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Silyl-Substituted Thioether Ligands and Their Ag(I) Complexes

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Silyl-substituted thioether ligands were prepared that differed in the identity and number of ligating groups attached to silicon and the nature of the alkyl groups on silicon. The ligand syntheses involved deprotonation of a thioether with *n*-butyllithium followed by reaction with the appropriate chlorosilane. Yields were 45−75% after purification. The majority of the ligands reacted with silver(I) triflate to give stable crystalline products in high yields that could be characterized by single-crystal X-ray crystallography. Depending on the ligand, the structures of the products ranged from discrete complexes to infinite polymeric structures. Apparent argentophilic interactions were commonly observed in the solid-state structures of the complexes (Ag−Ag = 2.909−3.196 Å).

Introduction

Recent research demonstrates that organosilicon moieties are important functional groups in ligand synthesis. A number of reasons exist for the increasing popularity of silicon in this regard. Organosilicon compounds in general are robust and relatively inert and can thus be handled freely in the laboratory. Furthermore, a large variety of silicon-containing starting materials is available at relatively low cost. From an electronic standpoint, the electron-releasing nature of a silicon atom within a molecule can alter the electron distribution within the molecule. Longer Si−X bonds (compared to C−X bonds) result in greater flexibility which can have a marked effect on strain and hence supramolecular geometry.[1] The presence of alkyl groups on silicon can increase the congestion in organosilicon ligands and thus affect binding behavior.[2] When combined with the proliferation of synthetic reactions in organosilicon chemistry, all of these factors make the incorporation of organosilicon groups into ligand structures an attractive proposition in terms of structural fine-tuning.

As a result of these attributes, silicon has played a unique and valuable role in ligand structure and design. For example, "silaplatin", a silicon-tethered analog of the antitumor drug cisplatin, demonstrated significant activity against cisplatin-resistant cancer lines,[3,4] in a study in which the authors exploited the versatility of organosilicon chemistry to easily change the substituents on silicon. In another study, silicon substituents on cyclopentadienyl ligands of metallocene complexes had a positive effect on catalytic activity for olefin polymerization.[5] Silicon has also played a major role as a *linking* moiety for cyclopentadienyl rings,[6−9] monothioether alkyl chains,[10−19] and pyridine rings[20−37] in a variety of multidentate ligand structures.

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(1) Sengupta, P.; Zhang, H.; Son, D. Y. *Inorg. Chem.* **2004**, *43*, 1828.
(2) Friesen, D. M.; Bowles, O. J.; McDonald, R.; Rosenberg, L. *J. Chem. Soc., Dalton Trans.* **2006**, 2671.
(3) Haugwitz, R. D.; Anderson, W. K.; Plowman, J.; Kaslinal, R.; Houston, D. M.; Narayanan, V. L. *Appl. Organomet. Chem.* **1990**, *4*, 375.
(4) Anderson, W. K.; Kasliwal, R.; Houston, D. M.; Wang, Y.-S.; Narayanan, V. L.; Haugwitz, R. D.; Plowman, J. *J. Med. Chem.* **1995**, *38*, 3789.
(5) Cuenca, T.; Royo, P. *Coord. Chem. Rev.* **1999**, *193−195*, 447.
(6) Prashar, S.; Antinolo, A.; Otero, A. *Coord. Chem. Rev.* **2006**, *250*, 133.
(7) Wang, B. *Coord. Chem. Rev.* **2006**, *250*, 242.
(8) Green, J. C. *Polyhedron* **2005**, *24*, 1382.
(9) Spaleck, W.; Kueber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.
(10) Yim, H. W.; Tran, L. M.; Pullen, E. E.; Rabinovich, D.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 6234.
(11) Yim, H. W.; Tran, L. M.; Dobbin, E. D.; Rabinovich, D.; Liable-Sands, L. M.; Incarvito, C. D.; Lam, K.-C.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 2211.
(12) Blackwell, W. C., III.; Bunich, D.; Concolino, T. E.; Rheingold, A. L.; Rabinovich, D. *Inorg. Chem. Commun.* **2000**, *3*, 325.
(13) Maye, M. M.; Chun, S. C.; Han, L.; Rabinovich, D.; Zhong, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 4958.
(14) Maye, M. M.; Luo, J.; Lim, I. I. S.; Han, L.; Kariuki, N. N.; Rabinovich, D.; Liu, T. B.; Zhong, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9906.
(15) Maye, M. M.; Lim, I. I. S.; Luo, J.; Rab, Z.; Rabinovich, D.; Liu, T.; Zhong, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 1519.
(16) Knorr, M.; Guyon, F.; Jourdain, I.; Kneifel, S.; Frenzel, J.; Strohmann, C. *Inorg. Chim. Acta* **2003**, *350*, 455.

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Although it is clear that many silicon-containing ligands have been reported, what is lacking is a systematic investigation that clearly demonstrates the versatile role silicon can play in ligand design. In this context, we describe the synthesis of a series of silyl-substituted ligands that differ in terms of the identity of the ligating group on silicon, the nature of the alkyl groups on silicon, and also the number of ligating groups on silicon. We also describe the complexes formed from the interactions of these ligands with silver triflate (AgOTf), using single-crystal X-ray crystallography as a primary characterization tool. For ligating groups, we chose bis(methylthio)methane, 1,3-dithiane, and 1,3,5-trithiane because they (1) possess multiple binding sites, (2) are commercially available, (3) are easily deprotonated with *n*-butyllithium (*n*-BuLi), and (4) are individually known to bind to Ag(I) to form supramolecular complexes.[38−43] In order to minimize the number of variables in this study, we chose primarily a 1:1 ligand/metal ratio and did not vary the counterion. Triflate was chosen as the counterion due to the good solubility of silver triflate in a range of organic solvents, and its versatility in serving as either a relatively noncoordinating anion or as a labile ligand through the sulfonate group.[44] As a whole, this investigation demonstrates the variability in supramolecular structures that can be obtained from simple manipulations of silicon-related variables.

Experimental Section

General Comments. All starting materials were obtained commercially and used as received (including compound **2**). Solvents were degassed and dried over activated molecular sieves. Unless otherwise noted, all reactions were carried out under an atmosphere of dry dinitrogen. All NMR spectra were recorded using a 400-MHz Bruker Avance DRX multinuclear NMR spectrometer. ^{29}Si NMR spectra were obtained using standard ^{1}H broadband decoupling methods. Elemental analyses were obtained using a CE Elantech Flash EA 1112 elemental analyzer. Vapor pressure osmometry (VPO) measurements were obtained using a Wescan Instruments, Inc., model 233 instrument. Average values of repeated measurements in chloroform or acetonitrile are reported.

Preparation of (Bis-methylsulfanyl-methyl)-trimethyl-silane (1a). A 250 mL round-bottomed single-necked flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with bis(methylthio)methane (3.25 g, 30.0 mmol) and 100 mL of THF. After cooling to −40 °C, *n*-BuLi (21.1 mL of 1.9 M solution, 40.0 mmol) was added slowly by syringe. After addition, the cooling bath was removed, and the temperature was allowed to rise to 0 °C. The solution was further stirred for 30 min at 0 °C. The solution was recooled to −78 °C, and chlorotrimethylsilane (7.60 mL, 60.0 mmol) was added slowly by syringe. After the addition, the cooling bath was removed and the temperature allowed to rise to −10 °C. Cold water was then added with vigorous stirring. The upper layer and two diethyl ether extracts were dried over anhydrous $MgSO_4$. All volatiles were removed using a rotary evaporator. Further purification of the crude product by distillation gave **1a** as a clear oil in 56% yield (3.06 g, bp 82 °C/10.0 mmHg, lit[45] bp 80 °C/12 mmHg). ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 9H, SiCH_3), 2.17 (s, 6H, SCH_3), 2.87 (s, 1H). ^{1}H NMR (CD_3CN): δ 0.15 (s, 9H, SiCH_3), 2.16 (s, 6H, SCH_3), 2.95 (s, 1H). ^{13}C NMR (CD_3CN): δ −1.50 (SiCH_3), 15.29 (SCH_3), 42.01 (SCHS). ^{29}Si NMR (CD_3CN): δ 4.98.

Preparation of (Bis-methylsulfanyl-methyl)-triisopropyl-silane (1b). A 250 mL round-bottomed single-necked flask equipped with a septum, a N_2 gas inlet, and a magnetic stir bar was charged with bis(methylthio)methane (1.76 g, 16.2 mmol) and 120 mL of THF. After cooling to −40 °C, *n*-BuLi (8.50 mL of 1.9 M solution, 16.2 mmol) was added slowly by syringe. After the addition, the solution was stirred for an additional 30 min at −20 to −30 °C. The solution was then recooled to −78 °C, and triisopropylsilyl chloride (3.50 mL, 16.2 mmol) was added slowly by syringe. After the addition, the cooling bath was removed and the temperature allowed to rise to −10 °C. Cold water was then added with vigorous stirring. The upper layer and two diethyl ether extracts were dried over anhydrous $MgSO_4$. All volatiles were removed using a rotary evaporator. Distillation of the crude mixture provided **1b** as a clear colorless oil in 71% yield (3.03 g, bp 91−93 °C/0.05 mmHg). Anal. calcd for $C_{12}H_{28}S_2Si$: C, 54.48; H, 10.67. Found: C, 54.85; H, 10.61. ^{1}H

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(17) Knorr, M.; Peindy, H. N.; Guyon, F.; Sachdev, H.; Strohmann, C. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1955.

(18) Peindy, H. N.; Guyon, F.; Knorr, M.; Smith, A. B.; Farouq, J. A.; Islas, S. A.; Rabinovich, D.; Golen, J. A.; Strohmann, C. *Inorg. Chem. Commun.* **2005**, *8*, 479.

(19) Peindy, H. N.; Guyon, F.; Jourdain, I.; Knorr, M.; Schildbach, D.; Strohmann, C. *Organometallics* **2006**, *25*, 1472.

(20) Schmitz, M.; Leininger, S.; Fan, J.; Arif, A. M.; Stang, P. J. *Organometallics* **1999**, *18*, 4817.

(21) Goodgame, D. M. L.; Lickiss, P. D.; Rooke, S. J.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2001**, *324*, 218.

(22) Jung, O.-S.; Lee, Y.-A.; Kim, Y. J. *Chem. Lett.* **2002**, 1096.

(23) Jung, O. S.; Kim, Y. J.; Kim, K. M.; Lee, Y. A. *J. Am. Chem. Soc.* **2002**, *124*, 7906.

(24) Jung, O.-S.; Lee, Y.-A.; Kim, Y. J.; Hong, J. *Cryst. Growth Des.* **2002**, *2*, 497.

(25) Lee, Y. A.; Yoo, K. H.; Park, K. M.; Jung, O. S. *Bull. Korean Chem. Soc.* **2002**, *23*, 1839.

(26) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Schmitz, M.; Stang, P. J. *Inorg. Chem.* **2002**, *41*, 2903.

(27) Goodgame, D. M. L.; Lickiss, P. D.; Rooke, S. J.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2003**, *343*, 61.

(28) Miura, Y.; Nanjo, M.; Mochida, K.; Iwamoto, T.; Kira, M. *Inorg. Chem. Commun.* **2004**, *7*, 1017.

(29) Garcia, F.; Hopkins, A. D.; Humphrey, S. M.; McPartlin, M.; Rogers, M. C.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **2004**, 361.

(30) Lee, Y.-A.; Kim, S. A.; Jung, S. M.; Jung, O.-S.; Oh, Y. H. *Bull. Korean Chem. Soc.* **2004**, *25*, 581.

(31) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Kang, S. W.; Choi, S. N. *Cryst. Growth Des.* **2004**, *4*, 23.

(32) Park, B. I.; Kim, Y. J.; Lee, Y. A.; Park, K. M.; Jung, O. S. *Bull. Korean Chem. Soc.* **2004**, *25*, 1969.

(33) Dikarev, E. V.; Chernyshev, V. V.; Shpanchenko, R. V.; Filatov, A. S.; Petrukhina, M. A. *J. Chem. Soc., Dalton Trans.* **2004**, *2004*, 4120.

(34) Lee, J. W.; Kim, E. A.; Kim, Y. J.; Lee, Y. A.; Pak, Y.; Jung, O. S. *Inorg. Chem.* **2005**, *44*, 3151.

(35) Park, B. I.; Lee, J. W.; Lee, Y.-A.; Hong, J.; Jung, O.-S. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1624.

(36) Rani, N.; Sengupta, P.; Singh, A. K.; Butcher, R. J. *Polyhedron* **2007**, *26*, 5477.

(37) Na, Y. M.; Noh, T. H.; Chun, I. S.; Lee, Y.-A.; Hong, J.; Jung, O.-S. *Inorg. Chem.* **2008**, *47*, 1391.

(38) Edema, J. J. H.; Buter, J.; Van Bolhuis, F.; Meetsma, A.; Kellogg, R. M. *Inorg. Chim. Acta* **1993**, *207*, 263.

(39) Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *Inorg. Chem.* **1996**, *35*, 4432.

(40) Rasanen, T. M.; Jaaskelainen, S.; Pakkanen, T. A. *J. Organomet. Chem.* **1997**, *548*, 263.

(41) Brammer, L.; Rodger, C. S.; Blake, A. J.; Brooks, N. R.; Champness, N. R.; Cunningham, J. W.; Hubberstey, P.; Teat, S. J.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4134.

(42) Knaust, J. M.; Keller, S. W. *CrystEngComm* **2003**, *5*, 459.

(43) Green, M.; Draganjac, M.; Jiang, Y.; Nave, P. M.; Cordes, A. W.; Bryan, C. D.; Dixon, J. K.; Folkert, S. L.; Yu, C. H. *J. Chem. Cryst.* **2003**, *33*, 473.

(44) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(45) Brandsma, L. In *Preparative Polar Organometallic Chemistry 2*; Springer-Verlag: Berlin, 1990; p 70.

NMR (CDCl$_3$): δ 1.16 (d, 18H, CC*H*$_3$, ^3J = 7.4 Hz), 1.31 (m, 3H, C*H*CH$_3$, ^3J = 7.4 Hz), 2.28 (s, 6H, SC*H*$_3$), 3.15 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 11.90 (*C*CH$_3$), 18.06 (S*C*H$_3$), 19.12 (C*C*H$_3$), 40.36 (S*C*HS). ^{29}Si NMR (CDCl$_3$): δ 7.21.

Preparation of (Bis-methylsulfanyl-methyl)-dimethyl-vinyl-silane (1c). The procedure used in the preparation of **1b** was employed here, but using chlorodimethylvinylsilane. Bis(methylthio)methane (4.33 g, 40.0 mmol), *n*-BuLi (21.1 mL of 1.9 M solution, 40.0 mmol), and chlorodimethylvinylsilane (6.90 mL, 50.0 mmol) were allowed to react in 200 mL of THF. Distillation of the crude mixture provided **1c** as a clear colorless oil in 65% yield (5.01 g, bp 45−46 °C/0.025 mmHg). Anal. calcd for $C_7H_{16}S_2Si$: C, 43.69; H, 8.38. Found: C, 43.26; H, 8.04. ^{1}H NMR (CDCl$_3$): δ 0.25 (s, 6H, SiC*H*$_3$), 2.15 (s, 6H, SC*H*$_3$), 2.90 (s, 1H), 5.79 (dd, 1H, CH═C*H*H, ^2J = 3.6 Hz, ^3J = 20.2 Hz), 6.04 (dd, 1H, CH═CH*H*, ^2J = 3.6 Hz, ^3J = 14.7 Hz), 6.23 (dd, 1H, C*H*CH$_2$, ^3J = 14.7 Hz, ^3J = 20.2 Hz). ^{13}C NMR (CDCl$_3$): δ −3.52 (Si*C*H$_3$), 14.97 (S*C*H$_3$), 40.60 (S*C*HS), 133.37 (CH*C*H$_2$), 136.77 (*C*HCH$_2$). ^{29}Si NMR (CDCl$_3$): δ −3.79. ^{1}H NMR (CD$_3$CN): δ 0.21 (s, 6H, SiC*H*$_3$), 2.14 (s, 6H, SC*H*$_3$), 3.02 (s, 2H), 5.81 (dd, 1H, CH═C*H*H, ^2J = 3.8 Hz, ^3J = 20.3 Hz), 6.03 (dd, 1H, CH═CH*H*, ^2J = 3.8 Hz, ^3J = 14.8 Hz), 6.23 (dd, 1H, C*H*CH$_2$, ^3J = 14.8 Hz, ^3J = 20.3 Hz). ^{13}C NMR (CD$_3$CN): δ −3.35 (Si*C*H$_3$), 15.34 (S*C*H$_3$), 41.11 (S*C*HS), 133.79 (CH*C*H$_2$), 137.74 (*C*HCH$_2$). ^{29}Si NMR (CD$_3$CN): δ −4.03.

Preparation of (Bis-methylsulfanyl-methyl)-trivinyl-silane (1d). The procedure used in the preparation of **1b** was employed here, but using chlorotrivinylsilane. Bis(methylthio)methane (2.16 g, 20.0 mmol), *n*-BuLi (12.0 mL of 1.9 M solution, 30.0 mmol), and chlorotrivinylsilane (4.60 mL, 30.0 mmol) were allowed to react in 100 mL of THF. Distillation of the crude mixture provided **1d** as a clear colorless oil in 65% yield (2.83 g, bp 67−69 °C/0.005 mmHg). Anal. calcd for $C_9H_{16}S_2Si$: C, 49.94; H, 7.45. Found: C, 49.49; H, 7.43. ^{1}H NMR (CDCl$_3$): δ 2.19 (s, 6H, SC*H*$_3$), 3.08 (s, 1H), 5.92 (dd, 3H, CH═C*H*H, ^2J = 5.9 Hz, ^3J = 17.9 Hz), 6.25 (m, 6H, CH═CH*H*, C*H*CH$_2$). ^{13}C NMR (CDCl$_3$): δ 15.15 (S*C*H$_3$), 38.94 (S*C*HS), 132.47 (CH*C*H$_2$), 136.62 (*C*HCH$_2$). ^{29}Si NMR (CDCl$_3$): δ −21.44. ^{1}H NMR (CD$_3$CN): δ 2.32 (s, 6H, SC*H*$_3$), 3.51 (s, 1H), 5.94 (dd, 3H, CH═C*H*H, ^2J = 5.2 Hz, ^3J = 18.6 Hz), 6.27 (m, 6H, CH═CH*H*, C*H*CH$_2$). ^{13}C NMR (CD$_3$CN): δ 15.74 (S*C*H$_3$), 39.60 (S*C*HS), 133.83 (CH*C*H$_2$), 137.12 (*C*HCH$_2$). ^{29}Si NMR (CD$_3$CN): δ −21.40.

Preparation of (Bis-methylsulfanyl-methyl)-tert-butyl-dimethyl-silane (1e). The procedure used in the preparation of **1b** was employed here, but using *t*-butyldimethylsilyl chloride. Bis(methylthio)methane (2.16 g, 20.0 mmol), *n*-BuLi (10.5 mL of 1.9 M solution, 20.0 mmol), and *t*-butyldimethylsilyl chloride (3.01 g, 20.0 mmol) were allowed to react in 150 mL of THF. Distillation of the crude mixture provided **1e** as a clear colorless oil in 62% yield (2.76 g, bp 50−52 °C/0.025 mmHg). Anal. calcd for $C_9H_{22}S_2Si$: C, 48.59; H, 9.97. Found: C, 48.96; H, 10.14. ^{1}H NMR (CDCl$_3$): δ 0.13 (s, 6H, SiC*H*$_3$), 0.98 (s, 9H, CC*H*$_3$), 2.14 (s, 6H, SC*H*$_3$), 2.96 (s, 1H). ^{13}C NMR (CDCl$_3$): δ −5.55 (Si*C*H$_3$), 15.00 (S*C*H$_3$), 17.79 (*C*CH$_3$), 27.15 (C*C*H$_3$), 39.04 (S*C*HS). ^{29}Si NMR (CDCl$_3$): δ 10.52.

Preparation of (Bis-methylsulfanyl-methyl)-dimethyl-silane (1f). The procedure used in the preparation of **1b** was employed here, but using chlorodimethylsilane. Bis(methylthio)methane (3.25 g, 30.0 mmol), *n*-BuLi (12.5 mL of 2.4 M solution, 30.0 mmol), and chlorodimethylsilane (4.50 mL, 40.0 mmol) were allowed to react in 150 mL of THF. Distillation of the crude mixture provided **1f** as a clear yellow-colored oil in 62% yield (3.10 g, bp 87 °C/11 mmHg). Anal. calcd for $C_5H_{14}S_2Si$: C, 36.10; H, 8.48. Found: C, 36.17; H, 8.17. ^{1}H NMR (CDCl$_3$): δ 0.15 (d, 6H, SiC*H*$_3$, ^3J = 3.8 Hz), 2.06 (s, 6H, SC*H*$_3$), 2.87 (d, 1H, ^3J = 3.3 Hz), 3.95 (m, 1H, Si*H*, ^3J = 3.3 Hz, ^3J = 3.8 Hz). ^{13}C NMR (CDCl$_3$): δ −4.66 (Si*C*H$_3$), 14.21 (S*C*H$_3$), 38.57 (S*C*HS). ^{29}Si NMR (CDCl$_3$): δ −12.71.

Preparation of Trimethyl-1,3,5-trithian-2-yl-silane (3). 2-Lithio-1,3,5-trithiane was prepared using a combination of literature procedures.[46,47] A 500-mL two-necked round-bottomed flask containing a magnetic stirring bar was charged with 1,3,5-trithiane (2.77 g, 20.0 mmol) and 150 mL of THF. The resulting mixture was refluxed in a nitrogen atmosphere until the trithiane had dissolved. The solution was then cooled rapidly to −40 °C, causing the trithiane to precipitate as fine crystals. *n*-BuLi (10.5 mL of 1.9 M solution, 20.0 mmol) was then added slowly by a syringe. The solution was stirred and kept at −20 to −30 °C for 2 h. The solution was recooled to −78 °C, and chlorotrimethylsilane (3.80 mL, 30.0 mmol) was added slowly by a syringe. After the addition, the cooling bath was removed and the temperature allowed to rise to room temperature. Cold water was then added with vigorous stirring. The upper layer and two diethyl ether extracts were dried over anhydrous MgSO$_4$. Evaporation of the solvent provided **3** as a white solid in 75% yield (3.16 g). Mp: 70−73 °C (lit[48] mp 72−73 °C). ^{1}H NMR (CDCl$_3$): δ 0.18 (s, 9H, SiC*H*$_3$), 3.78 (d, 2H, SC*H$_a$*HS, ^2J = 14.4 Hz), 4.07 (s, 1H), 4.46 (d, 2H, SCH*H$_e$*S, ^2J = 14.4 Hz). ^{13}C NMR (CDCl$_3$): δ −3.20 (Si*C*H$_3$), 36.14 (S*C*H$_2$S), 38.15 (S*C*HS). ^{29}Si NMR (CDCl$_3$): δ 4.67. ^{1}H NMR (CD$_3$CN): δ 0.11 (s, 9H, SiC*H*$_3$), 3.77 (d, 2H, SC*H$_a$*HS, ^2J = 14.7 Hz), 4.24 (s, 1H), 4.53 (d, 2H, SCH*H$_e$*S, ^2J = 14.7 Hz). ^{13}C NMR (CD$_3$CN): δ −3.37 (Si*C*H$_3$), 36.15 (S*C*H$_2$S), 38.11 (S*C*HS). ^{29}Si NMR (CD$_3$CN): δ 4.32.

Preparation of Bis(bis-methylsulfanyl-methyl)-dimethyl-silane (4). The procedure used in the preparation of **1b** was employed here, but using dichlorodimethylsilane. Bis(methylthio)methane (3.25 g, 30.0 mmol), *n*-BuLi (15.8 mL of 1.9 M solution, 30.0 mmol), and dichlorodimethylsilane (2.40 mL, 20.0 mmol) were allowed to react in 150 mL of THF. Purification of the crude product by distillation gave **4** as a clear light-pink-colored oil in 57% yield (2.33 g, bp 95∼100 °C/0.025 mmHg). The synthesis of **4** has been reported previously without spectral characterization.[49] ^{1}H NMR (CDCl$_3$): δ 0.29 (s, 6H, SiC*H*$_3$), 2.19 (s, 12H, SC*H*$_3$), 3.26 (s, 2H). ^{13}C NMR (CDCl$_3$): δ −3.76 (Si*C*H$_3$), 15.37 (S*C*H$_3$), 39.60 (S*C*HS). ^{29}Si NMR (CDCl$_3$): δ 5.83. ^{1}H NMR (CD$_3$CN): δ 0.27 (s, 6H, SiC*H*$_3$), 2.20 (s, 12H, SC*H*$_3$), 3.29 (s, 2H). ^{13}C NMR (CD$_3$CN): δ −3.67 (Si*C*H$_3$), 15.67 (S*C*H$_3$), 40.33 (S*C*HS). ^{29}Si NMR (CD$_3$CN): δ 5.48.

Preparation of Bis-1,3-dithian-2-yl-dimethyl-silane (5). In a 250 mL two-neck round-bottomed flask containing a magnetic stirring bar was placed 1,3-dithiane (1.20 g, 10.0 mmol) in 100 mL of THF. A 1,3-dithiane solution was refluxed in a nitrogen atmosphere until it dissolved. The solution was cooled rapidly to − 40 °C, and 1,3-dithiane precipitated as fine crystals. Then *n*-BuLi (4.00 mL of 2.5 M solution, 10.0 mmol) was added slowly with a syringe. The solution was stirred and kept at − 20 to − 30 °C for 1 h. The solution was recooled to −78 °C, and dichlorodimethylsilane (0.61 mL, 5.0 mmol) was added slowly with a syringe. After the addition, the cooling bath was removed and the temperature allowed to rise to room temperature. Cold water was then added with vigorous stirring. The upper layer and two diethyl ether extracts were dried over MgSO$_4$. After evaporation of the solvent, washing with cold hexanes gave **5** as a white solid in 43% yield (0.64 g). The synthesis

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(46) Seebach, D.; Beck, A. K. *Org. Synth.* **1971**, *51*, 39.

(47) Peach, M. E.; Schmidt, M.; Weissflog, E. *Can. J. Chem.* **1975**, *53*, 3720.

(48) Seebach, D.; Kolb, M.; Grobel, B.-T. *Chem. Ber.* **1973**, *106*, 2277.

(49) Shimizu, M.; Iwakubo, M.; Nishihara, Y.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 3193.

of **5** has been reported previously without spectral characterization.[50] ^{1}H NMR (CDCl$_3$): δ 0.20 (s, 6H, SiCH_3), 1.92 (m, 2H, SCH$_2$CHHCH$_2$S), 2.04 (m, 2H, SCH$_2$CHHCH$_2$S), 2.65 (m, 4H, SCH_2CH$_2$), 2.83 (m, 4H, SCH_2CH$_2$), 3.86 (s, 2H). ^{13}C NMR (CDCl$_3$): δ − 6.68 (SiCH$_3$), 25.89 (SCH$_2$$CH_2CH_2$S), 30.89 (S$CH_2CH_2$$CH_2$S), 31.21 (S$C$HS). ^{29}Si NMR (CDCl$_3$): δ 4.51. ^{1}H NMR (CD$_3$CN): δ 0.20 (s, 6H, SiCH_3), 2.10 (m, 2H, SCH$_2$CHHCH$_2$S), 2.12 (m, 2H, SCH$_2$CHHCH$_2$S), 2.70 (m, 4H, SCH_2CH$_2$), 2.89 (m, 4H, SCH_2CH$_2$), 3.98 (s, 2H). ^{13}C NMR (CD$_3$CN): δ −6.34 (SiCH$_3$), 26.92 (SCH$_2$$CH_2CH_2$S), 31.38 (S$CH_2CH_2$$CH_2$S), 31.92 (S$C$HS). ^{29}Si NMR (CD$_3$CN): δ 4.41.

Preparation of Dimethyl-bis-1,3,5-trithian-2-yl-silane (6). A 250 mL two-necked round-bottomed flask containing a magnetic stirring bar was charged with 1,3,5-trithiane (1.38 g, 10.0 mmol) and 100 mL of THF. The resulting mixture was refluxed in a nitrogen atmosphere until the trithiane had dissolved. The solution was cooled rapidly to −40 °C, causing the trithiane to precipitate as fine crystals. *n*-BuLi (4.00 mL of 2.5 M solution, 10.0 mmol) was then added slowly using a syringe. The solution was stirred and kept at −20 to −30 °C for 1 h. The solution was then recooled to −78 °C, and dichlorodimethylsilane (0.61 mL, 5.0 mmol) was added slowly with a syringe. After the addition, the cooling bath was removed and the temperature allowed to rise to room temperature. Cold water was then added with vigorous stirring. The upper layer and two diethyl ether extracts were dried over anhydrous MgSO$_4$. After evaporation of the solvent, purification by flash chromatography on silica gel using 4:1 chloroform/hexane gave **6** as a white solid in 54% yield (0.90 g). Mp 192−194 °C (lit[51] mp 196−197 °C). ^{1}H NMR (CDCl$_3$): δ 0.34 (s, 6H, SiCH_3), 3.81 (d, 4H, SCH_aHS, ^2J = 13.9 Hz), 4.34 (s, 2H), 4.52 (d, 4H, SCHH_eS, ^2J = 13.9 Hz). ^{13}C NMR (CDCl$_3$): δ −5.93 (SiCH$_3$), 35.79 (SCHS), 37.00 (SCH$_2$S). ^{29}Si NMR (CDCl$_3$): δ 4.82.

Preparation of [Ag-1a]$_2$(CF$_3$SO$_3$)$_2$ (1a-M). Silver triflate (80 mg, 0.31 mmol) in methanol (2 mL) was slowly added to a solution of **1a** (56 mg, 0.31 mmol) in methanol (2 mL). The reaction mixture was kept in a refrigerator and allowed to evaporate slowly to obtain colorless rods suitable for X-ray analysis. Yield: 77 mg (57%). Mp 167−169 °C (dec). Anal. calcd for C$_{14}$H$_{32}$Ag$_2$F$_6$O$_6$S$_6$Si$_2$: C, 19.22; H, 3.69. Found: C, 19.07; H, 4.09. ^{1}H NMR (CD$_3$CN): δ 0.18 (s, 9H, SiCH_3), 2.33 (s, 6H, SCH_3), 3.14 (s, 1H). ^{13}C NMR (CD$_3$CN): δ − 1.83 (SiCH$_3$), 18.07 (SCH$_2$S), 43.79 (SCHS). ^{29}Si NMR (CD$_3$CN): δ 5.70. The yield of **1a-M** could be increased to 91% using vapor diffusion methods. In this case, diethyl ether was allowed to diffuse into a solution of silver triflate and **1a** in methanol/acetone over two days at room temperature.

Preparation of [Ag-(1b)$_2$](CF$_3$SO$_3$) (1b-M). Silver triflate (66 mg, 0.26 mmol) in methanol (2 mL) was slowly added to a solution of **1b** (68 mg, 0.26 mmol) in methanol (2 mL). The reaction mixture was kept in a refrigerator and allowed to evaporate slowly to obtain colorless platelike crystals suitable for X-ray analysis. Yield: 30 mg (30%). Mp 132−135 °C (dec). Anal. calcd for C$_{25}$H$_{56}$AgF$_3$O$_3$S$_5$Si$_2$: C, 38.20; H, 7.18. Found: C, 37.90; H, 7.24. ^{1}H NMR (CDCl$_3$): δ 1.18 (d, 18H, CCH_3, ^3J = 7.3 Hz), 1.36 (m, 3H, CHCH$_3$, ^3J = 7.3 Hz), 2.72 (s, 6H, SCH_3), 3.19 (s, 1H). ^{13}C NMR (CDCl$_3$): δ 11.85 (CCH$_3$), 19.18 (CCH$_3$), 22.06 (SCH$_3$), 43.83 (SCHS). ^{29}Si NMR (CDCl$_3$): δ 8.85. The yield of **1b-M** could be increased to 95% using vapor diffusion methods. In this case, diethyl ether was allowed to diffuse into a solution of silver triflate and **1b** in acetonitrile over two days at room temperature.

Preparation of [Ag-1c]$_2$(CF$_3$SO$_3$)$_2$ (1c-M). Silver triflate (81 mg, 0.32 mmol) in methanol (2 mL) was slowly added to the solution of **1c** (61 mg, 0.32 mmol) in methanol (2 mL). The reaction mixture was kept in a refrigerator and allowed to evaporate slowly to obtain colorless platelike crystals suitable for X-ray analysis. Yield: 106 mg (74%). Mp 154 °C. Anal. calcd for C$_{16}$H$_{32}$Ag$_2$F$_6$O$_6$S$_6$Si$_2$: C, 21.38; H, 3.59. Found: C, 20.99; H, 3.57. ^{1}H NMR (CD$_3$CN): δ 0.28 (s, 6H, SiCH_3), 2.32 (s, 6H, SCH_3), 3.33 (s, 1H), 5.85 (m, 1H, CH═CHH), 6.19 (m, 2H, CH═CHH and CHCH$_2$). ^{13}C NMR (CD$_3$CN): δ −3.83 (SiCH$_3$), 17.65 (SCH$_3$), 43.40 (SCHS), 131.90 (CHCH$_2$), 134.27 (CHCH$_2$). ^{29}Si NMR (CD$_3$CN): δ −1.40.

Preparation of [Ag-1d](CF$_3$SO$_3$) (1d-M). Silver triflate (49 mg, 0.19 mmol) in acetonitrile (2 mL) was slowly added to a solution of **1d** (41 mg, 0.19 mmol) in acetonitrile (2 mL). Colorless needlelike crystals suitable for X-ray analysis were obtained by the vapor diffusion of diethyl ether into this solution at room temperature. Yield: 72 mg (80%). Mp 158−159 °C (dec). Anal. calcd for C$_{10}$H$_{16}$AgF$_3$O$_3$S$_3$Si: C, 25.37; H, 3.41. Found: C, 21.32; H, 3.14. ^{1}H NMR (CD$_3$CN): δ 2.28 (s, 6H, SCH_3), 3.40 (s, 1H), 5.93 (m, 3H, CH═CHH), 6.25 (m, 6H, CH═CHH and CHCH$_2$). ^{13}C NMR (CD$_3$CN): δ 17.11 (SCH$_3$), 41.23 (SCHS), 131.80 (CHCH$_2$), 137.11 (CHCH$_2$). ^{29}Si NMR (CD$_3$CN): δ −20.75.

Preparation of [Ag-2]$_2$(CF$_3$SO$_3$)$_2$ (2-M). Silver triflate (128 mg, 0.50 mmol) in methanol (2 mL) was slowly added to a solution of **2** (192 mg, 1.00 mmol) in dichloromethane (2 mL). The reaction mixture was kept at room temperature and was allowed to evaporate slowly to obtain light-yellow colorless plates suitable for X-ray analysis. Yield: 367 mg (82%). Mp 200−202 °C (dec). Anal. calcd for C$_{16}$H$_{32}$Ag$_2$F$_6$O$_6$S$_6$Si$_2$: C, 21.38; H, 3.59. Found: C, 21.36; H, 3.79. ^{1}H NMR (CD$_3$CN): δ 0.17 (s, 9H, SiCH_3), 1.99 (m, 1H, SCH$_2$CHHCH$_2$S), 2.26 (m, 1H, SCH$_2$CHHCH$_2$S), 2.83 (m, 2H, SCH_2CH$_2$), 3.03 (m, 2H, SCH_2CH$_2$), 3.87 (s, 1H). ^{13}C NMR (CD$_3$CN): δ −2.86 (SiCH$_3$), 28.19 (SCH$_2$$CH_2CH_2$S), 32.45 (S$CH_2CH_2$$CH_2$S), 36.63 (S$C$HS). ^{29}Si NMR (CD$_3$CN): δ 5.06. The yield of **2-M** could be increased to 90% using vapor diffusion methods. In this case, diethyl ether was allowed to diffuse into a solution of silver triflate and **2** in methanol/acetone over two days at room temperature.

Preparation of [Ag-3](CF$_3$SO$_3$) (3-M). Silver triflate (67 mg, 0.26 mmol) in methanol (2 mL) was slowly added to a solution of **3** (55 mg, 0.26 mmol) in methanol (2 mL). The reaction mixture was kept in a refrigerator and was allowed to evaporate slowly to obtain thin pale-yellow platelike crystals suitable for X-ray analysis. Yield: 83 mg (68%). Mp 77−79 °C. Anal. calcd for C$_7$H$_{14}$AgF$_3$O$_3$S$_4$Si: C, 17.99; H, 3.02. Found: C, 17.93; H, 3.09. ^{1}H NMR (CD$_3$CN): δ 0.17 (s, 9H, SiCH_3), 3.94 (d, 2H, SCH_aHS, ^2J = 14.5 Hz), 4.34 (s, 1H), 4.57 (d, 2H, SCHH_eS, ^2J = 14.5 Hz). ^{13}C NMR (CD$_3$CN): δ −3.28 (SiCH$_3$), 37.43 (SCH$_2$S), 38.95 (SCHS). ^{29}Si NMR (CD$_3$CN): δ 5.67. The yield of **3-M** could be increased to 91% using vapor diffusion methods. In this case, diethyl ether was allowed to diffuse into a solution of silver triflate and **3** in methanol over two days at room temperature.

Preparation of [Ag-4]$_2$(CF$_3$SO$_3$)$_2$ (4-M). Silver triflate (55 mg, 0.21 mmol) in methanol (2 mL) was slowly added to a solution of **4** (58 mg, 0.21 mmol) in methanol (2 mL). The reaction mixture was kept in a refrigerator and was allowed to evaporate slowly to obtain colorless rodlike crystals suitable for X-ray analysis. Yield: 63 mg (56%). Mp 153−156 °C (dec). Anal. calcd for C$_{18}$H$_{40}$Ag$_2$-

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(50) Shimizu, M.; Iwakubo, M.; Nishihara, Y.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 3197.

(51) Schmidt, V. M.; Weissflog, E. *Z. Anorg. Allg. Chem.* **1975**, *418*, 208.

(52) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431.

(53) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

(54) Seebach, D. *Synthesis* **1969**, *1*, 17.

Table 1. Crystal Data

	1a-M	**1b-M**	**1c-M**	**1d-M**
empirical formula	$C_{14}H_{32}Ag_2F_6O_6S_6Si_2$	$C_{25}H_{56}AgF_3O_3S_5Si_2$	$C_{16}H_{32}Ag_2F_6O_6S_6Si_2$	$C_{10}H_{16}AgF_3O_3S_3Si$
fw	874.68	786.05	898.70	473.37
temp	293(2) K	296(2) K	100(2) K	296(2) K
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$Pbca$
a, Å	27.463(2)	7.7185(8)	8.2234(9)	12.9776(14)
b, Å	8.2307(6)	14.5692(14)	10.6970(12)	15.3104(17)
c, Å	17.2878(13)	17.7565(18)	18.346(2)	17.5409(19)
α, deg	90	99.526(2)	90	90
β, deg	122.762(1)	97.962(2)	96.931(2)	90
γ, deg	90	99.398(2)	90	90
V, Å^3	3286.2(4)	1914.5(3)	1602.1(3)	3485.2(7)
Z	4	2	2	8
D, g/cm^3	1.768	1.364	1.863	1.804
μ, mm^{-1}	1.706	0.900	1.753	1.617
R_1 $[I > 2\sigma(I)]^a$	0.050	0.059	0.047	0.063
wR_2 (all data)^a	0.130	0.141	0.117	0.153

	2-M	**3-M**	**4-M**	**5-M**
empirical formula	$C_{18}H_{38}Ag_2F_6O_8S_6Si_2$	$C_7H_{14}AgF_3O_3S_4Si$	$C_{18}H_{40}Ag_2F_6O_6S_{10}Si_2$	$C_{34}H_{60}Ag_4F_{12}O_{12}S_{16}Si_3$
fw	960.76	467.38	1059.02	1917.53
temp	100(2) K	293(2) K	100(2) K	296(2) K
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_12_12$
a, Å	11.3531(16)	6.7399(4)	13.5726(10)	12.2869(5)
b, Å	12.4452(17)	8.6102(5)	16.4573(12)	27.6134(11)
c, Å	12.4835(17)	13.8426(9)	17.8509(13)	9.5143(4) Å
α, deg	90	90	90	90
β, deg	94.796(2)	93.571(1)	106.190(1)	90
γ, deg	90	90	90	90
V, Å^3	1757.6(4)	801.75(8)	3829.2(5)	3228.0(2)
Z	2	2	4	2
D, g/cm^3	1.815	1.936	1.837	1.973
μ, mm^{-1}	1.608	1.881	1.692	1.854
R_1 $[I > 2\sigma(I)]^a$	0.035	0.033	0.053	0.042
wR_2 (all data)^a	0.086	0.081	0.137	0.090

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

$F_6O_6S_{10}Si_2$: C, 20.41; H, 3.81. Found: C, 20.27; H, 3.73. ^{1}H NMR (CD_3CN): δ 0.40 (s, 6H, $\mathrm{SiC}\mathit{H}_3$), 2.40 (s, 12H, $\mathrm{SC}\mathit{H}_3$), 3.47 (s, 2H). ^{13}C NMR (CD_3CN): δ −3.14 ($\mathrm{Si}\mathit{C}\mathrm{H}_3$), 18.42 ($\mathrm{S}\mathit{C}\mathrm{H}_3$), 42.35 ($\mathrm{S}\mathit{C}\mathrm{HS}$). ^{29}Si NMR ($CD_3CN$): δ 6.73. The yield of **4-M** could be increased to 91% using vapor diffusion methods. In this case, diethyl ether was allowed to diffuse into a solution of silver triflate and **4** in methanol/acetonitrile over two days at room temperature.

Preparation of $[Ag_4\text{-}5_3](CF_3SO_3)_4$ (5-M). Silver triflate (26 mg, 0.10 mmol) in acetonitrile (2 mL) was slowly added to a solution of **5** (30 mg, 0.10 mmol) in chloroform (2 mL). Colorless rodlike crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into this solution at room temperature. Yield: 58 mg (90%). Mp 208−211 °C (dec). Anal. calcd for $C_{34}H_{60}Ag_4F_{12}O_{12}S_{16}Si_3$: C, 21.30; H, 3.15. Found: C, 21.56; H, 3.25. ^{1}H NMR (CD_3CN): δ 0.31 (s, 6H, $\mathrm{SiC}\mathit{H}_3$), 2.06 (m, 2H, $\mathrm{SCH_2C}\mathit{H}\mathrm{HCH_2S}$), 2.31 (m, 2H, $\mathrm{SCH_2CH}\mathit{H}\mathrm{CH_2S}$), 2.90 (m, 4H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 3.09 (m, 4H, $\mathrm{SC}\mathit{H}_2\mathrm{CH_2}$), 4.08 (s, 2H). ^{13}C NMR (CD_3CN): δ −5.48 ($\mathrm{Si}\mathit{C}\mathrm{H}_3$), 27.82 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2CH_2S}$), 32.73 ($\mathrm{S}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2S}$), 35.68 ($\mathrm{S}\mathit{C}\mathrm{HS}$). ^{29}Si NMR ($CD_3CN$): δ 5.23.

Preparation of $[Ag\text{-}6]_2(CF_3SO_3)_2$ (6-M). Silver triflate (26 mg, 0.10 mmol) in methanol (2 mL) was slowly added to a solution of **6** (33 mg, 0.10 mmol) in acetone (2 mL). Colorless rodlike crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into this solution at room temperature. Yield: 55 mg (94%). Mp 174−177 °C (dec). Anal. calcd for $C_{18}H_{32}Ag_2F_6O_6S_{14}Si_2$: C, 18.33; H, 2.74. Found: C, 18.88; H, 2.89. ^{1}H NMR (CD_3CN): δ 0.36 (s, 6H, $\mathrm{SiC}\mathit{H}_3$), 4.01 (d, 2H, $\mathrm{SC}\mathit{H}_a\mathrm{HS}$, ^2J = 14.6 Hz), 4.61 (s, 1H), 4.66 (d, 2H, $\mathrm{SCH}\mathit{H}_e\mathrm{S}$, ^2J = 14.6 Hz). ^{13}C NMR (CD_3CN): δ −6.02 ($\mathrm{Si}\mathit{C}\mathrm{H}_3$), 37.18 ($\mathrm{S}\mathit{C}\mathrm{H_2S}$), 38.37 ($\mathrm{S}\mathit{C}\mathrm{HS}$). ^{29}Si NMR ($CD_3CN$): δ 7.39.

Single-Crystal X-Ray Diffraction Studies. Data were collected on a Bruker APEX system with a CCD area detector. The structure was solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL program package (Sheldrick, G. M. *SHELXTL*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1990). Selected crystal parameters are listed in Table 1, and selected interatomic distances and bond angles are given in Table 2. The ORTEP diagram in Figure 7b was drawn using *Ortep-3 for Windows* (Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565).

Results and Discussion

Ligand Syntheses. The ligands we chose for this study are shown in Figure 1. With the exception of **2**, which is commercially available, all of the ligands were synthesized by the reaction of deprotonated bis(methylthio)methane, 1,3-dithiane, or 1,3,5-trithiane with the corresponding chlorosilanes. The deprotonation of these organosulfur starting materials with *n*-BuLi is well-known, as are subsequent reactions with a variety of electrophiles.[52−55] Although some of the ligands have been previously reported, we include our experimental details because in certain cases experimental details were not provided in the literature, and in other cases, we found it best to use slightly modified experimental procedures. The ligands were isolated as air- and moisture-stable liquids or solids in moderate to good yields. Characterization was accomplished with ^{1}H, ^{13}C, and

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(55) Brandsma, L. In *Preparative Polar Organometallic Chemistry 2*; Springer Verlag: Berlin, 1990; p 53.

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

1a-M		1b-M		1c-M[b]		1d-M[c]	
Ag(1)−Ag(2)	3.1133(7)	Ag−S(1)	2.4557(12)	Ag-AgA	3.1959(6)	Ag(1)−C(4)	2.434(2)
Ag(1)−S(1)	2.4305(9)	Ag−S(3)	2.4858(12)	Ag−O(1)	2.457(3)	Ag(1)−C(5)	2.461(2)
Ag(2)−S(2)	2.4775(11)	Ag−O(1)	2.519(16)	Ag−S(2A)	2.5158(10)	Ag(1)−S(2A)	2.5316(7)
Ag(2)−O(1)	2.564(4)			Ag−S(1)	2.5229(10)	Ag(1)−S(1)	2.5449(6)
				S(2)−AgA	2.5158(10)	C(6)−Ag(1B)	2.642(2)
				C(6)−AgA	2.518(4)	C(7)−Ag(1B)	2.643(3)
				C(7)−AgA	2.507(4)		

2-M[d]		3-M[e]		4-M		5-M	
Ag−AgA	3.0013(5)	Ag−S(1)	2.540(4)	Ag(1)−Ag(2)	2.9086(4)	Ag(1)−Ag(2)	2.9921(5)
Ag−S(2A)	2.4552(6)	Ag−S(3A)	2.577(5)	Ag(1)−O(1)	2.483(3)	Ag(1)−S(26)	2.5014(12)
Ag−S(1)	2.4679(6)	Ag−O(1)	2.578(16)	Ag(1)−S(1)	2.5154(8)	Ag(1)−O(1)	2.580(5)
Ag−O(1)	2.5811(17)			Ag(1)−S(7)	2.5623(8)	Ag(1)−S(12)	2.5943(12)
				Ag(1)−S(5)	2.5985(9)	Ag(1)−S(112)	2.6106(13)
				Ag(2)−O(4)	2.489(3)	Ag(2)−S(22)	2.4974(12)
				Ag(2)−S(8)	2.5201(8)	Ag(2)−S(116)	2.5332(13)
				Ag(2)−S(2)	2.5368(9)	Ag(2)−S(16)	2.5475(12)
				Ag(2)−S(3)	2.6452(9)		

1a-M[a]		1b-M		1c-M[b]		1d-M[c]	
S(1)−Ag(1)−S(1A)	163.84(5)	S(1)−Ag−S(3)	155.27(4)	O(1)−Ag−AgA	164.53(8)	C(4)−Ag(1)−C(5)	31.81(7)
S(1)−Ag(1)−Ag(2)	81.92(2)	S(1)−Ag−O(1)	107.9(5)	S(2A)−Ag−-AgA	71.70(2)	C(4)−Ag(1)−S(2A)	132.79(6)
S(1A)−Ag(1)−Ag(2)	81.92(2)	S(3)−Ag−O(1)	95.8(5)	S(1)−Ag−AgA	87.67(2)	C(5)−Ag(1)−S(2A)	102.26(7)
S(2)−Ag(2)−S(2A)	79.10(5)	C(1)−S(1)−Ag	99.42(19)	O(1)−Ag−S(2A)	110.23(9)	C(4)−Ag(1)−S(1)	90.55(5)
S(2)−Ag(2)−O(1)	88.49(10)	C(3)−S(1)−Ag	107.89(13)	O(1)−Ag−S(1)	79.95(8)	C(5)−Ag(1)−S(1)	117.14(6)
S(2A)−Ag(2)−O(1)	91.12(10)	C(13)−S(3)−Ag	106.72(17)	S(2A)−Ag−S(1)	132.48(3)	S(2A)−Ag(1)−S(1)	117.00(2)
S(2)−Ag(2)−O(1A)	91.12(10)	C(15)−S(3)−Ag	97.03(13)	S(1)−C(3)−S(2)	107.73(19)	S(2)−C(1)−S(1)	111.01(11)
S(2A)−Ag(2)−O(1A)	88.49(10)	S(4)−C(15)−S(3)	113.7(2)				
O(1)−Ag(2)−O(1A)	128.40(18)						
S(2)−Ag(2)−Ag(1)	90.45(3)						
S(2A)−Ag(2)−Ag(1)	90.45(3)						
O(1)−Ag(2)−Ag(1)	115.80(9)						
O(1A)−Ag(2)−Ag(1)	115.80(9)						
S(1)−C(1)−S(2)	117.8(2)						

2-M[d]		3-M[e]		4-M		5-M	
S(2A)−Ag−S(1)	179.282(19)	S(1)−Ag−S(3A)	160.80(15)	O(1)−Ag(1)−S(1)	94.99(7)	S(26)−Ag(1)−O(1)	85.96(12)
S(2A)−Ag−O(1)	88.12(4)	S(1)−Ag−O(1)	99.5(3)	O(1)−Ag(1)−S(7)	99.52(7)	S(26)−Ag(1)−S(12)	139.30(4)
S(1)−Ag−O(1)	91.64(4)	S(3A)−Ag−O(1)	99.7(4)	S(1)−Ag(1)−S(7)	148.00(3)	O(1)−Ag(1)−S(12)	101.39(10)
S(2A)−Ag−AgA	90.136(16)	C(3)−S(1)−Ag	103.4(6)	O(1)−Ag(1)−S(5)	87.48(6)	S(26)−Ag(1)−S(112)	136.68(4)
S(1)−Ag−AgA	90.525(16)	C(1)−S(1)−Ag	101.4(5)	S(1)−Ag(1)−S(5)	113.30(3)	O(1)−Ag(1)−S(112)	86.47(13)
O(1)−Ag−AgA	132.59(4)	C(3)−S(3)−AgB	94.3(7)	S(7)−Ag(1)−S(5)	95.78(3)	S(12)−Ag(1)−S(112)	83.98(4)
C(1)−S(1)−Ag	110.94(7)	C(2)−S(3)−AgB	96.1(5)	O(1)−Ag(1)−Ag(2)	174.03(6)	S(26)−Ag(1)−Ag(2)	85.85(3)
C(2)−S(1)−Ag	107.03(8)	S(2)−C(2)−S(3)	112.3(9)	S(1)−Ag(1)−Ag(2)	81.97(2)	O(1)−Ag(1)−Ag(2)	160.59(10)
C(1)−S(2)−AgA	111.93(7)			S(7)−Ag(1)−Ag(2)	80.77(2)	S(12)−Ag(1)−Ag(2)	96.29(3)
C(4)−S(2)−AgA	106.30(8)			S(5)−Ag(1)−Ag(2)	98.44(2)	S(112)−Ag(1)−Ag(2)	87.48(3)
S(2)−C(1)−S(1)	114.06(11)			O(4)−Ag(2)−S(8)	93.04(8)	S(22)−Ag(2)−S(116)	120.47(5)
				O(4)−Ag(2)−S(2)	104.43(7)	S(22)−Ag(2)−S(16)	145.16(4)
				S(8)−Ag(2)−S(2)	149.56(3)	S(116)−Ag(2)−S(16)	94.37(4)
				O(4)−Ag(2)−S(3)	86.60(7)	S(22)−Ag(2)−Ag(1)	93.37(3)
				S(8)−Ag(2)−S(3)	108.95(3)	S(116)−Ag(2)−Ag(1)	93.44(3)
				S(2)−Ag(2)−S(3)	96.98(3)	S(16)−Ag(2)−Ag(1)	83.73(3)
				O(4)−Ag(2)−Ag(1)	173.46(7)	C(11)−S(12)−Ag(1)	102.54(14)
				S(8)−Ag(2)−Ag(1)	80.42(2)	C(13)−S(12)−Ag(1)	109.82(17)
				S(2)−Ag(2)−Ag(1)	81.62(2)	C(15)−S(16)−Ag(2)	117.87(18)
				S(3)−Ag(2)−Ag(1)	95.20(2)	C(11)−S(16)−Ag(2)	110.40(15)
				S(2)−C(1)−S(1)	114.89(18)	C(111)−S(112)−Ag(1)	108.83(15)
				S(3)−C(2)−S(4)	114.33(18)	C(113)−S(112)−Ag(1)	112.56(19)
						C(111)−S(116)−Ag(2)	105.39(15)
						C(115)−S(116)−Ag(2)	110.5(2)
						C(21)−S(22)−Ag(2)	107.08(14)
						C(23)−S(22)−Ag(2)	103.09(19)
						C(21)−S(26)−Ag(1)	106.62(14)
						C(25)−S(26)−Ag(1)	116.80(19)
						S(12)−C(11)−S(16)	113.1(2)
						S(112)−C(111)−S(116)	114.1(2)
						S(26)−C(21)−S(22)	113.8(2)

[a] Symmetry operation: *A* = −*x*, *y*, 1/2 − *z*. [b] Symmetry operation: *A* = 1 − *x*, 2 − *y*, 1 − *z*. [c] Symmetry operations: *A* = 1/2 + *x*, *y*, 3/2 − *z*; *B* = −1/2 + *x*, *y*, 3/2 − *z*. [d] Symmetry operation: *A* = 1 − *x*, 1 − *y*, 2 − *z*. [e] Symmetry operations: *A* = 1 − *x*, −1/2 + *y*, 1 − *z*; *B* = 1 − *x*, 1/2 + *y*, 1 − *z*.

^{29}Si NMR spectroscopy, and compounds that were previously unknown were further characterized with elemental analysis.

From this ligand set, we were able to conduct three comparison studies. In one study, we changed the identities of

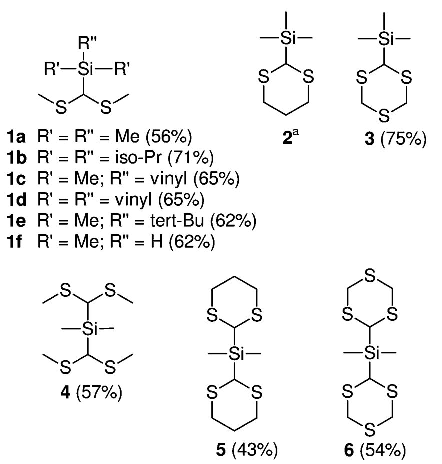

Figure 1. Organosilicon-thioether ligands utilized in this study. Isolated yields are in parentheses. Superscript a denotes commercially available.

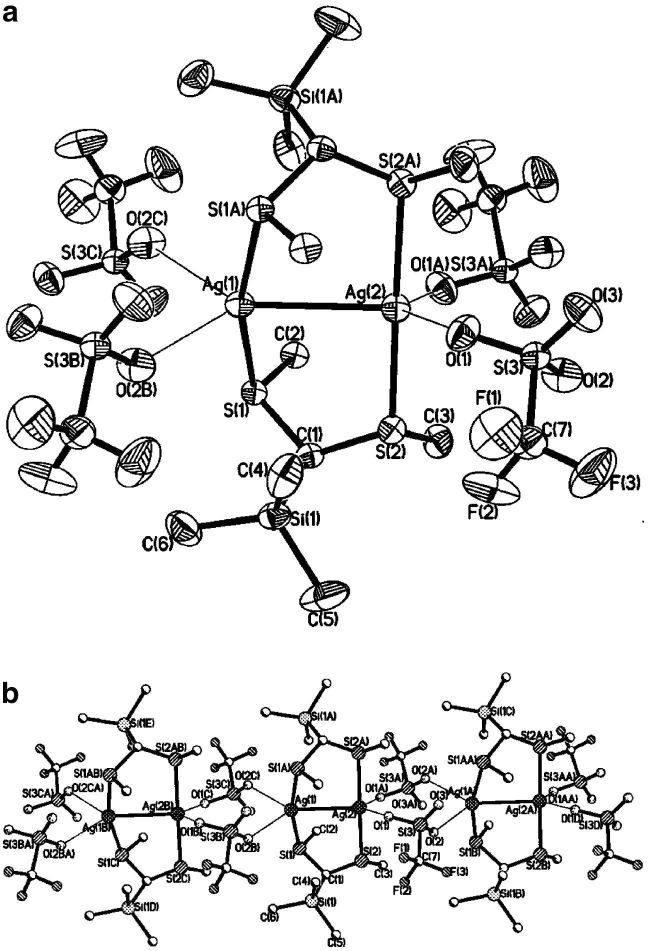

Figure 2. (a) ORTEP diagram of **1a-M** (50% ellipsoids). (b) Extended polymeric view of **1a-M**. Symmetry operations: $A = -x, y, 1/2 - z$; $B = x, -1 + y, z$; $C = -x, -1 + y, 1/2 - z$.

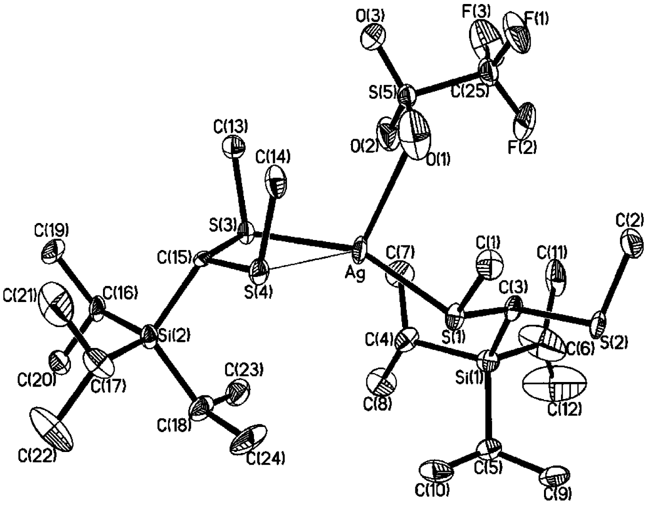

Figure 3. ORTEP diagram of **1b-M** (50% ellipsoids).

the alkyl groups on silicon in a series of silyl-substituted bis(methylthio)methanes (**1a**−**f**). In the second study, we changed the nature of the organosulfur ligating group on silicon (comparing **1a**, **2**, and **3**). In the third study, we increased the number of organosulfur ligating groups on silicon (comparing **4**, **5**, and **6** with **1a**, **2**, and **3**, respectively). Although none of these changes requires a variation in synthetic strategy, we can nonetheless induce changes in the ligand binding characteristics through these relatively simple modifications.

Changing Alkyl Groups on Silicon. Complexes 1a-M, 1b-M, 1c-M, and 1d-M. Ligands **1a**−**f** are silyl-substituted bis(methylthio)methanes that differ in the nature of the alkyl groups on the silicon atom. Ligands **1a**−**d** gave crystalline complexes upon reaction with silver triflate that were characterizable using single-crystal X-ray crystallography.

Complex **1a-M** was obtained as air-stable colorless rods. X-ray crystallography revealed a structure in which two molecules of **1a** support a Ag(1)−Ag(2) interaction (3.1133(7) Å; Figure 2a). Each silver atom is coordinated to two sulfur atoms from different ligand molecules (Ag(1)−S(1) = 2.4305(9) Å; Ag(2)−S(2) = 2.4775(11) Å) and is also coordinated to two oxygen atoms from two different triflate anions (Ag(1)−O(2) = 2.654(4) Å; Ag(2)−O(1) = 2.564(4) Å). The geometry about Ag(2) is a nearly perfect trigonal bipyramid with S(2A)−Ag(2)−S(2) = 179.10(4)° ($\tau = 0.85$), whereas the geometry about Ag(1) is a distorted trigonal bipyramid with the S(1A)−Ag(1)−S(1) angle more deviated from linearity (163.84(5)°; $\tau = 0.44$). By virtue of the oxygen atoms, the triflate anions serve to bridge the Ag−Ag dimeric units to form a one-dimensional linear polymer (Figure 2b). For comparison purposes, the reaction of unsubstituted bis(methylthio)methane with silver triflate has been reported to give a two-dimensional network without Ag−Ag interactions.[56]

Ligand **1b** differed from **1a** in that the methyl groups on silicon were replaced with isopropyl groups, thus giving the ligand considerably more steric bulk. X-ray structural analysis revealed **1b-M** to be a discrete mononuclear complex in which two molecules of **1b** surround a single tetracoordinate silver atom bonded to two sulfur atoms of one ligand, one sulfur atom from another ligand and an oxygen atom from a triflate anion (Figure 3). The Ag−S(1) and Ag−S(3) bond distances (2.4557(12) and 2.4858(12) Å, respectively) are comparable to Ag−S distances in similar

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(56) Awaleh, M. O.; Badia, A.; Brisse, F. *Cryst. Growth Des.* **2006**, *6*, 2674.

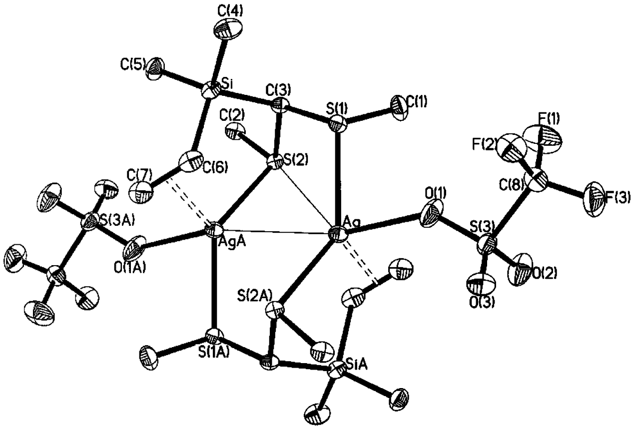

Figure 4. ORTEP diagram of **1c-M** (50% ellipsoids). Symmetry operation: $A = 1 - x, 2 - y, 1 - z$.

tetrahedral complexes in which silver is bonded to three sulfur atoms and a triflate anion (2.491−2.652 Å).[38,57−59] The Ag−O(1) distance (2.519(16) Å) is also comparable to literature values (2.325−2.960 Å).[38,57−59] The Ag−S(4) (3.0031(14) Å) interaction is slightly elongated compared to the other Ag−S bonds but still well within the sum of the silver and sulfur van der Waals radii (3.52 Å).[60]

From a steric standpoint, ligand **1c** has similarities to **1a**. However, in ligand **1c**, one of the methyl groups on silicon has been replaced with a vinyl group, which is a potential binding moiety. Like complex **1a-M**, X-ray structural analysis of **1c-M** (Figure 4) revealed a dimeric structure in which two ligands of **1c** support a Ag−Ag(A) interaction (3.1959(6) Å), with both silver atoms in a distorted trigonal-bipyramidal environment ($\tau = 0.53$). A further similarity is that each silver atom is bonded to two sulfur atoms, each from separate ligand molecules. The Ag−S distances are within accepted ranges for such interactions (2.5158(10) and 2.5229(10) Å). Sulfur atoms S(2) and the symmetry-generated S(2A) also interact marginally with Ag and Ag(A), respectively, with the 3.390 Å separation being slightly less than the sum of the van der Waals radii. The two vinyl groups in **1c-M** play a structurally significant role, each bonding in a η^2 fashion with a silver atom. The Ag−C distance to the less substituted carbon atom of the vinyl group is slightly shorter than the other Ag−C bond (2.507(4) vs 2.518(4) Å), with both distances being in the typical range for Ag−C η^2-coordination (2.345−2.680 Å).[61−64]

Ligand **1d** is similar to **1c**, but ligand **1d** now has three vinyl groups bonded to silicon instead of one, opening up the possibility of multiple η^2-coordination. X-ray crystallographic analysis of complex **1d-M** revealed a structure in which two molecules of **1d** coordinate tetrahedrally to a single silver atom (Figure 5). Each silver atom is coordinated to two sulfur atoms and two vinyl groups from different ligand molecules, resulting in the formation of a one-dimensional twisted polymer chain. The Ag−S distances are within the accepted ranges as before (2.5316(7) and 2.5449(6) Å). The vinyl groups in **1d-M** also show η^2 bonding to Ag, as in the case of **1c-M**. The Ag−C distances to one vinyl group (2.434(2) and 2.461(2) Å) are significantly shorter than the other Ag−C vinyl bond distances (2.642(2) and 2.643(3) Å), but the longer distances are still within comparable literature values.[61−64] Unlike the structure of **1c-M**, the distances between Ag and the *more* substituted carbon of the double bond are shorter in both cases, although the difference is slight between Ag(1B)−C(6) and Ag(1B)−C(7) (2.642(2) vs 2.643(3) Å). The third vinyl group in the ligand remains nonbonding.

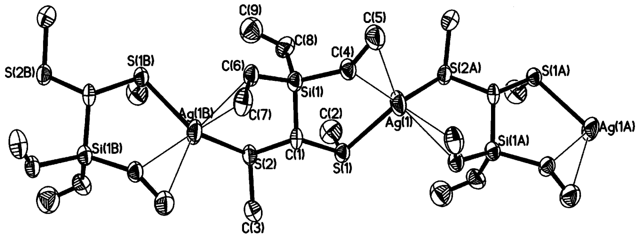

Figure 5. ORTEP diagram of **1d-M** (50% ellipsoids). Symmetry operations: $A = 1/2 + x, y, 3/2 - z$; $B = -1/2 + x, y, 3/2 - z$.

We were unable to obtain X-ray-quality crystals from the reactions of **1e** and **1f** with silver triflate. In reactions involving **1e**, we obtained fine powders that could not be redissolved in organic solvents. Reactions of **1f** with silver triflate gave instant silver mirror deposits on the walls of the reaction vial. The reduction of silver and other coinage metals by silyl hydrides is a well-known process.[65−69]

Changing the Nature of the Ligating Group on Silicon. Complexes 2-M and 3-M. Compared to ligand **1a**, the sulfur atoms in **2** are “tied-back” in a dithiane ring, which imposes certain mobility restraints on the binding moiety. Like **1a-M**, complex **2-M** exists as a dimeric structure in the solid state, in which two molecules of **2** support a Ag−Ag(A) interaction (3.0013(5) Å) (Figure 6). Despite the 1:1 ligand/metal ratio in the complex, we were only able to obtain a crystalline product by mixing the ligand and metal in a 2:1 ratio. Each silver atom is coordinated to two sulfur atoms from two different ligand molecules (Ag−S(1) = 2.4679(6) Å; Ag−S(2A) = 2.4552(6) Å) and to two oxygen atoms from a triflate anion (Ag−O(2) = 2.7049(17) Å) and a methanol solvent molecule (Ag−O(1) = 2.5811(17) Å). The two bridging 1,3-dithiane molecules adopt a chair conformation, as observed in similar 1,3-dithiane-Ag(I)

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(57) Li, K.; Xu, Z.; Fettinger, J. C. *Inorg. Chem.* **2004**, *43*, 8018.

(58) Fu, Y.-T.; Lynch, V. M.; Lagow, R. J. *Chem. Commun.* **2004**, 1068.

(59) Brooks, N. R.; Blake, A. J.; Champness, N. R.; Cunningham, J. W.; Hubberstey, P.; Teat, S. J.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2001**, 2530.

(60) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(61) Alyea, E. C.; Ferguson, G.; McAlees, A.; McCrindle, R.; Myers, R.; Siew, P. Y.; Dias, S. A. *J. Chem. Soc., Dalton Trans.* **1981**, 481.

(62) Hossain, M. B.; van der Helm, D. *J. Am. Chem. Soc.* **1968**, *90*, 6607.

(63) Cottam, J. R. A.; Steel, P. J. *J. Organomet. Chem.* **2006**, *691*, 2286.

(64) Burgess, J.; Cottam, J. R. A.; Steel, P. J. *Aust. J. Chem.* **2006**, *59*, 295.

(65) Anderson, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 5083.

(66) Purkayastha, A.; Baruah, J. B. *Polym. Prepr.* **2004**, *45*, 666.

(67) Purkayastha, A.; Baruah, J. B. *React. Polym.* **2005**, *63*, 177.

(68) Fukushima, M.; Hamada, Y.; Tabei, E.; Aramata, M.; Mori, S.; Yamamoto, Y. *Chem. Lett.* **1998**, 347.

(69) Takahashi, M.; Kamada, J.; Iwata, K.; Goto, K.; Watanabe, H.; Tamai, S. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 168.

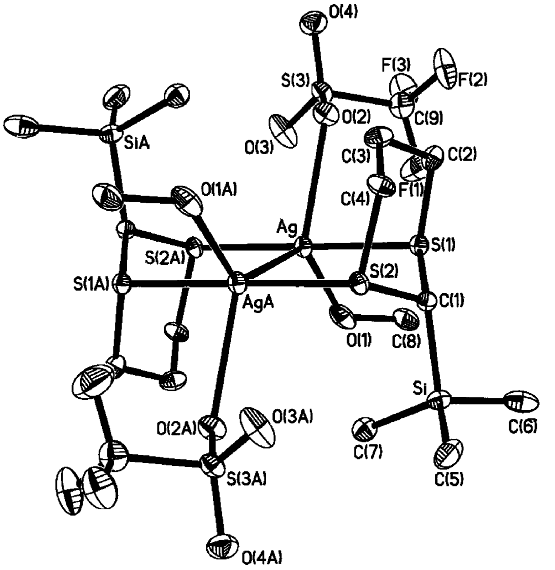

Figure 6. ORTEP diagram of **2-M** (50% ellipsoids). Symmetry operation: $A = 1 - x, 1 - y, 2 - z$.

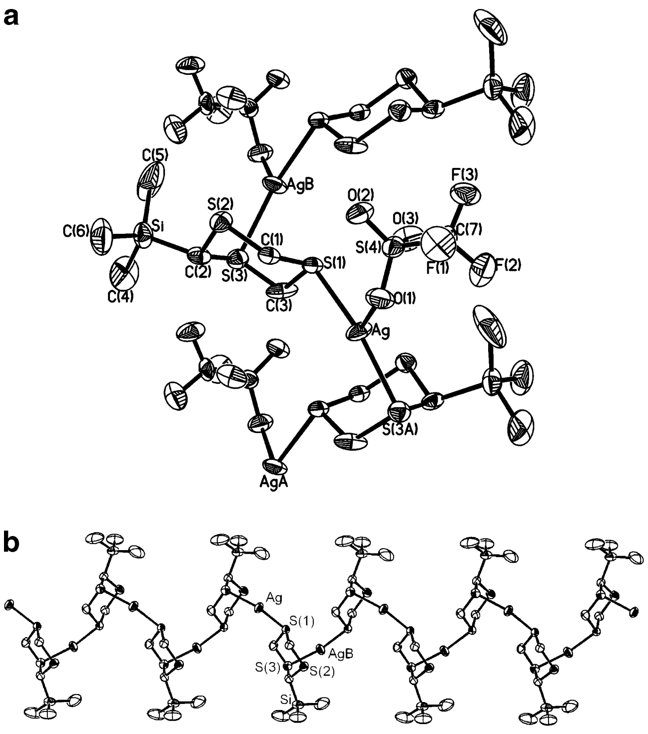

Figure 7. (a) ORTEP diagram of **3-M** (50% ellipsoids). (b) Extended polymeric view of **3-M**. Symmetry operations: $A = 1 - x, -1/2 + y, 1 - z$; $B = 1 - x, 1/2 + y, 1 - z$.

complexes.[41] The geometry about silver is nearly trigonal bipyramidal with S(1)−Ag−S(2A) = 179.282(19)° and $\tau = 0.78$.

In ligand **3**, the 1,3-dithiane ring is replaced with a 1,3,5-trithiane ring, which we originally believed to be a relatively minor modification. Unlike the structures of **1a-M** and **2-M**, however, the X-ray crystal structure of **3-M** shows no Ag−Ag interaction (Figure 7a). Each silver atom is coordinated to two sulfur atoms from different ligand molecules (Ag−S(1) = 2.540(4) Å; Ag−S(3A) = 2.577(5) Å) and is also coordinated to one oxygen atom from a triflate anion (Ag−O(1) = 2.578(16) Å). The geometry about Ag is somewhat T-shaped, with an S(1)−Ag−S(3A) angle of 160.80(15)° (S(1)−Ag−O(1) = 99.5(3) Å and S(3A)−Ag−O(1) = 99.7(4) Å). Comparable silver complexes in which silver is bonded to two thioether sulfur atoms and one triflate possess a distorted trigonal-planar geometry ($[Ag(PhS(CH_2)_4SPh)(CF_3SO_3)]_\infty$ and $[Ag_2(PhS(CH_2)_2SPh)(CF_3SO_3)_2]_\infty$).[70] The 1,3,5-trithiane groups adopt a chair conformation and behave as bidentate bridging ligands coordinated to two different silver atoms. As a result, complex **3-M** exists as a one-dimensional polymeric chain (Ag−Ag(B) = 5.6709(5) Å; Figure 7b). Of the two Ag−S contacts along the chain, one is equatorial with respect to the 1,3,5-trithiane ring and the other is axial, as in the case of unsubstituted 1,3,5-trithiane complexes with silver salts.[71,72] Although all three sulfur atoms in the trithiane ring can be coordinating,[72,73] in **3-M**, the relatively bulky trimethylsilyl group likely prevents the coordination of the third sulfur atom.

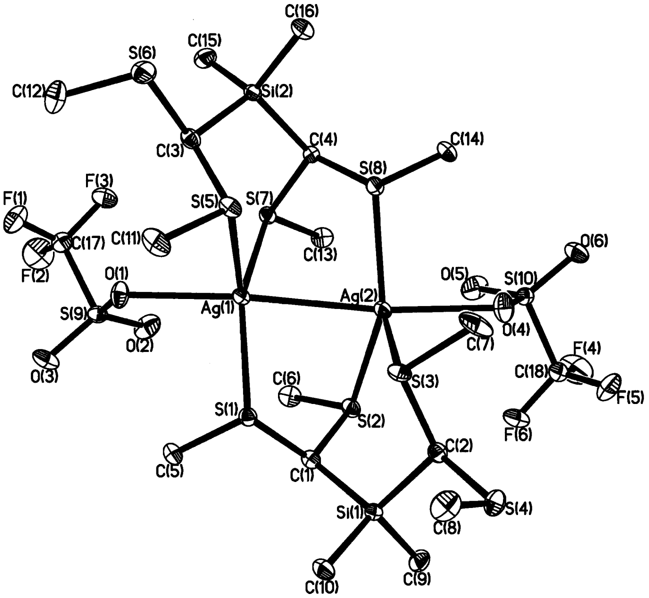

Figure 8. ORTEP diagram of **4-M** (50% ellipsoids).

Changing the Number of Ligating Groups on Silicon. Complexes 4-M, 5-M, and 6-M. Compared to **1a**, ligand **4** has an additional bis(methylthio)methane group, which increases the number of potential donor atoms but also makes the ligand considerably more congested around the silicon atom. X-ray crystallographic characterization of complex **4-M** showed it to be a discrete dimer (Figure 8). As in complexes **1a-M**, **1c-M**, and **2-M**, two ligand molecules in **4-M** support a Ag(1)−Ag(2) interaction (2.9086(4) Å), which is shorter than that observed in **1a-M** (3.1133(7) Å). The additional sulfur atoms available in **4** result in each silver in **4-M** being coordinated to two sulfur atoms from one ligand (Ag−S = 2.5368(9)−2.6452(9) Å) and one sulfur atom from the other (Ag−S = 2.5154(8) and 2.5201(8) Å), resulting in one sulfur atom on each ligand

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(70) Awaleh, M. O.; Badia, A.; Brisse, F.; Bu, X.-H. *Inorg. Chem.* **2006**, *45*, 1560.

(71) Domenicano, A.; Scaramuzza, L.; Vaciago, A.; Ashworth, R. S.; Prout, C. K. *J. Chem. Soc. A* **1968**, 866.

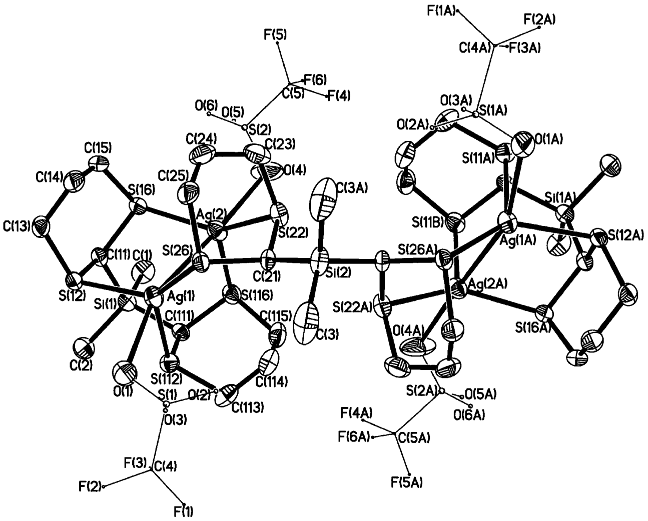

Figure 9. ORTEP diagram of **5-M** (50% ellipsoids). Symmetry operation: $A = -x, 1 - y, z$.

remaining nonbonding. One additional coordination site on silver is occupied by an oxygen atom from a triflate anion (2.483(3) and 2.489(3) Å). Both silver atoms are pentacoordinate ($\tau(\mathrm{Ag}(1)) = 0.43$, $\tau(\mathrm{Ag}(2)) = 0.40$). In contrast to **1a-M**, the triflate anions are not bridging, possibly the result of the increased steric bulk of **4**. Congestion of the organosulfur ligating groups around silicon may also be the reason for all six Ag−S bonds being longer than those in **1a-M**.

Replacing one of the methyl groups in ligand **2** with a 1,3-dithiane group gives ligand **5**, having two dithiane groups bound to silicon. Unlike the other reported complexes in this paper, X-ray structural analysis revealed **5-M** to be a 3:4 complex of **5** with silver triflate, in which three molecules of **5** support Ag(1)−Ag(2) interactions (2.9921(5) Å) in two symmetrically equivalent subsections of the complex (Figure 9). One of the three molecules of **5** serves as the linking unit between the two "halves", in addition to contributing a dithiane moiety to support the Ag−Ag interactions. Unlike in **2-M**, each Ag−Ag interaction is supported by a total of three dithiane moieties, one from the linking ligand and two from a separate molecule of **5** (Ag−S = 2.4974(12)−2.6106(13) Å). The 1,3-dithiane rings adopt the chair conformation, and all Ag−S contacts are in the axial position with respect to the 1,3-dithiane ring. One additional coordination site on each silver is occupied by an oxygen atom from a triflate anion (2.580(5) and 2.616(5) Å). Each silver atom in **5-M** is pentacoordinate ($\tau(\mathrm{Ag}(1)) = 0.35$, $\tau(\mathrm{Ag}(2)) = 0.51$), with the immediate coordinating environment about silver resembling that found in complex **4-M**.

Ligand **6** possesses two 1,3,5-trithiane groups bonded to silicon as compared to one in ligand **3**. Unfortunately, although crystals of **6-M** were obtained in high yield, the structure could not be satisfactorily refined due to disordered triflate anions.[74] It was determined that the asymmetric unit consists of two different discrete complexes, both of which contain two ligands of **6** supporting Ag−Ag interactions.

Table 3. VPO Data for All Complexes[a]

complex	MW based on solid state structure	MW determined by VPO	average MW of Ag, triflate, and ligand
1a-M	polymeric	248	145
1b-M	786	495	173
1c-M	899	222	149
1d-M	polymeric	216	157
2-M	961[b]	196	149(120[b])
3-M	polymeric	212	155
4-M	1059	278	264
5-M	1918	343	184

[a] All complexes were dissolved in acetonitrile with the exception of **1b-M**, which was dissolved in chloroform. [b] Value includes one molecule of methanol, which was present in the X-ray structure.

Nature of Complexes in Solution. Since all of the complexes reported herein are described in terms of their solid-state structures, it is of interest to consider the nature of the structures in solution. Of particular interest are the complexes in which an apparent argentophilic[75,76] interaction is present (**1a-M**, **1c-M**, **2-M**, **4-M**, and **5-M**). The Ag−Ag interaction is known to be relatively weak and similar in magnitude to Ag−aromatic interactions,[77] and therefore susceptible to rupture on dissolution. To investigate the identity of the complexes in solution, we utilized VPO to determine the average molecular weight of all species in solution. The results are listed in Table 3.

The data clearly suggest that the complexes do not retain their structure in solution. In all cases, the observed molecular weights are significantly lower than the molecular weights calculated from the crystal structures. Furthermore, the obtained molecular weights are somewhat higher than the values that would be obtained if the silver ion, triflate ion, and ligand were completely unassociated and free in solution (last column in Table 3). As a result, we believe that, although the solid-state structures do not remain intact in solution, there is some aggregation/solvation that occurs between the ligand and the silver ion. This conclusion is also supported by the NMR data of the complexes, which indicates measurable shifting of the ligand signals relative to the free ligand (see Experimental Section).

Conclusion

We have synthesized a series of multidentate organosilicon-thioether ligands that exhibit a variety of binding modes to silver depending on the type and number of thioether

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(72) Ashworth, R. S.; Prout, C. K.; Domenicano, A.; Vaciago, A. *J. Chem. Soc. A* **1968**, 93.

(73) Roesky, H. W.; Hofmann, H.; Jones, P. G.; Pinkert, W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1215.

(74) **6-M**: $C_{18}H_{32}Ag_2F_6S_{14}Si_2$, FW 1179.20, space group $P2_1/c$, $a = 21.4616(9)$, $b = 13.3888(6)$, $c = 30.7888(13)$ Å, $\beta = 96.273(1)°$, $V = 8794.0(7)$ Å^3, $Z = 8$, $D = 1.781$ Mg/m3, $\delta = 1.666$ mm^{-1}. The results of refinement are poor due to the disorder of three triflate anions. The disordered groups were restrained in the refinement. The final refinement parameters are R_1 [$I > 2\delta(I)$] = 0.113 and wR_2 [all data] = 0.343.

(75) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(76) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem.−Eur. J.* **1997**, *3*, 1451.

(77) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *221*, 155.

ligating groups on silicon. An additional structural influence is the type of alkyl substituent on silicon. Mostly discrete complexes are obtained in the solid state, but polymeric structures are possible when sterically accessible sulfur atoms exist (as in **3**) or additional nonsulfur ligating moieties are present in the ligand, such as the vinyl groups in **1d**. A common feature in the discrete complexes is an argentophilic interaction, evidenced by short Ag−Ag distances. Only when the ligand is sterically hindered (**1b**) is an argentophilic interaction prevented. Vapor pressure osmometry measurements suggest that the solid-state structures of the complexes are not retained in solution. As a whole, this study demonstrates the versatility of silicon as a tunable substituent in multidentate thioether ligands.

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Supporting Information Available: Complete crystal data in CIF format for all complexes described in this investigation. This material is available free of charge via the Internet at http://pubs.acs.org.

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