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One-Dimensional Copper(I) Coordination Polymers Based on a Tridentate Thioether Ligand

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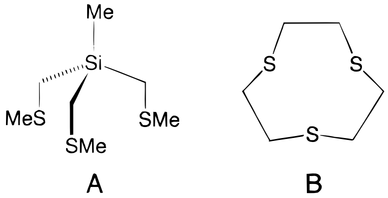
The one-dimensional copper(I) coordination polymers $Cu_3\{MeSi(CH_2SMe)_3\}_2X_3$ (X = Cl, Br) and $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]Y$ (Y = OSO_2CF_3, BF_4, PF_6) were readily obtained in very good to excellent yields (80−95%) by reacting CuX or $[Cu(NCMe)_4]Y$, respectively, with the tridentate thioether ligand $MeSi(CH_2SMe)_3$ in acetonitrile. The new complexes were characterized by a combination of analytical and spectroscopic techniques, including electrospray ionization mass spectrometry and, for the bromo and hexafluorophosphate derivatives, single-crystal X-ray diffraction. Both complexes exhibit one-dimensional chain structures with approximately tetrahedral copper centers and bridging unidentate/bidentate thioether ligands.

Introduction

Molecular architecture and self-assembly of complex structures are two of the most fascinating themes in modern inorganic chemistry.[1−3] Among the transition metals, copper(I) has played a central role in the construction of supramolecular arrays supported by a variety of nitrogen and sulfur donor ligands.[4] Although polymeric compounds built upon Cu(I) centers and simple dialkyl thioethers (R_2S) are relatively rare,[5−7] a number of species exhibiting extended solid-state structures have been reported for derivatives of polydentate or macrocyclic thioethers.[8−24] With the aim of exploring the chemistry of new acyclic polythioether ligands, we recently prepared the new tridentate thioether $MeSi(CH_2SMe)_3$ (Chart 1A) and structurally characterized its octahedral group 6 metal carbonyl derivatives $\{\eta^3\text{-}MeSi(CH_2SMe)_3\}M(CO)_3$ (M = Cr, Mo, W).[25] It occurred to us that the enhanced structural flexibility of $MeSi(CH_2SMe)_3$ compared to that of related "crown" thioethers such as 1,4,7-trithiacyclononane (commonly abbreviated ttcn or 9S3, Chart 1B) may facilitate the preparation of complexes with different coordination geometries and novel structures. Our assumption turned out to be correct, and we describe herein the syntheses and characterization of several copper(I) coordination polymers supported by $MeSi(CH_2SMe)_3$.

Chart 1. $MeSi(CH_2SMe)_3$ and ttcn (9S3) Ligands



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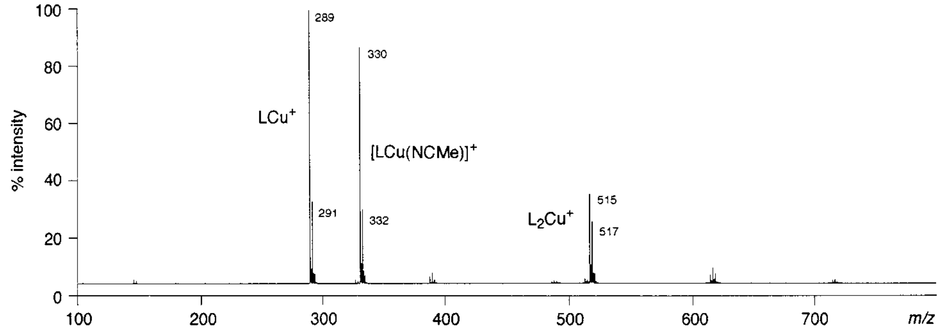
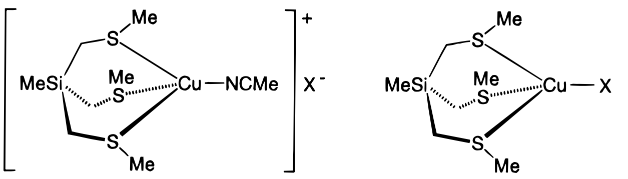


Figure 1. Positive ion ESI mass spectrum of $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Cl_3}$ in acetonitrile solution (cone voltage = 140 V).

Chart 2. Two Possible Mono(thioether) Cu(I) Complexes in Acetonitrile Solution (X = Cl, Br)



Results and Discussion

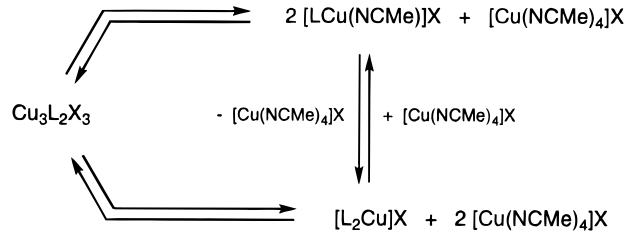
$\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2X_3}$ Complexes. An acetonitrile solution of copper(I) chloride reacted with $\mathrm{MeSi(CH_2SMe)_3}$ in the ratio 3:2 to give, within seconds and in excellent yield, an off-white precipitate of composition $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Cl_3}$, as determined by elemental analysis (eq 1). The use of an excess

$$3\,\mathrm{CuCl} + 2\,\mathrm{MeSi(CH_2SMe)_3} \xrightarrow{\mathrm{MeCN}} \mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Cl_3} \qquad (1)$$

of the thioether ligand (>1 equiv) or a higher reaction temperature (i.e., reflux) invariably led to the same product. Similarly, the bromo analogue $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$ was isolated (ca. 90% yield) from the corresponding reaction of CuBr. Both compounds are diamagnetic, fairly air-stable solids, only slightly soluble in polar coordinating solvents such as acetonitrile. Dissolution of the complexes in this solvent and precipitation of the solid, base-free complexes is reversible, and no signs of decomposition were observed after several cycles.

The nature of the $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2X_3}$ (X = Cl, Br) complexes in solution was initially investigated by ^{1}H NMR spectroscopy. The spectra of both compounds in $\mathrm{CD_3CN}$ showed only three resonances in the ratio 3:2:1, adscribed respectively to the methylthio, methylene, and methylsilyl protons of one or more (if equilibrated on the NMR time scale) complexes bearing facially coordinated tridentate thioether ligands. We tend to favor the presence in solution of the cationic acetonitrile adduct $\mathrm{[LCu(NCMe)]^+}$, rather than a neutral complex LCuX [L = $\mathrm{MeSi(CH_2SMe)_3}$, Chart 2], on the basis of the solubility and virtually identical spectroscopic data observed for both derivatives and the independent preparation and isolation of analogous complexes [LCu(NCMe)]X with noncoordinating anions (X = $\mathrm{OSO_2CF_3}$, $\mathrm{BF_4}$, $\mathrm{PF_6}$), as described below. In addition, electrospray ionization mass spectrometry (ESI-MS), an analytical technique that is increasingly being applied to investigate inorganic and organometallic systems,[26−29] was used to study the $\mathrm{Cu_3L_2X_3}$ complexes. The mass spectra of dilute acetonitrile solutions of both complexes are virtually identical, with that of the chloro derivative shown in Figure 1. The two main peaks correspond to the molecular ion $\mathrm{[LCu(NCMe)]^+}$ (*m*/*z* = 330) and the desolvated species $\mathrm{[LCu]^+}$ (*m*/*z* = 289), the latter presumably generated in the gas phase during the ionization process. Surprisingly, a peak corresponding to the bis(thioether) complex $\mathrm{[L_2Cu]^+}$ was also present at *m*/*z* = 515. While we are uncertain whether $\mathrm{[L_2Cu]^+}$ forms directly from $\mathrm{Cu_3L_2X_3}$ or from the comproportionation of two $\mathrm{[LCu(NCMe)]^+}$ fragments (Scheme 1), and we have not been able to independently synthesize such complex yet, it is worth noting that the related bis(crown thioether) complexes $[(\eta^3\text{-9S3})_2\mathrm{Cu}](\mathrm{BF_4})_2$,[30,31] $[(\eta^3\text{-9S3})\mathrm{Cu}(\eta^1\text{-9S3})]\mathrm{PF_6}$,[32] and $[(\eta^3\text{-12S3})\mathrm{Cu}(\eta^1\text{-12S3})]_2[\mathrm{Ru_6(CO)_{16}}(\mu_6\text{-C})]$[33] have been isolated and structurally characterized. Although no direct evidence has been found so far for the presence of the homoleptic tetrakis(acetonitrile) complex $\mathrm{[Cu(NCMe)_4]^+}$ upon dissolving the $\mathrm{Cu_3L_2X_3}$ complexes in acetonitrile, more detailed studies of these compounds are currently in progress.

Scheme 1. Potential Routes to the Bis(thioether) Complex $\mathrm{[L_2Cu]^+}$ in Acetonitrile Solution [L = $\mathrm{MeSi(CH_2SMe)_3}$]



Structure of $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$. Single crystals of $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$ suitable for an X-ray diffraction study were obtained by slow evaporation at room temperature of a concentrated acetonitrile solution.[34] The complex displays in the solid state a one-dimensional chain structure with each asymmetric unit consisting of three CuBr units and two bridging

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(34) The chloro complex was determined to be isomorphous to the bromo derivative on the basis of the following observed unit cell parameters: a = 16.0992(1) Å, b = 7.985(3) Å, c = 23.3462(10) Å, β = 103.394(10)°, V = 2919.8(17) Å^3. Liable-Sands, L. M.; Rheingold, A. L. Unpublished results.

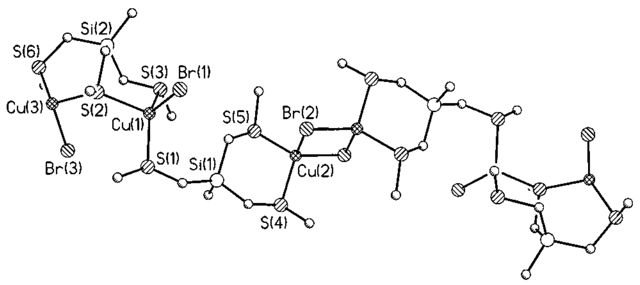

Figure 2. Two asymmetric units of the infinite chain structure of $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$ with hydrogen atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$

Cu(1)−S(1)	2.301(1)	Cu(1)−S(2)	2.429(1)
Cu(1)−S(3)	2.339(1)	Cu(1)−Br(1)	2.419(1)
Cu(2)−S(4)	2.314(1)	Cu(2)−S(5)	2.297(1)
Cu(2)−Br(2)	2.563(1)	Cu(2)−Br(2′)	2.425(1)
Cu(3)−S(2)	2.293(1)	Cu(3)−S(6)	2.299(1)
Cu(3)−Br(3)	2.503(1)	Cu(3)−Br(3′)	2.460(1)
S(1)−Cu(1)−S(2)	110.28(3)	S(1)−Cu(1)−S(3)	115.95(3)
S(1)−Cu(1)−Br(1)	116.95(3)	S(3)−Cu(1)−Br(1)	110.56(3)
S(3)−Cu(1)−S(2)	100.38(3)	Br(1)−Cu(1)−S(2)	100.20(3)
S(5)−Cu(2)−S(4)	105.82(4)	S(5)−Cu(2)−Br(2′)	127.59(3)
S(4)−Cu(2)−Br(2′)	109.74(3)	S(5)−Cu(2)−Br(2)	102.58(3)
S(4)−Cu(2)−Br(2)	109.01(3)	Br(2)−Cu(2)−Br(2′)	100.76(2)
S(2)−Cu(3)−S(6)	114.92(4)	S(2)−Cu(3)−Br(3′)	116.68(3)
S(6)−Cu(3)−Br(3′)	107.28(3)	S(2)−Cu(3)−Br(3)	103.96(3)
S(6)−Cu(3)−Br(3)	107.10(3)	Br(3)−Cu(3)−Br(3′)	106.12(2)
Cu(2′)−Br(2)−Cu(2)	79.24(2)	Cu(3′)−Br(3)−Cu(3)	73.88(2)

thioether ligands, as illustrated in Figure 2. Selected bond lengths and angles are included in Table 1.

Although all the copper centers are roughly tetrahedral, the flexibility of the polymeric structure in general and of the thioether ligands in particular is reflected in the wide range of observed Br−Cu−S and S−Cu−S angles, which vary from 100.2 to 127.6°. The thioether ligands exhibit two different coordination modes, namely (i) unidentate:bidentate (μ-η^1:η^2), as in the thioether containing Si(1), and (ii) bidentate:bidentate (μ-η^2:η^2), as in the ligand containing Si(2), in which one of the thioether arms bridges two copper centers. Alternatively, the structure can be described in terms of the two distinctive coordination environments for the three unique copper centers: (i) $\mathrm{CuS_3X}$, with one arm of a thioether ligand and two from another bonded to a CuBr unit, as for Cu(1), and (ii) $\mathrm{CuS_2X_2}$, with two arms of a thioether ligand bound to each copper atom in the Cu(μ-Br)$_2$Cu groups, as for Cu(2) and Cu(3). The geometries of the two $\mathrm{Cu_2Br_2}$ moieties in $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$ are similar to those observed in other complexes containing such dinuclear cores, for example $\mathrm{[CuBr(SMe_2)]}_n$,[7] $\mathrm{[CuBr(PPh_2Me)_2]_2}$,[35] and $\mathrm{[CuBr(PPh_3)(py)]_2}$.[36] The Cu(3)···Cu(3′) separation [2.9832(9) Å], while representing the shortest intermetallic distance in $\mathrm{Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3}$, indicates at most a weak copper−copper interaction. The Cu−S bond lengths (in the approximate range 2.29−2.43 Å) are within the range of the values observed for other Cu(I) thioether complexes.[5−24,32,33,37−53] Likewise, the Cu−Br bond distances, between 2.419(1) and 2.563(1) Å, appear to be normal,[54,55] as are the S−C and Si−C bond lengths (ca. 1.81 and 1.88 Å, respectively).[56]

[{MeSi(CH₂SMe)₃}Cu(NCMe)]X Complexes. To access the putative mononuclear complexes $\mathrm{[LCu(NCMe)]^+}$, copper(I) salts of less-coordinating anions were reacted with the thioether ligand. For example, white complexes of composition [LCu(NCMe)]X (X = $\mathrm{OSO_2CF_3}$, $\mathrm{BF_4}$, $\mathrm{PF_6}$) were prepared (80−90% yield) by reacting $\mathrm{MeSi(CH_2SMe)_3}$ with acetonitrile solutions of $\mathrm{CuOSO_2CF_3}$ (generated in situ from CuCl or CuI and $\mathrm{AgOSO_2CF_3}$) or $\mathrm{[Cu(NCMe)_4]X}$ (X = $\mathrm{BF_4}$, $\mathrm{PF_6}$), respectively (eq 2). The diamagnetic, slightly air-sensitive products were

$$\mathrm{[Cu(NCMe)_4]X} + \mathrm{L} \xrightarrow[\mathrm{L\,=\,MeSi(CH_2SMe)_3}]{\mathrm{MeCN}} \mathrm{[LCu(NCMe)]X} \qquad (2)$$

characterized by a combination of analytical and spectroscopic techniques. Significantly, acetonitrile solutions of all three [LCu(NCMe)]X derivatives display ESI mass spectra virtually identical to those of the $\mathrm{Cu_3L_2X_3}$ complexes. The presence of the acetonitrile ligands in [LCu(NCMe)]X was established by elemental analyses and verified by the observation of 1 equiv of liberated $\mathrm{CH_3CN}$/copper complex in their ^{1}H NMR spectra (obtained in $\mathrm{CD_3CN}$). In addition, their IR spectra (obtained as KBr pellets) show weak carbon−nitrogen stretching frequency bands (ν_{CN}) around 2275−2280 cm^{-1}, values which are typical of metal−acetonitrile complexes.[57−59]

Structure of [{MeSi(CH₂SMe)₃}Cu(NCMe)]PF₆. To verify if the [LCu(NCMe)]X complexes were indeed mononuclear, an X-ray diffraction study was performed for the hexafluorophosphate derivative $\mathrm{[LCu(NCMe)]PF_6}$, single crystals of which were

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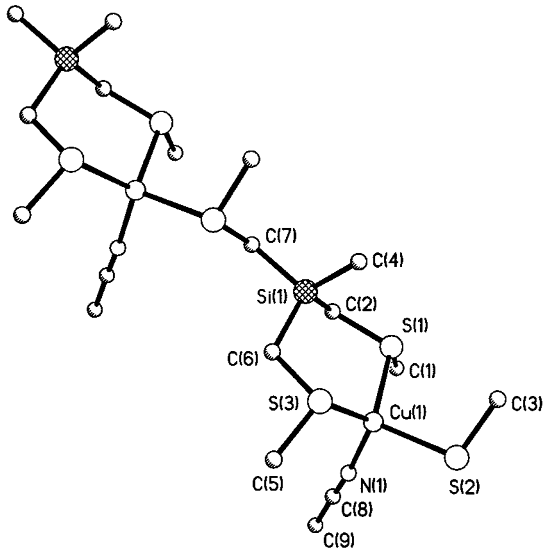

Figure 3. Two asymmetric units of the infinite chain structure of the cation in [{MeSi($CH_2SMe)_3$}Cu(NCMe)]PF_6·MeCN with hydrogen atoms, the lattice molecule of acetonitrile, and the PF_6^- counterions omitted for clarity.

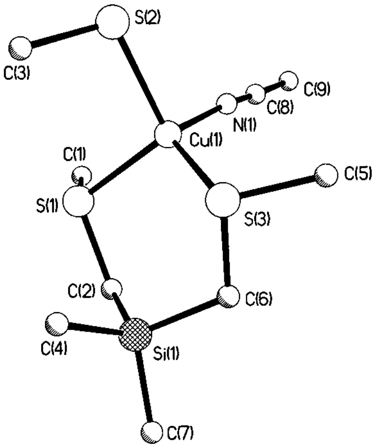

Figure 4. Copper coordination sphere in [{MeSi($CH_2SMe)_3$}Cu(NCMe)]$^+$ with hydrogen atoms omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [{MeSi($CH_2SMe)_3$}Cu(NCMe)]PF_6·MeCN

Cu(1)−S(1)	2.319(2)	Cu(1)−S(2)	2.339(2)
Cu(1)−S(3)	2.273(2)	Cu(1)−N(1)	1.985(7)
N(1)−C(8)	1.154(1)	C(8)−C(9)	1.435(1)
S(1)−Cu(1)−S(2)	106.3(1)	S(1)−Cu(1)−S(3)	109.3(1)
S(1)−Cu(1)−N(1)	107.1(2)	S(2)−Cu(1)−S(3)	110.4(1)
S(2)−Cu(1)−N(1)	104.0(2)	S(3)−Cu(1)−N(1)	119.0(2)
Cu(1)−N(1)−C(8)	172.8(7)	N(1)−C(8)−C(9)	179.0(9)

obtained from a concentrated acetonitrile solution at −30 °C. To our surprise, we found that [LCu(NCMe)]PF_6 was *also* polymeric in the solid state, with cationic [Cu(NCMe)]$^+$ fragments linked by bridging (μ-η^1:η^2) thioether ligands (Figure 3) and no close contacts with the PF_6^- counterions. Selected bond lengths and angles are shown in Table 2. The four-coordinate copper centers (Figure 4) are approximately tetrahedral, with the S−Cu−S and S−Cu−N angles varying from 104.0 to 119.0°. The Cu−S bond lengths observed in [LCu(NCMe)]PF_6, in the range 2.273(2)−2.339(2) Å, are comparable to those found in Cu_3\{MeSi($CH_2SMe)_3$\}$_2Br_3$, and the Cu−N bond length [1.985(7) Å] is on the long side, but within the range, of the corresponding distances reported for other tetrahedral acetonitrile complexes of copper(I) supported by nitrogen or sulfur donor ligands.[57−74] The binding of the acetonitrile ligands is fairly linear [Cu(1)−N(1)−C(8) = 172.8(7)°], and the rest of the metrical data (i.e., S−C, Si−C, N−C, and C−C bond lengths) are unexceptional as well.

Conclusions

In summary, the copper(I) complexes Cu_3\{MeSi($CH_2SMe)_3$\}$_2X_3$ (X = Cl, Br) and [{MeSi($CH_2SMe)_3$}Cu(NCMe)]X (X = OSO_2CF_3, BF_4, PF_6) have been prepared in excellent yield from suitable starting materials and the thioether MeSi($CH_2SMe)_3$. In contrast to the formation of octahedral group 6 metal complexes LM(CO)$_3$, which display tridentate, facially coordinated thioether ligands, MeSi($CH_2SMe)_3$ exhibits a marked tendency to bridge metal centers and form one-dimensional coordination polymers in the context of copper(I) chemistry. We are currently investigating the synthesis and reactivity of the bulkier tridentate thioether ligands MeSi($CH_2SR)_3$ (R = Ph, Bu^t) as well as exploring the corresponding reactions of other copper(I) salts. For example, CuI also reacts with MeSi($CH_2SMe)_3$ but forms instead a 1:1 product of stoichiometry LCuI and a dimeric structure in the solid state, results to be reported in due course.

Experimental Section

General Considerations. All reactions were performed under dry oxygen-free nitrogen in an Innovative Technology System One-M-DC glovebox or under argon using a combination of high-vacuum and Schlenk techniques.[75−77] Solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. MeSi($CH_2SMe)_3$[25] and [Cu(NCMe)$_4$]X (X = BF_4, PF_6)[78] were prepared as reported. ^1H and ^{13}C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts (δ) are reported in parts per million relative to $SiMe_4$ (δ = 0 ppm) and were referenced internally with respect to the residual protio solvent resonances (δ 1.94 for CD_2HCN, δ 1.39 for CD_3CN); coupling constants are given in hertz (Hz). IR spectra were recorded as KBr pellets on a Midac Collegian FT spectrophotometer and are reported in cm^{-1}; relative intensities of the absorptions are

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indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Electrospray ionization mass spectra were obtained on a PerSeptive Biosystems Mariner ESI-TOF mass spectrometer by direct infusion using acetonitrile solutions and a flow rate of 10 μL/min. Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA), or Desert Analytics (Tucson, AZ).

Synthesis of $Cu_3\{MeSi(CH_2SMe)_3\}_2Cl_3$. A stirred solution of CuCl (1.00 g, 10.10 mmol) in acetonitrile (20 mL) was treated with $MeSi(CH_2SMe)_3$ (1.40 mL, 7.05 mmol), resulting in the immediate formation of an off-white precipitate. The suspension was stirred for an additional 20 min and concentrated under reduced pressure to ca. 10 mL. After addition of diethyl ether (25 mL), the product was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo for 1 h (2.32 g, 92%). NMR data (in CD_3CN): ^{1}H δ 0.24 (s, 3 H, CH_3Si), 2.08 (s, 6 H, CH_2), 2.26 (s, 9 H, SCH_3); $^{13}C\{^1H\}$ δ −4.8 (s, 1 C, *C*H_3Si), 20.1 (s, 3 C, *C*H_2), 22.4 (s, 3 C, S*C*H_3). IR data: 2912 (m), 2870 (w), 1420 (s), 1389 (m), 1313 (m), 1250 (s), 1242 (m), 1162 (w), 1140 (s), 1113 (w), 1098 (w), 1081 (w), 971 (s), 949 (s), 831 (s), 806 (s), 774 (s), 759 (s), 741 (m), 717 (m). Anal. Calcd for $C_{14}H_{36}Cl_3Cu_3S_6Si_2$: C, 22.4; H, 4.8. Found: C, 22.5; H, 4.8.

Synthesis of $Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3$. (a) From $CuBr{\cdot}SMe_2$. A stirred orange-red suspension of $CuBr{\cdot}SMe_2$ (2.06 g, 10.10 mmol) in acetonitrile (35 mL) was treated with $MeSi(CH_2SMe)_3$ (1.40 mL, 7.05 mmol), resulting in the immediate formation of an off-white precipitate. The suspension was stirred for an additional 30 min and concentrated under reduced pressure to ca. 10 mL. After addition of diethyl ether (30 mL), the product was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo for 1 h (2.86 g, 97%). NMR data (in CD_3CN): ^{1}H δ 0.23 (s, 3 H, CH_3Si), 2.10 (s, 6 H, CH_2), 2.26 (s, 9 H, SCH_3); $^{13}C\{^1H\}$ δ −4.8 (s, 1 C, *C*H_3Si), 20.3 (s, 3 C, *C*H_2), 22.5 (s, 3 C, S*C*H_3). IR data: 2911 (m), 2869 (w), 1419 (s), 1387 (m), 1312 (m), 1251 (s), 1244 (m), 1163 (w), 1140 (s), 1114 (w), 1099 (w), 1082 (w), 971 (s), 951 (m), 830 (vs), 805 (vs), 774 (s), 757 (m), 739 (m), 717 (m). Anal. Calcd for $C_{14}H_{36}Br_3Cu_3S_6Si_2$: C, 19.0; H, 4.1. Found: C, 19.6; H, 4.2.

(b) From CuBr. A stirred red solution of CuBr (1.45 g, 10.10 mmol) in acetonitrile (20 mL) was treated with $MeSi(CH_2SMe)_3$ (1.40 mL, 7.05 mmol), resulting in the immediate formation of an off-white precipitate. The suspension was stirred for an additional 15 min, and the product was isolated by filtration, washed with diethyl ether (2 × 20 mL), and dried in vacuo for 45 min (2.60 g, 87%). The product exhibits the same spectroscopic properties as those of the compound obtained in method a.

Synthesis of $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]OSO_2CF_3$. (a) From CuCl. A stirred solution of CuCl (0.19 g, 1.92 mmol) in acetonitrile (15 mL) was treated with $AgOSO_2CF_3$ (0.49 g, 1.91 mmol), resulting in the formation of a gray precipitate (AgCl). After the mixture was stirred for 20 min, the solution was filtered and the filtrate was treated with $MeSi(CH_2SMe)_3$ (0.45 mL, 2.27 mmol). After stirring the solution for 15 min, the solvent was removed under reduced pressure to give a clear oily residue. Trituration with diethyl ether (15 mL) led to the separation of a white solid, which was isolated by filtration, washed with pentane (20 mL), and dried in vacuo for 18 h (0.64 g, 66%). NMR data (in CD_3CN): ^{1}H δ 0.25 (s, 3 H, CH_3Si), 1.96 (s, 3 H, free CH_3CN), 2.11 (s, 6 H, CH_2), 2.30 (s, 9 H, SCH_3); ^{13}C δ −4.8 (q, $^1J_{C-H}$ = 122, 1 C, *C*H_3Si), 20.3 (t, $^1J_{C-H}$ = 133, 3 C, *C*H_2), 22.8 (q, $^1J_{C-H}$ = 140, 3 C, S*C*H_3). IR data: 2976 (w), 2912 (w), 2873 (w), 2311 (w), 2277 (w), 1420 (w), 1387 (w), 1258 (vs), 1232 (m), 1175 (m), 1044 (s), 1031 (m), 969 (w), 829 (m), 806 (m), 775 (w), 668 (w), 658 (m), 638 (m), 580 (w), 520 (w). Anal. Calcd for $C_{10}H_{21}CuF_3NO_3S_4Si$: C, 25.0; H, 4.4; N, 2.9; S, 26.7. Found: C, 25.0; H, 4.4; N, 2.7; S, 26.8.

(b) From CuI. A stirred solution of CuI (0.74 g, 3.89 mmol) in acetonitrile (25 mL) was treated with $AgOSO_2CF_3$ (1.00 g, 3.89 mmol), resulting in the formation of a yellow precipitate (AgI). After stirring the mixture for 45 min, the solution was filtered and the filtrate was treated with $MeSi(CH_2SMe)_3$ (0.82 mL, 4.13 mmol). After the solution was stirred for 20 min, the solvent was removed under reduced pressure to give a clear oily residue. Trituration with diethyl ether (20 mL) led to the separation of a white solid, which was isolated by filtration, washed with pentane (20 mL), and dried in vacuo for 30 min (1.62 g, 83%). The product exhibits the same spectroscopic properties as those of the compound obtained in method a.

Table 3. Crystallographic Data for $Cu_3L_2Br_3$ and $[LCu(NCMe)]PF_6{\cdot}MeCN$ [L = $MeSi(CH_2SMe)_3$]

	$Cu_3L_2Br_3$	$[LCu(NCMe)]PF_6{\cdot}MeCN$
formula	$C_{14}H_{36}Br_3Cu_3S_6Si_2$	$C_{11}H_{24}CuF_6N_2PS_3Si$
fw	883.32	517.10
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
T, K	218(2)	173(2)
a, Å	16.3025(1)	8.4288(2)
b, Å	8.1492(1)	20.8982(2)
c, Å	23.6934(1)	12.5855(2)
β, deg	104.475(1)	99.7998(9)
V, Å^3	3047.80(4)	2184.55(5)
Z	4	4
D_c, g cm^{-3}	1.925	1.572
μ(Mo Kα), cm^{-1}	65.01	14.62
R_1/wR_2 [$I > 2\sigma(I)$]^a	0.0336/0.0712	0.0785/0.2619
R_1/wR_2 (all data)^a	0.0464/0.0871	0.0874/0.2684

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w^{-1} = \sigma^2(F_o) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2,0)]/3$.

Synthesis of $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]BF_4$. A stirred solution of $[Cu(NCMe)_4]BF_4$ (0.50 g, 1.59 mmol) in acetonitrile (15 mL) was treated with $MeSi(CH_2SMe)_3$ (0.34 mL, 1.71 mmol). The resulting clear pale yellow solution was stirred for 15 min and filtered. The filtrate was concentrated under reduced pressure to ca. 5 mL. Addition of diethyl ether (35 mL) induced the formation of a white precipitate and a small amount of a colorless oily substance which redissolved upon stirring the mixture for 15 min. The white product was isolated by filtration, washed with diethyl ether (30 mL), and dried in vacuo for 45 min (0.59 g, 89%). NMR data (in CD_3CN): ^{1}H δ 0.25 (s, 3 H, CH_3Si), 1.96 (s, 3 H, free CH_3CN), 2.07 (s, 6 H, CH_2), 2.26 (s, 9 H, SCH_3); ^{13}C δ −4.8 (q, $^1J_{C-H}$ = 125, 1 C, *C*H_3Si), 20.3 (t, $^1J_{C-H}$ = 132, 3 C, *C*H_2), 22.8 (q, $^1J_{C-H}$ = 140, 3 C, S*C*H_3). IR data: 3003 (w), 2944 (w), 2918 (w), 2895 (w), 2308 (w), 2276 (w), 1434 (m), 1378 (w), 1259 (m), 1149 (m), 1053 (vs), 971 (m), 829 (s), 805 (s), 774 (m), 759 (w), 728 (w), 697 (w), 618 (w), 521 (w). Anal. Calcd for $C_9H_{21}BCuF_4NS_3Si$: C, 25.9; H, 5.1; N, 3.4. Found: C, 26.0; H, 5.1; N, 3.9.

Synthesis of $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]PF_6$. A stirred solution of $[Cu(NCMe)_4]PF_6$ (0.50 g, 1.34 mmol) in acetonitrile (15 mL) was treated with $MeSi(CH_2SMe)_3$ (0.28 mL, 1.41 mmol). The resulting clear solution was stirred for 15 min and filtered. The filtrate was concentrated under reduced pressure to ca. 5 mL, resulting in the formation of a white precipitate. After addition of diethyl ether (40 mL), the white product was isolated by filtration, washed with diethyl ether (15 mL), and dried in vacuo for 45 min (0.57 g, 89%). NMR data (in CD_3CN): ^{1}H δ 0.25 (s, 3 H, CH_3Si), 1.96 (s, 3 H, free CH_3CN), 2.10 (s, 6 H, CH_2), 2.29 (s, 9 H, SCH_3); ^{13}C δ −4.8 (q, $^1J_{C-H}$ = 119, 1 C, *C*H_3Si), 20.3 (t, $^1J_{C-H}$ = 130, 3 C, *C*H_2), 22.7 (q, $^1J_{C-H}$ = 140, 3 C, S*C*H_3). IR data: 2911 (w), 2374 (w), 2366 (w), 2362 (w), 2357 (w), 2346 (w), 2333 (w), 2287 (w), 2273 (w), 1420 (w), 1388 (w), 1312 (w), 1251 (w), 1141 (w), 1082 (w), 971 (m), 836 (vs), 806 (s), 775 (m), 758 (w), 560 (s). Anal. Calcd for $C_9H_{21}CuF_6NPS_3Si$: C, 22.7; H, 4.5; N, 2.9. Found: C, 23.0; H, 4.3; N, 3.3.

X-ray Structure Determinations. Crystal data collection and refinement parameters are given in Table 3. Suitable crystals for data collection were selected and mounted in nitrogen-flushed, thin-walled capillaries. Data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector using Mo Kα radiation (λ = 0.710 73 Å). The systematic absences in the diffraction data were uniquely consistent with the reported space groups. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Empirical absorption corrections were applied to the data using SADABS. All non-hydrogen atoms were refined with anisotropic displacement coefficients. For $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]PF_6$, a molecule of acetonitrile was located in the asymmetric unit, and hydrogen atoms on both the coordinated and the lattice acetonitrile molecules were located from the difference map. All other hydrogen atoms in both structures were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structures of $Cu_3\{MeSi(CH_2SMe)_3\}_2Br_3$ and $[\{MeSi(CH_2SMe)_3\}Cu(NCMe)]PF_6{\cdot}MeCN$. This material is available free of charge via the Internet at http://pubs.acs.org.

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