

Synthesis and Characterization of Copper(I) and Silver(I) Telluroates and Selenolates. The X-ray Crystal Structures of $\{\text{Cu}[\text{SeC}(\text{SiMe}_3)_3]\text{PCy}_3\}_2$ and the Homoleptic Silver Selenolate $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$

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Homoleptic copper(I) and silver(I) selenolates of empirical formula $\text{M}[\text{SeC}(\text{SiMe}_3)_3]$ ($\text{M} = \text{Cu}, \text{Ag}$) were prepared by reaction of $(\text{DME})\text{LiSeC}(\text{SiMe}_3)_3$ ($\text{DME} = 1,2\text{-dimethoxyethane}$) with CuCl or AgNO_3 in DME. At -20°C , $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$ crystallized from concentrated hexane solution as a hexane solvate in the monoclinic space group $P2_1/c$ with $a = 17.848(4) \text{ \AA}$, $b = 20.017(3) \text{ \AA}$, $c = 23.997(3) \text{ \AA}$, $\beta = 92.90(2)^\circ$, $V = 8563(4) \text{ \AA}^3$, $d_{\text{calcd}} = 1.47 \text{ g cm}^{-3}$, and $Z = 4$. Reaction of CuCl with $(\text{DME})\text{LiSeC}(\text{SiMe}_3)_3$ in benzene afforded the salt $[\text{Li}(\text{DME})_2]\text{-}\{\text{Cu}[\text{SeC}(\text{SiMe}_3)_3]\}_2$. Related reactions between $\text{CuBF}_4(\text{PCy}_3)_2$ or $\text{AgBr}(\text{PCy}_3)_2$ and $(\text{THF})_2\text{LiTeC}(\text{SiMe}_3)_3$ or $(\text{DME})\text{LiSeC}(\text{SiMe}_3)_3$ in either toluene or diethyl ether gave the tricyclohexylphosphine complexes $\text{M}(\text{ER})(\text{PCy}_3)$ ($\text{E} = \text{Se}, \text{Te}$; $\text{R} = \text{C}(\text{SiMe}_3)_3$). $\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)$ is dimeric in the solid state; it crystallized from hexane at -20°C in the space group $P2_12_12_1$ with $a = 12.039(2) \text{ \AA}$, $b = 14.800(2) \text{ \AA}$, $c = 37.615(6) \text{ \AA}$, $V = 6702(3) \text{ \AA}^3$, $d_{\text{calcd}} = 1.30 \text{ g cm}^{-3}$, and $Z = 4$.

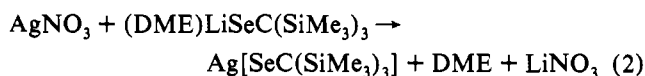
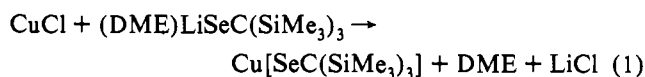
Introduction

We recently reported a series of new gold chalcogenolates¹ and now wish to describe our efforts to extend this chemistry to the lighter coinage metals, copper and silver. The chemistry of Cu and Ag compounds with the heavier group 16 elements is dominated by complexes involving selenide and telluride ligands.^{2–11} Specific examples include: $(\text{PPh}_4)_4[\text{Cu}_2\text{Te}_{12}]$,⁸ $\text{K}_4\text{Cu}_8\text{Te}_{11}$,³ and $[(\text{Ph}_4\text{P})\text{AgSe}_4]_n$.⁶ Interest in this class of compounds derives in part from their various applications in electronics ranging from superconductivity^{4,5,12} to photovoltaics.^{3,13,14} Interestingly, selenolate and telluroate complexes of these metals are rare. Only a handful of homoleptic copper telluroates^{15–17} (EtTeCu , $^n\text{BuTeCu}$, $(\text{C}_5\text{H}_{11})\text{TeCu}$, PhTeCu and $(p\text{-EtOC}_6\text{H}_4)\text{TeCu}$) and a single example of a copper selenolate $[(\text{Ph}_3\text{P})_2\text{CuIn}(\text{SeEt})_4]$ have been described.¹³ The copper telluroates are reported to be brown, insoluble powders whose structures are presently unknown. The copper selenolate has been shown to be a solid-state precursor to the ternary selenide, CuInSe_2 , one of the most

efficient solar cell materials known to date.^{13,14} The structure of the silver thienyl telluroate $[\text{Ph}_4\text{P}]_2[\text{Ag}_4(\text{TeC}_4\text{H}_3\text{S})_6]$ was described recently.¹⁸ We know of no reports of silver selenolates.

Results and Discussion

Homoleptic Selenolates. We have previously shown¹⁹ that CuCl and AgCl will quantitatively oxidize the telluroate anion $^-\text{TeSi}(\text{SiMe}_3)_3$ to the ditelluride $(\text{Me}_3\text{Si})_3\text{SiTeTeSi}(\text{SiMe}_3)_3$.^{20–27} In contrast, reactions of CuCl or AgNO_3 with the less reducing selenolate derivative $(\text{DME})\text{LiSeC}(\text{SiMe}_3)_3$ ^{28–30} in DME led to formation of homoleptic metal selenolates with empirical formulae $\text{Cu}[\text{SeC}(\text{SiMe}_3)_3]$ and $\text{Ag}[\text{SeC}(\text{SiMe}_3)_3]$ (eqs 1 and 2). Yields



of the two compounds generally range from 30 to 50% after crystallization from hexane. The colorless, crystalline materials contain substantial quantities of hexane which is rapidly lost on

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filtration and drying. The solvent is readily apparent in the X-ray structure of the silver derivative which also shows the complex to be tetrameric in the solid state (see below). The infrared spectra of the Ag and Cu complexes are quite similar, and we therefore assume the solid-state structures are analogous. Over several hours at room temperature under nitrogen, solutions of both compounds slowly decompose to give complex mixtures. These solutions are rapidly oxidized to the orange diselenide (Me₃-Si)₃CSeSeC(SiMe₃)₃ on exposure to air.

Interestingly, when the same reactions were carried out in benzene, rather than DME, the 1:1 salts [Li(DME)₂][Cu[SeC(SiMe₃)₃]₂] and [Li(DME)₂][Ag[SeC(SiMe₃)₃]₂] were obtained. Beige-pink flakes of [Li(DME)₂][Cu[SeC(SiMe₃)₃]₂] were isolated in 27% yield. The compound behaved as a 1:1 electrolyte in MeCN with $\Lambda_M = 160 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The silver salt proved impossible to isolate in pure form and was not fully characterized.

Reactions between Cu(BF₄)(PCy₃)₂ and (THF)₂LiTeC(SiMe₃)₃ or (DME)LiSeC(SiMe₃)₃ afforded Cu[TeC(SiMe₃)₃](PCy₃) and Cu[SeC(SiMe₃)₃](PCy₃), respectively. The tellurolate was isolated from hexane or toluene as very small, orange needles in 50% yield, while yellow crystals of the selenolate were isolated in yields of ca. 35%. ¹H NMR data showed the expected signals for the two ligands involved. In benzene-*d*₆ at 25 °C, the ³¹P{¹H} chemical shifts for Cu[TeC(SiMe₃)₃](PCy₃) and Cu[SeC(SiMe₃)₃](PCy₃) were 18.5 and 21.7 ppm, respectively. For comparison, free PCy₃ resonates at 10.2 ppm under similar experimental conditions. Unfortunately, ¹²⁵Te{¹H} or ⁷⁷Se{¹H} NMR signals could not be detected even at temperatures as low as -80 °C.

In a similar fashion, reaction of AgBr(PCy₃)₂ with (DME)LiSeC(SiMe₃)₃ in diethyl ether afforded Ag[SeC(SiMe₃)₃](PCy₃) as bright yellow crystals in ca. 30% yields after recrystallization from hexane. Recrystallizations were essential as the crude product was contaminated with 1 equiv of PCy₃ and small amounts (ca. 5%) of Se=PCy₃. The identity of the phosphine selenide was verified by comparison to an authentic sample (benzene-*d*₆, δ 58.3, $J_{\text{PSe}} = 707 \text{ Hz}$).³¹⁻³³ Ag[SeC(SiMe₃)₃](PCy₃) was also formed when AgBr, PCy₃, and (DME)LiSeC(SiMe₃)₃ were combined in equimolar proportions in ether; however, small amounts of Se=PCy₃ persisted in crops of the crude silver selenolate. Analogous reactivity was observed when Ag[SeC(SiMe₃)₃](PPh₃) was generated *in situ* from either AgBr(PPh₃)₂ and (DME)LiSeC(SiMe₃)₃, or AgBr, PPh₃, and (DME)LiSeC(SiMe₃)₃. In this case, small amounts of Se=PPh₃ (δ 35.8, $J_{\text{PSe}} = 756 \text{ Hz}$) were detected. Attempts to isolate the latter PPh₃ adduct yielded only the homoleptic derivative Ag₄[SeC(SiMe₃)₃]₄, containing bridging selenolates as discussed below. Since steric and entropic factors can be discounted, this result indicates that the basicity of the selenolate ligand toward silver(I) is greater than the poorly basic PPh₃.

X-ray Crystallography. The molecular structure of the Ag[SeC(SiMe₃)₃]₃ tetramer is shown in ORTEP³⁴ views in Figures 1 and 2. A packing diagram is given in Figure S1 and selected bond lengths and angles are given in Table 2. The compound crystallizes as tetrameric units packed in the unit cell with normal van der Waals contacts between the methyl groups of each tetramer and other nearby tetramer and also to the atoms of the disordered hexane solvent. The structural motif of the metal complex is similar to the related gold tellurolate Au₄[TeC(SiMe₃)₃]₄ and thiolate Au₄[SC(SiMe₃)₃]₄.¹ Of particular note is the planar Ag₄Se₄ core of Ag₄[SeC(SiMe₃)₃]₄. This contrasts

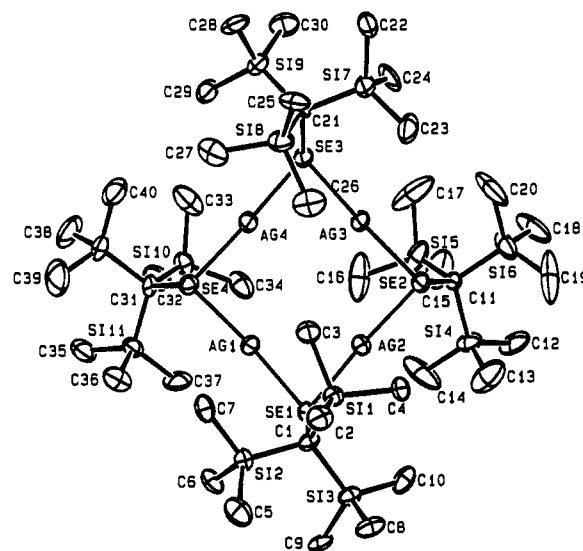


Figure 1. ORTEP view of Ag₄[SeC(SiMe₃)₃]₄ perpendicular to the Ag₄ plane. Hydrogens are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

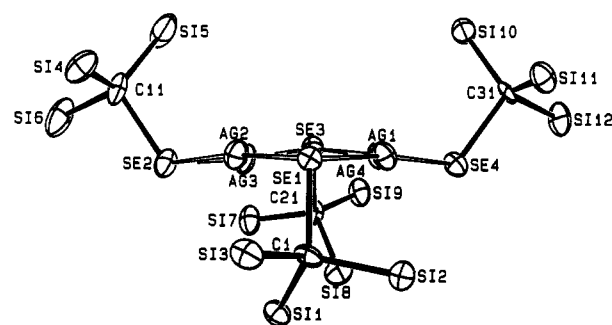


Figure 2. ORTEP view of Ag₄[SeC(SiMe₃)₃]₄ parallel to the Ag₄ plane. Methyl groups are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

Table 1. Crystallographic Parameters for Ag₄[SeC(SiMe₃)₃]₄ and Cu[SeC(SiMe₃)₃](PCy₃)

	Ag ₄ [SeC(SiMe ₃) ₃] ₄ ·2.5hexane	Cu[SeC(SiMe ₃) ₃](PCy ₃)
formula (empirical)	Ag ₄ Se ₄ Si ₁₂ C ₃₅ H ₁₄₃	SeCuPSi ₃ C ₂₈ H ₆₀
mol wt	1889.1	654.52
space group	P2 ₁ /c	P2 ₁ 2 ₁
a/Å	17.848(4)	12.039(2)
b/Å	20.107(3)	14.800(2)
c/Å	23.997(3)	37.615(6)
β/deg	92.800(16)	90
vol/Å ³	8563.2(43)	6702.1(30)
T/°C	-135	-97
Z	4	8
d _{calc} /g cm ⁻³	1.47	1.30
cryst size/mm	0.32 × 0.33 × 0.40	0.24 × 0.25 × 0.26
radiation type		Mo Kα (0.710 73 Å)
2θ range/deg	3–45	3–45
collcn range	+h,+k,±l	+h,+k,+l
abs coeff, μ/cm ⁻¹	27.7	19.0
abs cor	none	T _{min} = 0.937
(T _{max} = 1)		
no. of unique reflcns	11147	4884
no. of reflcns with F ² > 3σ(F ²)	5641	3185
no. params	661	613
final R, R _w	4.47, 4.12	4.71, 4.05
GOF	1.302	1.185

with the core in Au₄[TeC(SiMe₃)₃]₄ where the dihedral angle between two least squares planes (each containing half of the Au₄Te₄ core) was found to be 144.98(6)°, but is similar to the essentially planar Au₄S₄ core in the thiolate analogue, where the corresponding dihedral angle is 4.2(6)°. Similar planar geom-

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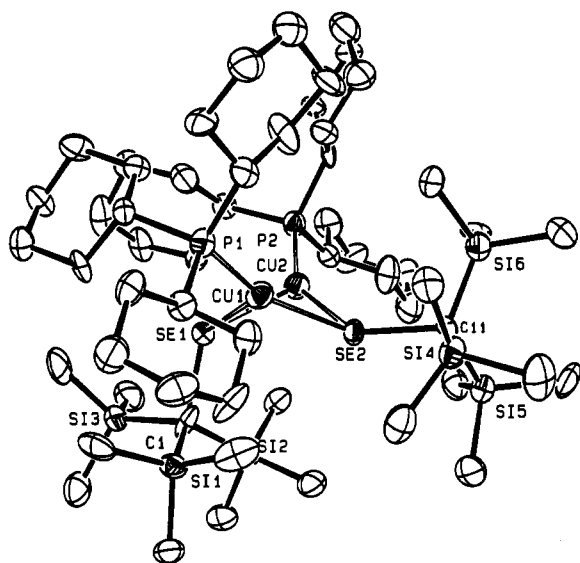
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Table 2. Selected Metrical Data for $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$

Bond Distances (Å)			
Ag1–Se1	2.488(2)	Se1–C1	2.044(10)
Ag1–Se4	2.486(2)	Se2–C11	2.025(11)
Ag2–Se1	2.480(2)	Se3–C21	2.031(11)
Ag2–Se2	2.473(2)	Se4–C31	2.055(10)
Ag3–Se3	2.479(2)	C1–Si1	1.913(11)
Ag4–Se3	2.481(2)	C1–Si2	1.913(11)
Ag4–Se4	2.479(2)	C1–Si3	1.886(10)

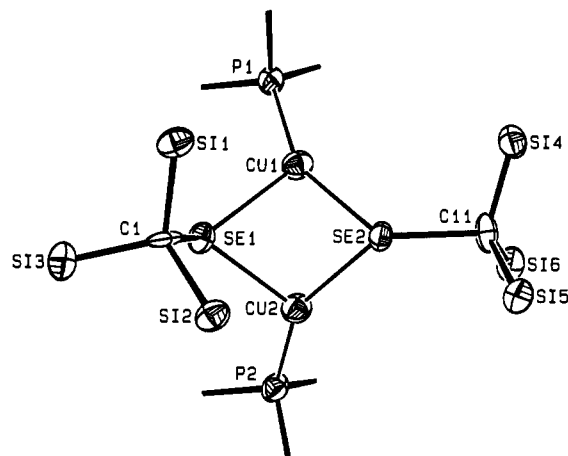
Bond Angles (deg)			
Se1–Ag1–Se4	172.45(6)	Ag3–Se3–C21	110.6(3)
Se1–Ag2–Se2	172.64(6)	Ag1–Se4–Ag4	90.97(5)
Se2–Ag3–Se3	175.05(6)	Ag1–Se4–C31	110.9(3)
Se3–Ag4–Se4	177.22(6)	Ag4–Se4–C31	109.4(3)
Ag1–Se1–Ag2	80.71(5)	Se1–C1–Si1	111.5(5)
Ag1–Se1–C1	108.2(3)	Se1–C1–Se2	104.5(5)
Ag2–Se1–C1	108.0(3)	Se1–C1–Si3	103.1(5)
Ag2–Se2–C11	110.0(3)	Si1–C1–Si2	111.4(5)
Ag3–Se2–C11	108.8(3)	Si1–C1–Si3	112.3(5)
Ag3–Se3–Ag4	81.77(5)		

**Figure 3.** ORTEP view of $[\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)_2]_2$. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

etries around Ag are seen in the silver selenide $[(\text{Ph}_4\text{P})\text{AgSe}_4]_n$,⁶ and the silver telluride $(\text{PPh}_4)_4[\text{Ag}_2\text{Te}_{12}]$.⁸

Each silver atom in $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$ is 2-coordinate, with an average Ag–Se distance of 2.480 [5] Å. This is significantly shorter than Ag–Se bond lengths determined for various silver selenides and diselenides containing Ag atoms with higher coordination numbers. Examples include $[(\text{Ph}_4\text{P})\text{AgSe}_4]_n$, where the 3-coordinate Ag–Se bond distances range from 2.545(2) to 2.672(2) Å,⁶ and $[(\text{PPh}_3)_2\text{AgSe}_2\text{WSe}_2\text{Ag}(\text{PPh}_3)]$, where both 3- and 4-coordinate Ag–Se interactions were determined (average values: 2.545(4) and 2.637(4) Å, respectively).⁹ In $[\text{Ag}_2(\text{Ph}_2\text{Se}_2)_4][\text{AsF}_6]_2$, where the Ag atoms are 5-coordinate, the Ag–Se bond lengths range from 2.580(2) to 2.711(2) Å.¹⁰ Finally, Ag–Se bond lengths in 6-coordinate $\{\text{Ag}[(\text{CH}_2\text{Se})_3]_2\}[\text{AsF}_6]$ range from 2.86(1) to 3.05(1) Å. The Se atoms in $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$ are trigonally coordinated, with Ag–Se–Ag angles ranging from 80 to 92° and Ag–Se–C angles from 108 to 111°. The Ag–Ag contacts come in two pairs: Ag1–Ag2 (3.217(1) Å) and Ag3–Ag4 (3.247(1) Å) and Ag2–Ag3 (3.560(1) Å) and Ag1–Ag4 (3.541(1) Å). The Se–C bonds average 2.039(13) Å, and the range of Si–C bonds is reasonable given the thermal motion and the disorder on some of the Si atoms.

An ORTEP³⁴ view of the molecular structure of $[\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)_2]_2$ is shown in Figures 3 and 4, with selected bond lengths and angles collected in Table 3. The structure

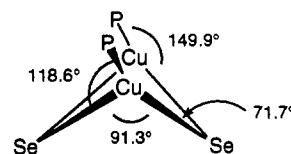
**Figure 4.** ORTEP view of $[\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)_2]_2$ emphasizing the distorted Cu_2Se_2 core. Peripheral carbon and hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.**Table 3.** Selected Metrical Data for $[\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)_2]_2$

Bond Distances (Å)			
Se1–Cu1	2.519(2)	C1–Si1	1.900(12)
Se1–Cu2	2.477(2)	C1–Si2	1.907(12)
Se2–Cu1	2.396(2)	C1–Si3	1.920(13)
Se2–Cu2	2.411(2)	Si1–C2	1.868(14)
Cu1–P1	2.245(4)	Si1–C3	1.871(16)
Cu2–P2	2.238(4)	Si1–C4	1.840(16)
C1–Se1	2.039(14)	C11–Si4	1.870(13)
C11–Se2	2.088(11)	C11–Si5	1.942(14)
C1–Se1	2.039(14)	C11–Si6	1.889(13)

Bond Angles (deg)			
Se1–Cu1–Se2	90.91(6)	Cu1–Se2–Cu2	73.31(7)
Se1–Cu1–P1	117.64(12)	Cu1–Se2–C11	131.4(4)
Se2–Cu1–P1	151.43(13)	Cu2–Se2–C11	134.6(4)
Se1–Cu2–Se2	91.57(7)	Se2–C11–Si4	106.0(6)
Se1–Cu2–P2	119.56(12)	Se2–C11–Si5	101.8(6)
Se2–Cu2–P2	148.33(13)	Se2–C11–Si6	110.3(6)
Cu1–Se1–Cu2	70.11(6)	Si4–C11–Si5	111.4(7)
Cu1–Se1–C1	122.4(3)	Si4–C11–Si6	114.3(7)
Cu2–Se1–C1	122.0(3)	Si5–C11–Si6	112.0(6)

consists of dimers packed in the unit cell with normal van der Waals contacts between molecules. The central core of the molecule is the expected structure with two selenolate ligands bridging two Cu–P fragments to give each Se two Cu neighbors and each Cu two Se neighbors and one P neighbor.

The Cu–Se–Cu–Se core has a butterfly shape, but the two Se ligands are bent in opposite directions from the average plane of the “butterfly”. In addition, while the two copper and two phosphorus atoms form a plane as expected, this plane does not bisect the angle between the two Cu_2Se_2 planes. Instead, it is bent away from that bisecting plane to form angles of 93.6(1) and 142.7(1)° to the planes containing Se1 and Se2 respectively. The consequences of this tilt also show up in the angles around the copper atoms: the coordination around each copper atom is planar, but the P–Cu–Se angles are very different. A sketch of this distortion, with angles that are the average of the chemically equivalent angles in the structure, is as follows:



As a result of the asymmetrical disposition of the two bulky phosphines, the Cu–Se distances to Se1 (2.519(2), 2.477(2) Å) and Se2 (2.396(2), 2.411(2) Å) are substantially different from each other, even given the relatively poor agreement between the

geometrically equivalent bonds. The Cu–Se bonds more directly *trans* to the Cu–P bond are almost 0.1 Å shorter than the ones that are *cis*. The Cu–Cu distance (2.871(2) Å) is unremarkable (cf. Cu–Cu distances of 2.782 and 3.404 Å in [Cu(PPh₃)₄(μ²-SPH)₂(μ³-SPH)₂]³⁵ and 2.581 Å in Cu₂(μ-OAc)₄(HOAc)₂³⁶).

Only one other copper selenolate derivative, (Ph₃P)₂CuIn-(SeEt)₄,¹³ has been structurally characterized. In this complex, the 4-coordinate copper is bound by two PPh₃ ligands and two bridging –SeEt ligands with average Cu–Se and Cu–P distances (2.526[2] and 2.275[3] Å) that are longer than those observed for {Cu[SeC(SiMe₃)₃](PCy₃)₂}.

Experimental Section

General Data. Our standard operating procedures and instrumentation were as described previously.^{19,37} All preparations were carried out with dry, oxygen-free solvents using Schlenk and glovebox techniques. Literature methods were used to prepare CuBF₄(PCy₃)₂,³⁸ AgBr(PCy₃)₂,³⁹ (THF)₂LiTeC(SiMe₃)₃,²⁸ and (DME)LiSeC(SiMe₃)₃,^{28,30} CuCl (Strem), AgBr (Elmer & Amend), AgNO₃ (Allied Chemical), and PCy₃ and PPh₃ (Aldrich), were used as received. Melting points were determined in capillaries sealed under N₂ and are uncorrected. Samples for FT IR spectroscopy were prepared as Nujol mulls between KBr plates. Chemical shifts for ¹H NMR spectra are relative to tetramethylsilane and were calibrated by measurement of the chemical shifts of the residual protons in the deuterated solvents used. Chemical shifts for ¹³C{¹H} NMR spectra are relative to tetramethylsilane and were calibrated by measurement of the chemical shifts of the deuterated solvents. Chemical shifts for ¹²⁵Te{¹H} NMR spectra are relative to Me₂Te are were calibrated with external Te(OH)₆ (δ 712 ppm). Elemental analyses were performed at the microanalytical laboratory in the College of Chemistry, University of California, Berkeley, CA.

Cu[SeC(SiMe₃)₃]. CuCl (0.24 g, 2.5 mmol) and (DME)LiSeC(SiMe₃)₃ (1.0 g, 2.5 mmol) were combined in a 100 mL round-bottomed flask. The solids were cooled to –78 °C, and DME (40 mL) was added. After removing the cold bath, the brown solution was stirred for 1 h by which point it had warmed to room temperature. The solvent was removed under reduced pressure and the solid was extracted with hexane (2 × 30 mL). Filtration afforded a clear yellow solution that was concentrated (20 mL) and cooled to –40 °C overnight. The colorless microcrystalline product was isolated by filtration (0.28 g, 31%). Mp: 160–165 °C dec. EI MS: *m/z* 622 [(Me₃Si)₃CSe]₂, 73 (SiMe₃). IR: 1250 s, 844 s, 772 sh, m, 679 m, 653 m cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 0.42 (s). ¹³C{¹H} NMR (C₆D₆): δ 3.63. Anal. Calcd for C₁₀H₂₇CuSeSi₃: C, 32.1; H, 7.27. Found: C, 31.9; H, 7.48.

[Li(DME)₂][Cu[SeC(SiMe₃)₃]. Benzene (100 mL) was added to CuCl (0.037 g, 0.37 mmol) and (DME)LiSeC(SiMe₃)₃ (0.30 g, 0.74 mmol) combined in a 100 mL round-bottomed flask wrapped in aluminum foil. After the dark cloudy solution was stirred for 1.5 h, the solvent was removed under reduced pressure, and the white residue was extracted with toluene (20 mL). Filtration afforded a clear yellow solution, which was cooled to –40 °C overnight. Colorless platelike crystals, which became opaque on drying, were isolated by filtration (0.066 g, 23%). Mp: 154–157 °C. IR: 1247 s, 1238 s, 1191 w, 1119 m, 1080 s, 1028 w, 1017 w, 861 s, 839 s, 769 w, 679 m, 652 m, 613 w, 602 w cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 3.25 (s, 6 H), 2.99 (s, 4 H), 0.50 (s, 27 H). ¹³C{¹H} NMR (C₆D₆): δ 70.2, 59.4, 3.92. Λ_M (MeCN, 1.9 mM): 160 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₂₈H₇₄CuLiO₄Se₂Si₆: C, 38.6; H, 8.56. Found: C, 39.4; H, 9.03.

Ag[SeC(SiMe₃)₃]. DME (40 mL) was added to AgNO₃ (0.21 g, 1.2 mmol) and (DME)LiSeC(SiMe₃)₃ (0.5 g, 1.2 mmol) combined in a 100 mL round-bottomed flask wrapped in aluminum foil. The red-brown mixture was stirred for 3 h, and then the solvent was removed under reduced pressure, leaving a gray residue that was extracted with hexane (2 × 30 mL). Filtration afforded a clear, light orange-brown solution, which darkened to a red-brown color on concentration (20 mL). After the solution was cooled at –40 °C overnight, large, colorless crystals of

the hexane solvate were isolated by filtration (0.29 g, 56%). These crystals quickly became opaque as they were dried. The analytical sample was dried under vacuum for several hours to produce solvent-free material. Mp: 200–205 °C dec. EI MS: *m/z* 622 [(Me₃Si)₃CSe]₂, 541 ((Me₃-Si)₃CSeC(SiMe₃)₃), 73 (SiMe₃). IR: 1250 s, 856 s, 772 s, 680 w, 656 w cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 0.47 (s). ¹³C{¹H} NMR (C₆D₆): δ 3.73. Anal. Calcd for C₁₀H₂₇AgSeSi₃: C, 28.7; H, 6.50. Found: C, 28.5; H, 6.50.

Cu[SeC(SiMe₃)₃](PCy₃). A solution of (DME)LiSeC(SiMe₃)₃ (0.29 g, 0.70 mmol) dissolved in ether (25 mL) was added to a suspension of CuBF₄(PCy₃)₂ (0.50 g, 0.74 mmol) in 15 mL of ether forming a clear, light yellow solution. The mixture was stirred for 30 min, and the ether was removed under reduced pressure leaving a colorless solid. The solid was extracted with hexane (40 mL), and the solution was filtered. Concentration to 20 mL, followed by cooling to –40 °C overnight, led to the formation of yellow crystals (0.16 g, 35%). Mp: 163–168 °C. IR: 1246 s, 1239 s, 857 vs, 838 s, 769 w, 677 m, 653 m, 611 w, 519 m, 474 w, 457 w cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 1.73–1.50 (m, PCy₃), 1.25–1.13 (m, PCy₃), 1.01 (m, PCy₃), 0.61 (s, SiMe₃). ¹³C{¹H} NMR (C₆D₆): δ 31.8, 30.9, 27.3, 26.1, 4.08. ³¹P{¹H} NMR (C₆D₆): δ 21.7. Anal. Calcd for C₂₈H₆₀CuPSeSi₃: C, 51.4; H, 9.24. Found: C, 51.5; H, 8.80.

Cu[TeC(SiMe₃)₃](PCy₃). A solution of (THF)LiTeC(SiMe₃)₃ (0.30 g, 0.59 mmol) dissolved in toluene (30 mL) was added to a solution of CuBF₄(PCy₃)₂ (0.42 g, 0.59 mmol) in 15 mL of toluene forming a clear, brown-yellow solution. The mixture was stirred for 20 min and then allowed to settle. Filtration and concentration (15 mL), followed by cooling to –40 °C overnight, led to the formation of a copper-colored powder that was isolated by filtration (0.21 g, 51%). Mp: 160–163 °C. IR: 1247 m, 1240 m, 1113 w, 1001 w, 855 vs, 839 s, 767 w, 677 w, 646 m, 614 w, 559 m, 510 w, 473 w cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 1.91–1.63 (m, PCy₃), 1.42–1.35 (m, PCy₃), 1.27–1.11 (m, PCy₃), 0.63 (s, SiMe₃). ¹³C{¹H} NMR (C₆D₆): δ 31.8, 30.9, 27.7, 26.7, 5.63. ³¹P{¹H} NMR (C₆D₆): δ 18.5. Anal. Calcd for C₂₈H₆₀CuPTeSi₃: C, 47.8; H, 8.60. Found: C, 48.8; H, 8.60.

Ag[SeC(SiMe₃)₃](PCy₃). Diethyl ether (40 mL) was added to AgBr(PCy₃)₂ (0.60 g, 0.80 mmol) and (DME)LiSeC(SiMe₃)₃ (0.33 g, 0.80 mmol) in a 100-mL round-bottomed flask covered with aluminum foil. The mixture was stirred for 20 min and then allowed to settle. Filtration afforded a pale yellow solution that was evaporated to dryness. The resulting solid was extracted with toluene (30 mL), and the solution was concentrated to ca. 15 mL and cooled to –40 °C overnight. Yellow crystals (0.16 g, 30%) were isolated by filtration. Mp: 150–154 °C. IR: 1247 m, 1238 s, 1111 w, 1002 m, 858 vs, 840 vs, 766 m, 680 m, 650 m, 614 w, 591 m, 509 m, 470 m cm⁻¹. ¹H NMR (300 MHz, C₆D₆): δ 1.71–1.52 (m, PCy₃), 1.23–1.07 (m, PCy₃), 1.04–1.01 (m, PCy₃), 0.64 (s, 27 H). ¹³C{¹H} NMR (C₆D₆): δ 32.2, 31.2, 27.4, 26.2, 4.00. ³¹P{¹H} NMR (C₆D₆): δ 33.1. Anal. Calcd for C₂₈H₆₀AgPSeSi₃: C, 48.1; H, 8.65. Found: C, 48.5; H, 8.67.

X-ray Structural Studies. Crystals of Ag₄[SeC(SiMe₃)₃]₄ immediately became opaque on drying in a nitrogen atmosphere; therefore, they were removed from their mother liquor in a glovebox and quickly covered with Paratone N hydrocarbon oil. A suitable crystal was cut and mounted on a glass fiber using the Paratone N, which solidified on cooling to data collection temperatures.

Cell dimensions and their esds for Ag₄[SeC(SiMe₃)₃]₄ and [Cu[SeC(SiMe₃)₃](PCy₃)₂] were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 26° and 30° (Table 1). Intensity standards were measured on the diffractometer using graphite-monochromated Mo Kα radiation. Intensity check reflections were measured after every hour of data collection. Standards for both compounds revealed a reduction of 10% of the original intensity over the data collection period. Three reflections were checked for centering after every 250 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10° from their predicted positions; reorientations were carried out twice for both compounds. Linear corrections for decay and appropriate empirical absorption corrections based on azimuthal scan data were made.

The crystal structure of Ag₄[SeC(SiMe₃)₃]₄ was solved by Patterson methods,⁴⁰ while that of [Cu[SeC(SiMe₃)₃](PCy₃)₂] was solved by direct methods using SHELXS-86.⁴¹ In the structure of Ag₄[SeC(SiMe₃)₃]₄,

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Table 4. Positional Parameters and Their Estimated Standard Deviations for $[\text{AgSeC}(\text{SiMe}_3)_4]^a$

atom	x	y	z	$B/\text{Å}^2$
Ag1	0.15943(1)	0.17583(1)	0.10543(1)	2.43(2)
Ag2	0.33973(1)	0.16917(1)	0.11167(1)	2.55(2)
Ag3	0.34583(1)	0.31525(1)	0.19637(1)	2.87(2)
Ag4	0.16402(1)	0.32406(1)	0.18604(1)	2.70(2)
Se1	0.24603(6)	0.09135(1)	0.06801(1)	1.99(3)
Se2	0.43850(6)	0.23453(6)	0.16282(1)	2.57(3)
Se3	0.25886(6)	0.40374(6)	0.22568(1)	2.61(3)
Se4	0.06449(6)	0.24764(6)	0.14858(1)	2.33(3)
Si1	0.2794(2)	0.0258(2)	0.1916(1)	2.11(7)
Si2	0.1390(2)	-0.0170(2)	0.1144(1)	2.35(7)
Si3	0.3039(2)	-0.0531(2)	0.0801(1)	2.43(8)
Si4	0.5291(2)	0.2157(2)	0.0549(2)	3.38(9)
Si5	0.4536(2)	0.3552(2)	0.0756(2)	4.7(1)
Si6	0.5884(2)	0.3031(2)	0.1561(2)	4.8(1)
Si7	0.3547(2)	0.4229(2)	0.3373(1)	3.31(9)
Si8	0.2158(2)	0.3248(2)	0.3379(1)	3.23(8)
Si9	0.1892(2)	0.4798(2)	0.3220(2)	3.26(9)
Si10	0.0557(2)	0.3646(2)	0.0557(2)	2.87(9)
Si11	-0.0338(2)	0.2284(2)	0.0374(2)	2.89(9)
Si12	-0.0799(2)	0.3296(2)	0.1305(2)	3.7(1)
C1	0.2426(6)	0.0079(5)	0.1169(4)	1.9(3)
C2	0.2518(6)	-0.0425(6)	0.2399(5)	3.3(3)
C3	0.2457(6)	0.1047(6)	0.2223(4)	3.0(3)
C4	0.3825(6)	0.0293(6)	0.1996(5)	3.2(3)
C5	0.1270(7)	-0.1079(6)	0.1317(5)	4.2(3)
C6	0.0896(6)	-0.0032(6)	0.0451(5)	3.4(3)
C7	0.0824(6)	0.0291(6)	0.1647(5)	2.8(3)
C8	0.3276(7)	-0.1293(6)	0.1236(5)	3.7(3)
C9	0.2581(6)	-0.0838(5)	0.0140(4)	2.8(3)
C10	0.3951(6)	-0.0170(6)	0.0612(5)	3.4(3)
C11	0.5037(6)	0.2814(6)	0.1082(5)	2.6(3)
C12	0.6151(7)	0.2404(7)	0.0190(5)	5.2(4)
C13	0.5461(8)	0.1321(7)	0.0859(7)	6.8(4)
C14	0.4534(8)	0.2044(8)	0.0000(5)	8.1(5)
C15	0.5022(8)	0.3844(7)	0.0120(7)	7.2(5)
C16	0.3541(7)	0.3379(8)	0.0528(6)	7.6(4)
C17	0.4503(9)	0.4294(7)	0.1253(8)	10.3(5)
C18	0.6496(8)	0.3660(8)	0.1202(6)	8.1(5)
C19	0.6472(7)	0.229(1)	0.1762(7)	8.8(5)
C20	0.5616(8)	0.3463(9)	0.2221(6)	9.5(5)
C21	0.2545(5)	0.4057(5)	0.3101(4)	1.9(2)
C22	0.3574(6)	0.4563(7)	0.4107(5)	3.7(3)
C23	0.4145(7)	0.3448(7)	0.3384(5)	4.6(4)
C24	0.4028(7)	0.4842(7)	0.2930(5)	4.9(4)
C25	0.2353(7)	0.3162(6)	0.4153(4)	3.4(3)
C26	0.2551(7)	0.2492(6)	0.3046(5)	4.4(3)
C27	0.1111(7)	0.3175(6)	0.3259(5)	4.2(3)
C28	0.1539(7)	0.4756(6)	0.3942(5)	4.4(3)
C29	0.1069(6)	0.4821(6)	0.2721(5)	3.7(3)
C30	0.2366(8)	0.5624(6)	0.3146(6)	5.0(4)
C31	-0.0008(5)	0.2964(5)	0.0886(4)	2.0(3)
C32	0.0069(7)	0.3939(6)	-0.0103(6)	4.7(4)
C33	0.0673(8)	0.4418(7)	0.1014(6)	6.0(4)
C34	0.1513(7)	0.3382(7)	0.0375(5)	4.6(4)
C35	-0.1206(7)	0.2561(7)	-0.0043(5)	4.7(4)
C36	-0.0580(7)	0.1481(6)	0.0710(5)	4.6(4)
C37	0.0370(8)	0.2084(7)	-0.0153(5)	5.0(4)
C38	-0.1350(8)	0.3943(8)	0.0903(7)	6.9(4)
C39	-0.1464(7)	0.2601(8)	0.1505(6)	6.7(4)
C40	-0.0490(7)	0.3697(7)	0.1979(5)	4.9(4)

^a The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,2)]$, where a , b , and c are real cell parameters, and $\beta(i,j)$ are anisotropic β 's.

two of the ligands have apparent disorder of the SiMe_3 groups. When fractional-occupancy Si atoms were included, the R -value dropped significantly. Distances and angles to the fractional-occupancy Si atoms are given in the tables as well as those to the majority component.

Positional and thermal parameters were refined by full-matrix least-squares methods. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w (=1/\sigma^2(F_o))$ was the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 for both compounds. In the final cycle of the refinement, all parameter shift/

Table 5. Positional Parameters and Their Estimated Standard Deviations for $\text{Cu}[\text{SeC}(\text{SiMe}_3)_3]\text{PCy}_3^a$

atom	x	y	z	$B/\text{Å}^2$
Se1	0.2119(1)	0.13434(7)	0.12412(1)	2.33(2)
Se2	0.2006(1)	-0.10171(7)	0.13030(1)	2.23(2)
Cu1	0.3007(1)	0.0133(1)	0.16166(1)	2.79(3)
Cu2	0.2653(1)	0.0044(1)	0.08630(1)	2.78(3)
P1	0.4239(3)	0.0570(2)	0.20304(9)	2.52(8)
P2	0.3579(3)	0.0288(2)	0.03560(9)	2.67(8)
Si1	0.0121(3)	0.1619(3)	0.17936(9)	2.65(8)
Si2	-0.0450(3)	0.1054(3)	0.09987(9)	2.53(8)
Si3	0.0538(3)	0.2975(2)	0.1170(1)	2.88(9)
Si4	0.1929(3)	-0.2671(2)	0.18352(9)	2.98(8)
Si5	0.0668(3)	-0.2756(2)	0.1102(1)	2.87(9)
Si6	0.3300(3)	-0.2903(2)	0.1125(1)	3.13(9)
C1	0.050(1)	0.1725(7)	0.1305(3)	2.7(3)
C2	-0.140(1)	0.1794(8)	0.1868(3)	3.3(3)
C3	0.081(1)	0.248(1)	0.2084(3)	4.1(4)
C4	0.045(1)	0.050(1)	0.1982(3)	4.5(4)
C5	-0.179(1)	0.1674(9)	0.0907(3)	3.4(3)
C6	-0.090(1)	-0.0038(9)	0.1189(3)	3.6(3)
C7	0.020(1)	0.0770(8)	0.0563(3)	3.4(3)
C8	-0.069(1)	0.3626(8)	0.1323(4)	4.3(4)
C9	0.056(1)	0.3150(9)	0.0675(4)	4.8(4)
C10	0.175(1)	0.3607(7)	0.1345(4)	4.4(4)
C11	0.203(1)	-0.2423(7)	0.1349(3)	2.6(3)
C12	0.149(1)	-0.3858(8)	0.1924(3)	4.8(4)
C13	0.095(1)	-0.1954(9)	0.2086(3)	4.0(4)
C14	0.327(1)	-0.2531(9)	0.2071(4)	4.5(4)
C15	0.065(1)	-0.3995(9)	0.0990(4)	4.2(4)
C16	-0.061(1)	-0.2572(9)	0.1372(3)	3.7(3)
C17	0.044(1)	-0.2171(8)	0.0671(3)	3.7(3)
C18	0.348(1)	-0.4143(8)	0.1212(4)	4.6(4)
C19	0.461(1)	-0.2388(8)	0.1288(4)	3.8(3)
C20	0.331(1)	-0.2702(9)	0.0637(4)	4.3(4)
C21	0.5418(9)	-0.0205(8)	0.2118(3)	2.8(3)
C22	0.6387(9)	0.0143(9)	0.2336(3)	2.9(3)
C23	0.724(1)	-0.0595(8)	0.2403(3)	3.8(3)
C24	0.765(1)	-0.1028(8)	0.2067(3)	3.6(3)
C25	0.670(1)	-0.1352(8)	0.1842(4)	3.9(3)
C26	0.587(1)	-0.0595(9)	0.1772(3)	4.1(3)
C27	0.345(1)	0.0644(8)	0.2451(3)	2.6(3)
C28	0.291(1)	-0.0268(8)	0.2648(3)	3.1(3)
C29	0.209(1)	-0.161(9)	0.2850(3)	4.0(3)
C30	0.262(1)	0.0265(9)	0.3176(3)	3.8(3)
C31	0.316(1)	0.1149(8)	0.3083(3)	4.0(3)
C32	0.400(1)	0.1038(8)	0.2783(3)	3.3(3)
C33	0.485(1)	0.1708(7)	0.1953(3)	2.6(3)
C34	0.397(1)	0.2445(8)	0.1970(3)	2.7(3)
C35	0.440(1)	0.3376(8)	0.1876(3)	3.1(3)
C36	0.497(1)	0.3364(8)	0.1512(3)	3.0(3)
C37	0.588(1)	0.2680(8)	0.1513(3)	3.3(3)
C38	0.5446(9)	0.1737(7)	0.1595(3)	2.5(3)
C39	0.400(1)	0.1464(8)	0.0264(3)	2.5(3)
C40	0.299(1)	0.2074(7)	0.0222(3)	3.2(3)
C41	0.330(1)	0.3062(8)	0.0144(3)	4.0(3)
C42	0.408(1)	0.3411(8)	0.0430(3)	4.9(3)
C43	0.510(1)	0.2815(9)	0.0479(4)	3.8(3)
C44	0.475(1)	0.1844(9)	0.0559(4)	4.2(4)
C45	0.488(1)	-0.0377(7)	0.0314(3)	2.3(3)
C46	0.5722(9)	-0.0059(8)	0.0035(3)	2.6(3)
C47	0.670(1)	-0.0723(8)	0.0017(3)	3.4(3)
C48	0.723(1)	-0.0881(9)	0.0369(4)	4.5(4)
C49	0.641(1)	-0.1174(9)	0.0643(4)	4.2(4)
C50	0.542(1)	-0.0541(8)	0.0660(3)	3.5(3)
C51	0.2679(9)	0.0007(8)	-0.0031(3)	3.0(3)
C52	0.222(1)	-0.0955(9)	-0.0002(3)	4.6(4)
C53	0.136(1)	-0.1134(9)	-0.0278(4)	4.9(4)
C54	0.174(1)	-0.0952(9)	-0.0651(4)	5.1(4)
C55	0.221(1)	-0.002(1)	-0.0680(3)	4.5(3)
C56	0.314(1)	0.0165(9)	-0.0401(3)	4.1(3)

^a The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \gamma)\beta(2,3)]$, where a , b , and c are real cell parameters, and $\beta(i,j)$ are anisotropic β 's.

error values were less than 0.01σ . The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors

were corrected for both real and imaginary components of anomalous dispersion. The largest peaks in the final difference Fourier maps for $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$ and $[\text{Cu}[\text{SeC}(\text{SiMe}_3)_3](\text{PCy}_3)]_2$ were 0.75 and 0.66 $\text{e}/\text{\AA}^3$, respectively, and the lowest excursions were -0.20 and -0.17 $\text{e}/\text{\AA}^3$, respectively.

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Supplementary Material Available: Tables of crystallographic data, temperature factor expressions, positional parameters, intramolecular distances and angles, least-squares planes, torsional angles and anisotropic thermal parameters for both structures and a view (Figure S1) of the disordered hexane in $\text{Ag}_4[\text{SeC}(\text{SiMe}_3)_3]_4$ (33 pages). Ordering information is given on any current masthead page.