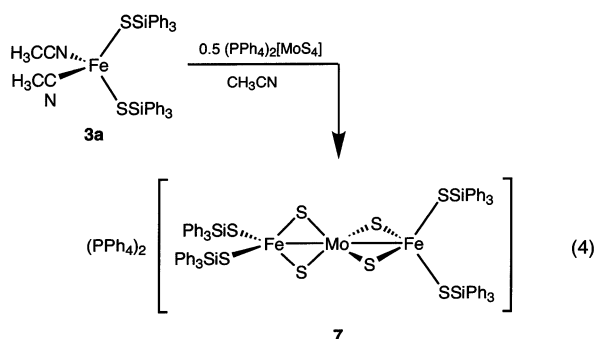
**Figure 3.** Structure of the anion part of  $(\text{NEt}_4)_2[\text{Fe}_2(\text{SSiPh}_3)_2\text{Cl}_4]$  (**8**) showing 50% probability ellipsoids.

According to the X-ray diffraction analysis, the manganese complex **4** was crystallized in the triclinic  $P\bar{1}$  space group, being isomorphic to **3d**, while **5** and **6** were crystallized in the monoclinic  $C2/c$  space group. Crystals of **3d** and **4** contain one  $\text{CH}_2\text{Cl}_2$  molecule in per asymmetric unit, and those of **5** and **6** contain two  $\text{CH}_2\text{Cl}_2$  molecules. The molecular structures of **4**, **5**, and **6**, are very similar to that of **3d** shown in Figure 3, and their geometrical parameters are added to Table 3. In a distorted tetrahedral geometry, the dihedral angles between the  $\text{MN}_2$  and  $\text{MS}_2$  planes in **3d** ( $84.6^\circ$ ) and **4** ( $84.9^\circ$ ) are slightly larger than those of **5** ( $83.0^\circ$ ) and **6** ( $82.4^\circ$ ). The  $\text{N–M–N}$  angles of **3d** [ $82.9(2)^\circ$ ] and **4** [ $82.4(4)^\circ$ ] are smaller than those of **5** [ $87.0(2)^\circ$ ] and **6** [ $87.7(2)^\circ$ ], and the  $\text{S–M–S}$  angles are in the range between  $133.56(6)^\circ$  and  $140.82(7)^\circ$ . No obvious correlation can be seen between these slight distortions from tetrahedral geometry and steric effects. The  $\text{M–N}$  distances decrease in the following order, **4** ( $\text{Mn}$ ,  $2.26 \text{ \AA}$  av) > **3d** ( $\text{Fe}$ ,  $2.205 \text{ \AA}$ ) > **5** ( $\text{Co}$ ,  $2.130 \text{ \AA}$ ) > **6** ( $\text{Ni}$ ,  $2.099 \text{ \AA}$ ), paralleling the ionic radii of the metal atoms. Although the  $\text{M–S}$  distances in **4** ( $2.386 \text{ \AA}$ ), **3d** ( $2.324 \text{ \AA}$ ), and **5** ( $2.274 \text{ \AA}$ ) follow the same trend, the average  $\text{Ni–S}$  distance in **6** is as long as the  $\text{Co–S}$  distance of **5**. The reason for the long  $\text{Ni–S}$  bond in **6** is not clear.<sup>14</sup>

**Reactions of Bis(triphenylsilanethiolato) Complexes.** The stability of the iron bis(triphenylsilanethiolato) com-

plexes  $\text{Fe}(\text{SSiPh}_3)_2(\text{L})_2$  in THF solution varies depending on the lability of the ligand L. The acetonitrile and pyridine adducts, **3a** and **3b**, decompose in THF at room temperature within several hours to form an insoluble black solid, while degradation of the phosphine adduct **3c** occurs more slowly and its colorless THF solution turns brown overnight. Attempts to characterize the degradation products have not been successful. During the degradation process, the ligands L might be replaced by THF molecules to produce an unstable intermediate  $\text{Fe}(\text{SSiPh}_3)_2(\text{thf})_2$ , which then leads to unidentified polymers/oligomers. On the other hand, the tmeda adduct **3d** did not show any sign of decomposition in THF at room temperature for 4 days, as monitored by UV–visible spectroscopy. The related neutral four-coordinate Fe(II) complexes,  $\text{Fe}(\text{E}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(1\text{-methylimidazole})_2$  (E = S, Se)<sup>13</sup> and  $\text{Fe}(\text{OCPh}_3)_2(\text{thf})_2$ ,<sup>15</sup> are known to be stable in solution. Thus, the instability of **3a–c** in THF may have something to do with the reactivity of the silicon–sulfur bond upon dissociation of L (and THF).

The facile dissociation of acetonitrile from **3a** prompted us to examine its reactions with  $(\text{PPh}_4)_2[\text{MoS}_4]$ ,  $(\text{NEt}_4)_2[\text{FeCl}_4]$ , and  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ . The treatment of **3a** with 0.5 equiv of  $(\text{PPh}_4)_2[\text{MoS}_4]$  in  $\text{CH}_3\text{CN}$  proceeded smoothly, and an  $\text{Fe}_2\text{Mo}$  cluster,  $(\text{PPh}_4)_2[\text{MoS}_4\{\text{Fe}(\text{SSiPh}_3)_2\}_2]$  (**7**), was isolated as black crystals in 71% yield after recrystallization



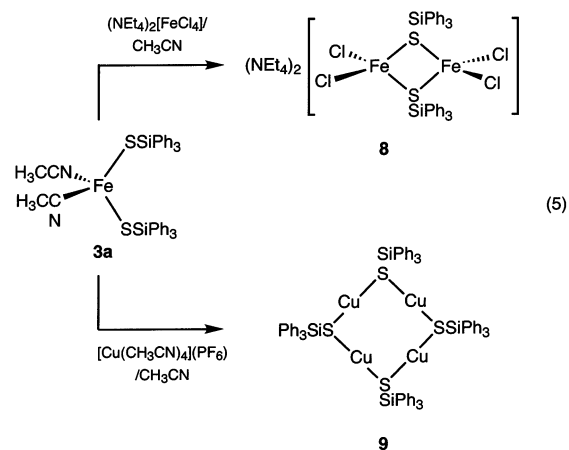
of the crude product from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . The IR spectrum of **7** shows a weak absorption at  $413\text{ cm}^{-1}$  assignable to the bridging Mo–S stretching vibrations, and no Mo=S stretching bands were observed. While the X-ray structure analysis of **7** was carried out,<sup>16</sup> the poor quality of the crystal prevents us from discussing its metric parameters in detail. However, the data clearly show a linear Fe–Mo–Fe cluster, which is similar to the core geometry of  $[\text{MoS}_4(\text{FeCl}_2)_2]^{2-}$ .<sup>17</sup> Each iron

**Table 4.** Selected Bond Distances (Å) and Angles (deg) in  $(\text{NEt}_4)_2[\text{Fe}_2(\text{SSiPh}_3)_2\text{Cl}_4]$  (**8**)

Fe–Fe'	3.589(2)	Fe–S	2.416(2)
Fe–S'	2.450(2)	Fe–Cl1	2.259(2)
Fe–Cl2	2.257(2)	S–Si	2.116(2)
S–Fe–S'	84.92(6)	Fe–S–Fe'	95.08(6)
Fe–S–Si	116.34(8)	Fe'–S–Si	128.82(9)
Cl1–Fe–Cl2	115.06(7)		

atom is tetrahedrally coordinated by two triphenylsilane-thiolato ligands and two sulfur atoms of the  $\text{MoS}_4$  unit.

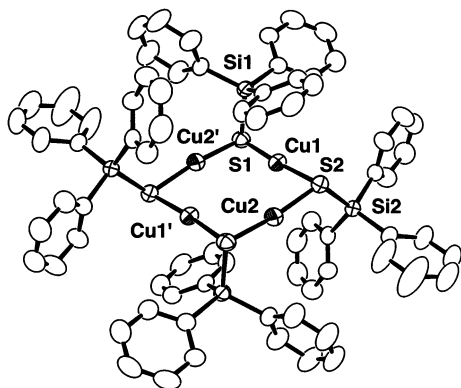
Treatment of **3a** with 1 equiv of  $(\text{NEt}_4)_2[\text{FeCl}_4]$  in  $\text{CH}_3\text{CN}$  immediately gave a brown homogeneous solution. Considering the facile silicon–sulfur bonds in **3a**, we anticipated that this reaction might proceed via silicon–sulfur bond cleavage to give a sulfido cluster of iron. However, a dinuclear chlorido/triphenylsilanethiolato complex,  $(\text{NEt}_4)_2[\text{Fe}_2(\text{SSiPh}_3)_2\text{Cl}_4]$  (**8**), was isolated as colorless crystals in 91% yield, as a result of ligand redistribution between **3a** and  $(\text{NEt}_4)_2[\text{FeCl}_4]$ . The IR spectrum indicated the presence of the tetraethylammonium cation and the triphenylsilane-thiolate group. The combustion analysis is consistent with the formulation of **8**, and the dinuclear structure was revealed by X-ray diffraction analysis.



The structure of the anion of **8** is shown in Figure 3, and Table 4 lists selected bond distances and angles. A crystallographic inversion center lies in the middle of the  $\text{Fe}_2\text{S}_2$  core. The two  $\text{Fe}^{\text{II}}$  centers assume a distorted tetrahedral coordination geometry, and are bridged by two silanethiolate sulfurs. Two chlorides are bound to each Fe center, and the dihedral angle between the  $\text{FeS}_2$  and  $\text{FeCl}_2$  planes is  $83.2^\circ$ . The two triphenylsilyl groups are oriented trans to each other to avoid steric repulsion. The  $\text{Fe}_2\text{S}_2$  core is planar with an Fe–Fe separation of  $3.589(2)\text{ Å}$ , which is longer by  $0.61\text{ Å}$  than that of **1**, and there is no Fe–Fe bonding interaction. The large Fe–S–Fe angle of  $95.08(6)^\circ$  is consistent with the absence of the Fe–Fe bonding. In the  $\text{Fe}_2\text{S}_2$  core, there are two sets of unequal Fe–S bond distances differing by  $0.034\text{ Å}$ . The average Fe–S distance of  $2.433\text{ Å}$  is obviously longer than that of **1** ( $2.343\text{ Å}$ ), because of the four-coordinated nature of the Fe centers for **8**.

When **3a** was treated with 2 equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  in  $\text{CH}_3\text{CN}$ , a ligand transfer reaction took place, and a cyclic tetranuclear complex  $\text{Cu}_4(\text{SSiPh}_3)_4$  (**9**) was obtained as

- (14) In a series of tetrahedral tetrakis-thiolato complexes,  $(\text{PPh}_4)_2[\text{M}(\text{SPh})_4]$ , the M–S distances decrease substantially in going from Mn (av  $2.442\text{ Å}$ ) to Fe ( $2.353\text{ Å}$ ) to Co ( $2.328\text{ Å}$ ) to Ni ( $2.288\text{ Å}$ ). (a) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932–1934. (b) Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350–3362.
- (15) Bartlett, R. A.; Ellison, J. J.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, *30*, 2888–2894.
- (16) Crystal data for **7**· $2\text{CH}_2\text{Cl}_2$ :  $\text{C}_{122}\text{H}_{104}\text{S}_8\text{Si}_4\text{P}_2\text{Cl}_4\text{Fe}_2\text{Mo}$ ,  $M = 2350.38$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 17.573(5)\text{ Å}$ ,  $b = 26.297(3)\text{ Å}$ ,  $c = 27.633(9)\text{ Å}$ ,  $\beta = 93.59(3)^\circ$ ,  $V = 12744.3(5)\text{ Å}^3$ ,  $Z = 4$ ,  $R = 0.167$ ,  $R_w = 0.204$ .
- (17) Coucouvanis, D.; Baenziger, N. C.; Simhon, E. D.; Stremple, P.; Swenson, D.; Simopoulos, A.; Kostikas, A.; Petrouleas, V.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1980**, *102*, 1732–1734.



**Figure 4.** Structure of  $\text{Cu}_4(\text{SSiPh}_3)_4$  (**9**) showing 50% probability ellipsoids.

**Table 5.** Selected Bond Distances (Å) and Angles (deg) in  $\text{Cu}_4(\text{SSiPh}_3)_4$  (**9**)

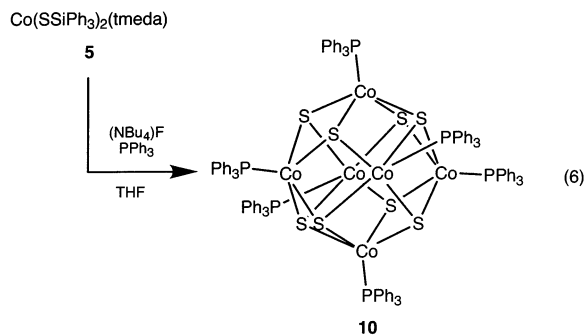
Cu1–Cu2	2.852(1)	Cu1–Cu2'	3.027(1)
Cu1–S1	2.168(1)	Cu1–S2	2.168(1)
Cu2–S2	2.157(1)	Cu2–S1'	2.160(1)
S1–Si1	2.153(2)	S2–Si2	2.142(2)
Cu1–Cu2–Cu1'	87.64(4)	Cu2–Cu1–Cu2'	92.36(4)
S1–Cu1–S2	174.18(4)	S1'–Cu2–S2	167.13(4)
Cu1–S1–Cu2'	88.79(5)	Cu1–S2–Cu2	82.50(5)
Cu1–S1–Si1	92.56(6)	Cu2'–S1–Si1	102.25(6)
Cu1–S2–Si2	100.03(6)	Cu2–S2–Si2	115.10(6)

colorless crystals. The soft silanethiolato ligand appears to prefer the softer Cu(I) center to Fe(II). The X-ray derived structure is shown in Figure 4, and selected bond distances and angles are listed in Table 5. The molecule consists of an eight-membered  $\text{Cu}_4\text{S}_4$  ring, and two halves of the tetrameric structure are related by an inversion center. Thus the  $\text{Cu}_4$  core is crystallographically planar, and the sulfur atoms are slightly off the  $\text{Cu}_4$  plane ( $-0.26$  Å for S1 and  $+0.22$  Å for S2). This planar arrangement of four copper atoms resembles the geometry of  $[\text{Cu}(\text{SR})_4]$  [ $\text{R} = \text{C}_6\text{H}_3\text{-2,6-(SiMe}_3)_2, \text{Si(O}^t\text{Bu)}_3$ ].<sup>5f,18</sup> The two triphenylsilyl groups of adjacent silanethiolato ligands are situated above the  $\text{Cu}_4\text{S}_4$  plane, and the other two groups are below the  $\text{Cu}_4\text{S}_4$  plane. The S–Cu–S angles slightly deviate from linearity with the average being  $170.66^\circ$ , while the average Cu–S–Cu angle is  $85.64^\circ$ . The  $\text{Cu}_4$  square geometry is slightly distorted in such a way that two Cu–Cu distances [ $2.852(1)$  Å] are shorter than the other two [ $3.027(1)$  Å]. It is also worthy to note that the Si–S bonds of the bridging silanethiolate ligands (av  $2.143$  Å for **1**, **8**, and **9**) are longer than those of

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the terminal silanethiolates (av  $2.104$  Å for **3a–d**, **4**, **5**, and **6**). The elongation of the Si–S bond implies that the S–Si  $p\pi-d\pi$  overlap interactions are smaller for the bridging silanethiolates, and that the  $\text{Si}^{\delta+}-\text{S}^{\delta-}$  ionic bond character increases.

Finally, we attempted to induce an S–Si bond cleaving reaction of the Co complex, **5**, with  $(\text{NBu}_4)\text{F}$ . Thus, when **5** was treated with  $(\text{NBu}_4)\text{F}$  in THF in the presence of  $\text{PPh}_3$ , the solution immediately darkened to black. Recrystallization of the crude product from  $\text{CH}_2\text{Cl}_2$  afforded the known hexanuclear cobalt–sulfido cluster  $\text{Co}_6(\mu_3\text{-S})_8(\text{PPh}_3)_6$  (**10**), albeit in low yield.<sup>19</sup> Compound **10** was identified by X-ray analysis, and the structure has an octahedral  $\text{Co}_6$  core, and each  $\text{Co}_3$  face is capped by  $\mu_3\text{-S}$ .<sup>20</sup> In addition, each Co atom is further coordinated by a phosphine ligand. An obvious driving force for the S–Si bond rupture of **5** is the formation of a thermally stable silicon–fluorine bond. We anticipate that the series of triphenylsilanethiolato complexes reported in this paper will be utilized, perhaps with appropriate desilylation reagents, as convenient precursors for the synthesis of metal/sulfide clusters.



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

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- (20) Crystal data for  $\text{10}\cdot\text{CH}_2\text{Cl}_2$ :  $\text{C}_{109}\text{H}_{92}\text{S}_8\text{Cl}_2\text{P}_6\text{Co}_6$ ,  $M = 2268.75$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 13.9808(8)$  Å,  $b = 15.011(2)$  Å,  $c = 15.352(1)$  Å,  $\alpha = 118.138(3)^\circ$ ,  $\beta = 114.736(3)^\circ$ ,  $\gamma = 92.432(7)^\circ$ ,  $V = 2462.1(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $R = 0.049$ ,  $R_w = 0.079$ .