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Mercury–Silver Sulfur Complexes

Stable -ESiMe₃ Complexes of Cu¹ and Ag¹ (E = S, Se) with NHCs: Synthons in Ternary Nanocluster Assembly

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Abstract: As a part of efforts to prepare new "metallachalcogenolate" precursors and develop their chemistry for the formation of ternary mixed-metal chalcogenide nanoclusters, two sets of thermally stable, N-heterocyclic carbene metalchalcogenolate complexes of the general formula [(IPr)Ag– ESiMe₃] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; E = S, 1; Se, 2) and [(*i*Pr₂-bimy)Cu–ESiMe₃]₂ (*i*Pr₂bimy = 1,3-diisopropylbenzimidazolin-2-ylidene; E = S, 4; Se, 5) are reported. These are prepared from the reaction between the corresponding carbene metal acetate, [(IPr)-AgOAc] and [(*i*Pr-bimy)CuOAc] respectively, and E(SiMe₃)₂ at low temperature. The reaction of [(IPr)Ag–ESiMe₃] 1 with mercury(II) acetate affords the heterometallic complex [{($|Pr\rangleAgS$ }_2Hg] **3** containing two ($|Pr\rangleAg-S^-$ fragments bonded to a central Hg^{II}, representing a mixed mercury-silver sulfide complex. The reaction of [(iPr_2 -bimy)Cu-SSiMe_3]₂, which contains a smaller N-heterocyclic-carbene, with mercuric(II) acetate affords the high nuclearity cluster, [(iPr_2 -bimy)₆Cu₁₀S₈Hg₃] **6**. The new N-heterocyclic carbene metal-chalcogenolate complexes **1**, **2**, **4**, **5** and the ternary mixed-metal chalcogenolate complex **3** and cluster **6** have been characterized by multinuclear NMR spectroscopy (¹H and ¹³C), elemental analysis and single-crystal X-ray diffraction.

Introduction

To date, the exploration of binary, late d-block molecular metal-chalcogenide nanoclusters has been much more extensive^{[1]} than that of ternary (MM'E) (E=S, Se, Te) systems. This may be attributed, in part, to a lack of suitable "binary" reagents that can be employed to yield ternary chalcogenide clusters in a controlled manner. A general molecular synthetic route to access ternary nanoclusters is desirable since the incorporation of different metals in ternary clusters can markedly affect, for example, the photophysical properties,^[2] mirroring the tailoring of optical and electronic properties in extended solid materials.^[3] In this regard, metal-chalcogenolate complexes of the d-block containing trimethylsilyl moieties (M- $ESiMe_3$; E = S, Se, Te), continue to draw considerable attention^[4] due to their optimized reactivity, which can be used for the controlled assembly of ternary cluster and nanocluster complexes.^[5] This is achieved via the selective cleavage of the E-Si

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bond when the "binary" silyl reagent, M–ESiMe₃, is reacted with a second metal salt, M′–X, to yield M–E–M′ units along with XSiMe₃ and form, ultimately, a ternary polynuclear complex. This strategy has been demonstrated with the formation of phosphine stabilized ternary clusters from the reaction between [(R₃P)_nCu–ESiMe₃] (E=S, Se) with In, Ga, Ag, and Hg salts.^[6]

Not only do the steric and electronic properties of the ancillary phosphine play a role in the final size and shape of ternary metal chalcogenide nanocluster cores, but they are key components in the formation of the metal chalcogenolate precursors as well.^[1a] Despite their utility, the coordination complexes of Cu and, especially, Ag are thermally sensitive even when isolated from solvent. Although enhanced thermal stability can be achieved with larger substituents about the silicon center, this ultimately prohibits selective silicon bond cleavage with other metal salts. As part of the continued interest in developing the chemistry of metal chalcogenolate precursors,^[7] we recently communicated the use of an alternate ancillary ligand, such as the N-heterocyclic carbene IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene), to increase the thermal stability of Cu-ESiMe₃, at the same time promoting an oriented coordination on the copper center with the preparation of [(IPr)Cu-ESiMe₃]. We also demonstrated that the strong bonding of IPr with Cu^I would enhance the kinetic stability first formed Cu-S-M' complexes.^[8] More recently, Zhai and coworkers reported the synthesis of the dimetallic $Cu_2^{I}(\mu$ -S) complex via ligation of the bulkier carbene 1,3-bis(2,6-(diphenylmethyl)-4-methlphenyl)imidazol-2-ylidene as the ancillary ligand.^[9]

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In this vein, access to a range of [(NHC)M–ESiMe₃] (NHC = N-heterocyclic carbene; M = Cu, Ag; E = S, Se) is of fundamental importance for the formation of new ternary metal chalcogenide nanocluster architectures. For a comparison with the recently reported [(IPr)Cu–ESiMe₃]^[8] and to evaluate the influence of metal or ancillary ligand change on the structural features and thermal stability, herein we report the synthesis, crystal structures, and spectroscopic characterization of the new silver(I) and copper(I) (trimethylsilyl)chalcogenolates stabilized with IPr and (*i*Pr₂-bimy), respectively: [(IPr)Ag–ESiMe₃] (E = S, 1; E = Se, 2) and [(*i*Pr₂-bimy)Cu–ESiMe₃]₂ (E = S, 4; E = Se, 5). We also describe details of the reactivity of 1 and 4 via the reaction with mercuric(II) acetate and the formation of the ternary mixed-metal complex [{(IPr)AgS}₂Hg] 3 and cluster [{(*i*Pr-bimy)₆Cu₁₀S₈Hg₃] 6.

Results and Discussion

The facile synthetic route to **1** and **2** involves dissolving [(IPr)-AgOAc] with one equivalent of bis(trimethylsilyl)chalcogenide in tetrahydrofuran at low temperature (-70°C; Scheme 1a). We have already shown that the large N-heterocyclic carbene ligand is critical for the stabilization of [(IPr)Cu–ESiMe₃], as it is essential to occupy/block the coordination sites around metal center and to force terminal coordination of the formed silyl-chalcogenolate, thus avoiding the generation of polynuclear copper–chalcogenide complexes. Unlike the phosphine ligated



Scheme 1. Synthesis of a) [(IPr)Ag–ESiMe_3] (E=S, 1; E=Se, 2); b) [{(IPr)-Ag–E}_2Hg] 3.

metal silylchalcogenolates where an excess amount of phosphine is required to force terminal coordination of the chalcogenolate ligand, applying a large volume NHC^[10] such as the ligand IPr ensures such a terminal coordination on the metal center. When a solution of the N-heterocyclic carbene silver acetate adduct [(IPr)AgOAc] is cooled to -70 °C and one equivalent of bis(trimethylsilyl)chalcogenide is added, [(IPr)Ag–ESiMe₃] forms selectively in good yields. Under these conditions, there is selective displacement of one of the two E–SiMe₃ bonds to yield 1 (S) and **2** (Se). Solutions are warmed to -25 °C and kept at that temperature for 10-12 h, followed by layering with cold pentane to crystallize the coordination complexes.

Complexes 1 and 2 crystallize as colorless blocks with relatively high melting points (1: 175-179; 2: 170-175 °C). The high thermal stability of 1 and 2 contrasts with those for $[(R_3P)_nAg-ESiMe_3]$ (T < 10 °C) and arises from the use of the ancillary ligand IPr. Such an improvement in the thermal stability, which also has already been shown for $[(IPr)Cu-ESiMe_3]$, facilitates their crystal growth, purification, and their "bottleability" for use in subsequent cluster-forming reaction steps. Complete structural information was obtained for 1 and 2 from single-crystal X-ray crystallographic analyses (Tables 1 and 2). The molecular structures of $[(IPr)Ag-SSiMe_3]$ 1 and $[(IPr)Ag-SeSiMe_3]$ 2 are illustrated in Figure 1 and the Supporting Information, Figure S1, respectively. The complexes 1 and 2 are the first examples of structurally characterized silver chalcogenolates containing the –ESiMe_3 moiety.

Compounds 1 and 2 crystallize in space group $P\overline{1}$. Selected angles and bond distances, as well as those for the related [(IPr)Cu–ESiMe₃] for comparison, are summarized in Table 1. Compounds 1 and 2 display a slightly less distorted linear coordination geometry (C-Ag-E \approx 175°) compared to their copper analogues (C-Cu-E \approx 171°).^[8] Expectedly, 1 and 2 display longer metal-chalcogen and metal-carbon bonds versus [(IPr)Cu– ESiMe₃]. These longer metal-chalcogen and metal-carbon distances are accompanied by a larger torsion angle between the pendent trimethylsilyl group and the plane defined by the imidazolin-2-ylidene ring of the carbene ligand. The M-E-Si angles in 1 and 2 are slightly larger than those for [(IPr)Cu–SSiMe₃] and [(IPr)Cu–SeSiMe₃].^[8] The silver–chalcogen and chalcogen– silicon bond lengths show the expected increase from sulfur to selenium.

Although 1 and 2 are unstable in solution above 0° C, they remain stable in solvent for extended periods at lower temperatures. Monitoring the reactions for the formation of 1 and 2 via ¹H NMR spectroscopy at low temperatures indicates the

Table 1. Selected bond lengths [Å], angles [°], and torsion angle [°] ^(a) of 1, 2, and the isostructural copper complexes. ⁽⁸⁾										
	C-M-E [°]	M–C [Å]	M—E [Å]	C3–N2···E–Si [°]	M-E-Si [°]	E—Si [Å]				
[(IPr)Ag–SSiMe ₃] 1	175.2(2)	2.089(6)	2.431(2)	15.3(3)	104.65(5)	2.093(3)				
[(IPr)Ag—SeSiMe ₃] 2	175.18(9)	2.093(3)	2.4334(9)	2.70(2)	100.42(2)	2.238(2)				
[(IPr)Cu—SSiMe ₃]	171.6(1)	2.133(1)	2.133(1)	85.1(5)	101.6(1)	2.105(2)				
[(IPr)Cu—SeSiMe ₃]	170.68(5)	1.884(1)	2.2431(7)	85.2(3)	98.53(4)	2.2502(7)				
[a] Defined as being between the plane defined by the central ring of the IPr ligand and the E–Si vector.										

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Table 2. Crystallographic data and parameters for compounds 1–6. ^[a]									
	1	2	3	4	5	6			
Formula	$C_{30}H_{45}AgN_2SSi\cdotTHF$	C ₃₀ H ₄₅ AgN ₂ SeSi·THF	$C_{54}H_{72}Ag_{2}HgN_{4}S_{2}\cdot4THF$	$C_{32}H_{54}Cu_2N_4S_2\text{-}THF$	$C_{32}H_{54}Cu_2N_4Se_2{\cdot}2THF$	C ₇₈ H ₁₀₈ Cu ₁₀ Hg ₃ N ₁₂ S ₈ ·5.5THF			
Formula weight	673.80	720.70	1546.02	814.27	980.18	3103.44			
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic			
Space group	PĨ	ΡĨ	PĪ	C2/c	P2 ₁ /c	P2 ₁ /n			
a [Ă]	10.196(2)	10.309(3)	14.614(3)	10.379(3)	20.371(5)	17.820(4)			
b [Å]	12.625(3)	12.604(5)	16.118(3)	16.442(4)	21.812(5)	34.856(4)			
c [Å]	16.038(5)	16.151(5)	16.572(3)	24.602(7)	21.819(6)	21.289(4)			
α [°]	67.516(13)	68.375(15)	88.030(8)	90	90	90			
β [°]	79.534(12)	78.886(13)	66.251(8)	94.930(13)	101.334(10)	100.093(10)			
γ [°]	71.104(9)	71.154(11)	87.115(9)	90	90	90			
V [ų]	1800.8(9)	1839.9(10)	3567.8(11)	4182.7(19)	9506(4)	13018(4)			
Ζ	2	2	2	4	8	4			
$ ho_{cal} [gcm^{-3}]$	1.243	1.301	1.439	1.293	1.370	1.583			
<i>M</i> (Mo _{Kα}) [mm ⁻¹]	0.677	1.595	2.795	1.206	2.512	5.295			
F(000)	712	748	1580	1728	4064	6151			
T [K]	110	110	110	110	110	110			
$\theta_{\min}, \theta_{\max}$ [°]	2.64, 30.00	2.60, 34.22	2.95, 28.17	2.48, 34.85	2.51, 29.25	2.61, 28.66			
Total reflns	20047	25554	31783	69222	209634	561862			
Unique reflns	5584	5942	21890	9133	29090	63135			
R(int)	0.0507	0.0377	0.0562	0.0422	0.0306	0.1237			
<i>R</i> 1	0.0610	0.0333	0.0534	0.0277	0.0494	0.0686			
wR2 [$l \ge 2\sigma$ (l)]	0.1740	0.1028	0.1399	0.0904	0.1433	0.1879			
R1 (all data)	0.0735	0.0382	0.0967	0.0422	0.1237	0.1875			
wR2 (all data)	0.1945	0.1180	0.1954	0.1205	0.1713	0.2464			
GOF	1.141	1.125	1.075	1.175	1.033	1.038			
$[a] R_1 = \Sigma(F_o - F_c) / \Sigma F_{o'} wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(wF_o^2)]^{1/2}, \text{ GOF} = [\Sigma(w(F_o^2 - F_c^2)^2) / (N_{observns} - N_{params})]^{1/2}.$									



Figure 1. The molecular structure of [(IPr)Ag–SSiMe₃] **1** (elipsoids set at 40% probability; hydrogen atoms are omitted); Selected bond lengths [Å] and angles [°]: C1–Ag1 2.089(6), Ag1–S1 2.341(2), S1–Si1 2.093(3); C1-Ag1-S1 175.2(2), Ag1-S1-Si1 101.6(1).

quantitative replacement of the acetate group with –ESiMe₃ to form [(IPr)Ag–ESiMe₃] and AcOSiMe₃. Along with a set of resonances assigned to one molecule of AcOSiMe₃ and the coordinated IPr ligand, a high-field signal is observed at –0.13 and –0.02 ppm from the coordinated –SSiMe₃ and –SeSiMe₃, respectively, which satisfactorily integrates as nine hydrogen atoms versus IPr. The chemical shifts of –ESiMe₃ are at slightly lower field compared to those reported for their copper analogues (IPrCuSSiMe₃: δ , –0.17; IPrCuSeSiMe₃: –0.04 ppm) and at considerably higher field compared to those reported in tetrahedral [L₃Ag–ESiMe₃] (L=R₃P: δ , 0.10–0.34 ppm). ¹³C{¹H} NMR spectroscopy can also be used confirm coordination of $-ESiMe_3$ ligands, with a peak observed at 7.0 and 7.6 ppm for $-ESiMe_3$ in 1 and 2, respectively.

The pendent –SSiMe₃ in [(IPr)Cu–SSiMe₃] has been shown to react with Hg(OAc)₂ to yield the heterometallic complex [{(IPr)-CuS}₂Hg], which contains two (IPr)Cu–S⁻ fragments bonded to a central Hg^{II}.^[8] This builds upon the reaction of [(Pr₃P)₃Cu–SSiMe₃] with Hg(OAc)₂ which has been shown to lead to the ternary cluster [Hg₁₅Cu₂₀S₂₅(PPr₃)₁₈] by activation of S–Si bonds and the ligand stabilized assembly of the forming Cu–S–Hg units.^[6a]

The known reactivity of silver salts toward -ESiMe₃ reagents in the assembly of Ag₂S megaclusters^[11] makes Ag-ESiMe₃ extremely attractive targets for the assembly of polynuclear Ag-E-M species. Efforts to use $[(L)_n Ag-SSiMe_3]$ (L=tertiary phosphine) for reactions with Hg^{II} metal salts for ternary Ag-S-Hg ternary complex formation have proven more difficult than those for Cu regarding formation of monosdisperse clusters. However, the more stable chalcogenolates 1 offer an entry point for the formation of a mercury-silver-sulfide ternary complex. When 1 is treated with 0.5 equivalents of Hg(OAc)₂ at low temperatures, the trimetallic complex [{(IPr)AgS}₂Hg] 3 forms (Scheme 1b). This is achieved via the controlled cleavage of the S-Si and the formation of mercury-sulfur bonds via the generation of AcOSiMe₃. Layering reaction solutions with pentane at -25°C leads to the formation of colorless, crystal blocks suitable for single-crystal X-ray analysis after 4-5 days. The structure of 3 in the crystal consists of two independent [{(IPr)AgS}₂Hg] molecules in the asymmetric unit (Figure 2), and each resides about a crystallographic inversion center. Data in



Figure 2. Molecular structure of $[{(|Pr)AgS}_2Hg]$ 3 in the crystal (ellipsoids set at 40% probability; hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: C-Ag 2.088(6), Ag–S 2.326(2), S–Hg 2.313(2), Hg–Ag 3.3211(8); C-Ag-S 175.9(2)-, Ag-S-Hg 91.46(8).

the text refer to molecule 1. Molecules of **3** show near-linear S–Hg–S arrangements with Hg–S distances of 2.326(2) Å. The Ag-S-Hg angle (91.46(8)°) is significantly smaller than \gtrless Ag-S-Si in **1** (104.65(5)°) resulting in a short Ag-Hg distance (3.3211(8) Å). While such an acute \gtrless M-S-M' (and Hg-Cu 3.044(1) Å) was observed in [{(IPr)CuS}₂Hg], calculations at the DFT level did not suggest any significant Hg-Cu interactions.^[8] The structural arrangement emphasizes the description of the (IPr)Ag–S⁻ as an "argentathiolate" moiety, two of which bond to Hg^{II} to yield the complex **3**.

The demonstrated, straightforward preparative chemistry for the formation of [(IPr)M–ESiMe₃] suggested that other NHC ligated M–ESiMe₃ could also be targeted, which would provide flexibility in the assembly of different ternary frameworks (see below). In analogy with the work developed for PR₃ ligands on metal–chalcogenide frameworks,^{[11} this would open an interesting opportunity to begin the development of NHC/cluster relationships. In this vein the smaller NHC *i*Pr₂-bimy (*i*Pr₂-bimy= 1,3-diisopropylbenzimidazolin-2-ylidene) was selected. The %V_{bur} (at *d*=2.00 and *r*=3.5 Å) for *i*Pr₂-bimy=27.9, versus 44.5 for the larger IPr.^[12] The approach for the synthesis of [(*i*Pr₂bimy)Cu–ESiMe₃)]₂ complexes **4** and **5** parallels the procedure developed for the formation of the silver complexes **1** and **2** and reported [(IPr)Cu–ESiMe₃]. Thus [(*i*Pr₂-bimy)Cu–OAc] was reacted with E(SiMe₃)₂ at -70 °C (Scheme 2a) and complexes **4**



Scheme 2. Synthesis of a) $[(iPr_2-bimy)Cu-ESiMe_3]_2$ (E=S, 4; E=Se, 5); b) $[\{(iPr_2-bimy)_6Cu_{10}S_8Hg_3\}$ 6.

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and **5** crystallize as colorless block and needle crystals, respectively. Complex **4** shows relatively high thermal stability with the melting point of 91–93 °C, while **5**, unexpectedly, is much more thermally sensitive, decomposing at temperatures above -25 °C in the solid state. Indeed, due to this sensitivity, complex **5** can ultimately only be isolated as a pure product a few single crystals at a time, although monitoring reaction solutions via NMR spectroscopy indicate selective formation of **5**.

Complexes **4** and **5** were satisfactorily solved and refined in the space groups C2/c and $P2_1/c$, respectively (Figure 3 and Figure 4). Crystals of **5** contain two virtually identical but independent molecules in the asymmetric unit; details in the text refer to molecule 1. Both **4** and **5** exist as $[(iPr_2-bimy)_2Cu_2(\mu$ -



Figure 3. The molecular structure of $[(iPr_2-bimy)Cu-SSiMe_3]_2$ 4 (ellipsoids set at 40% probability; hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: C1-Cu1 1.918(1), Cu1-S1 2.3105(9), S1-Si1 2.1133(7); C1-Cu1-S1 138.04(4), Cu1-S1-Si1 109.04(2).



Figure 4. The molecular structure of $[(iPr_2-bimy)Cu-SeSiMe_3]_2$ 5 (ellipsoids set at 40% probability; hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: C-Cu 1.916(4)–1.924(4), Cu-Se 2.3853(7)–2.5149(8), Se–Si1 2.257(1)–2.259(2); C-Cu-Se 115.3(1)-140.3(1), Se-Cu-Se 104.23(2)-104.44(2), Cu-Se-Cu 63.00(2)-65.82(2), Cu-Se-Si 96.79(4)-104.96(4).

ESiMe₃)₂] dimers in the solid state, with a hinged butterfly shaped E₂Cu₂ central ring (hinge angle: E=S **4**, 119°; E=Se **5**, 138°). Obviously the smaller size of the ancillary carbene (*i*Pr₂bimy) compared to IPr provides access to the additional coordination sites around the Cu metal and enables such a dimerization of two Cu–ESiMe₃. All copper centers in **4** and **5** assume distorted, trigonal planar coordination geometry at the wingtip positions of the butterfly structure, ligated by one NHC and two μ_2 -ESiMe₃ moleties.



In **4**, the dimeric molecule resides about a two-fold axis. Interestingly both $-SiMe_3$ groups in **4** are found on the same side (*cis*) of the hinged central ring and oriented towards the wingtip positions. In this molecule the Cu–S bond lengths range from 2.3105(9) to 2.3408(7) Å, the Cu–C bonds are 1.918(1) Å and the Cu-Cu separation (2.7047(8) Å) is slightly shorter than the sum of the van der Waals radii for $2 \times Cu^1$ (2.80 Å). In the dimeric molecules of **5**, the $-SiMe_3$ moieties adopt a *trans* orientation. The Cu-Se-Cu angles of **5** are smaller (63.00(2)°) compared to the related angles in **4** (71.19(2)°). On the other hand the Se-Cu-Se angle in **5** (103.86(2)°) is considerably larger than the related angle in **4** (89.01(2)°). Consequently molecules of **5** show shorter Cu-Cu separation (2.6125(9) Å) than is observed in **4**.

¹H and ¹³C{¹H} NMR spectra of **4** were obtained at low temperature by dissolving crystalline samples in CDCl₃. Owing to the lower stability of 5 in solution, spectral analysis was completed by monitoring reaction solutions. A clear, colorless reaction solution of [(*i*Pr₂-bimy)CuOAc] in deuterated chloroform was cooled to $-40\,^\circ\text{C}$ and treated with one equiv of Se(SiMe₃)₂. The ¹H and ¹³C{¹H} NMR spectra of the reaction solution display, along with the peaks of ligated carbene, those arising from the formed AcOSiMe₃ and the appearance of an additional signal in the high-field region, which is assigned to -SeSiMe₃. There is an evident downfield shift observed in the ¹H NMR spectra for the SiMe₃ signals on going from S (0.25 ppm) to Se (0.45 ppm; Supporting Information, Figure S2). These chemical shifts are themselves well downfield from those of [(IPr)Cu–ESiMe₃] (S: δ , -0.17 Se: -0.04),^[8] and this may suggest that the bridging interaction of the E-SiMe₃ is retained in solution. Monitoring the ¹H NMR spectra of **5** over a period of one hour at -35 °C revealed that the intensity of the peaks corresponding to 5 decreases accompanied by the growth of a new set of resonances for a *i*Pr₂-bimy-containing species (Supporting Information, Figure S3), together with an overall darkening of the color of the reaction solution to dark brown. Our attempts at isolating related silver [(iPr2bimy)Aq-ESiMe₃] (E = S, Se) have not proven successful. Here, too, reactions are accompanied by a darkening of the color of solutions, with resonances from multiple *i*Pr₂-bimy containing species observed in ¹H NMR spectra, even at low temperatures.

The reactivity of the E-Si bond and the effect of the smaller NHC ligand in [(iPr₂-bimy)Cu-SSiMe₃]₂ are both demonstrated with the formation of the nanocluster $[(iPr_2-bimy)_6Cu_{10}S_8Hg_3]$ 6, when a solution of 4 is treated with 0.5 equivalents of [Hg(OAc)₂] (Scheme 2b). Storage of the reaction solution at -25 °C leads to the selective formation of yellow crystals of 6 (yield = 50%). X-ray analysis indicates that 6 is composed of 10 copper and 3 mercury atoms and 8 sulfide bridging ligands, and this core is stabilized with six surface *i*Pr₂-bimy. This framework can be contrasted with that of [{(IPr)CuS}₂Hg], which forms with the larger NHC under similar reaction conditions.^[8] In cluster 6 there are four, two-coordinate near-linear Cu¹ bonded to two adjacent bridging sulfide atoms, one in the center (\gtrless S-Cu-S 176.32°) and three on the edges of the cluster (২S-Cu-S 175.08(9)–177.14(9)°; Figure 5). The other six Cu^I assume distorted trigonal planar geometry, bonded to two μ_3 -



Figure 5. Molecular structure of $[(iPr_2-bimy)_6Cu_{10}S_8Hg_3]$ **6** in the crystal. a) ORTEP diagram (ellipsoids set at 40% probability; hydrogen atoms omitted); b) space-filling diagram of the (iPr_2-bimy) surface ligands together with a ball-and-stick diagram of the $Cu_{10}S_8Hg_3$ core.

bridging sulfide ligands and each terminally bonded to a *i*Pr₂bimy. There is little variation observed in the Cu-C bond lengths (1.910(1)-1.959(9) Å), which are themselves similar to those in the precursor 4. The three Hg^{II} are each bonded to two sulfide ligands, leading to a distorted linear S-Hg-S arrangement (₹ S-Hg-S 172.42(8)–173.29(7)°). The Hg–S bond lengths range from 2.322(2) to 2.336(3) Å. Six sulfide ligands adopt μ_3 face-capping coordination modes with one Hg and two Cu atoms. The other two sulfide ligands are μ_4 -bonded to the central Cu and three additional Cu. The closest Cu-Cu and Cu-Hg contacts are 2.762(1) and 2.971(1) Å, respectively, consistent with the d¹⁰ electron configurations on the metal.^[13] Structurally, cluster 6 can be viewed as being intermediate in size between the trinuclear [{(IPr)CuS}₂Hg] and the phosphine ligated $[Hg_{15}Cu_{20}S_{25}(PPr_3)_{18}]$,^[6a] although, clearly, the varying Cu:Hg ratio prevents a more in depth comparison. Each of these represents a rare example of a Cu^l/Hg^{ll}-sulfide cluster.

Crystals of $[(iPr_2-bimy)_6Cu_{10}S_8Hg_3]$ **6** have a broad emission at about 800 nm; this can be contrasted with the recent reports by Eichhöfer and co-workers on the luminescent properties of similarly sized $[Cu_{12}S_6(L\cap L)]$ clusters $(L\cap L = bidentate phosphine ligand)$, with strong, sharp emissions being observed at about 700 nm.^[14] Crystals of **6** are stable under an inert atmos-

phere at room temperature; however, in solution the clusters decompose quickly, as evidenced by the formation of a black-colored suspension in the reaction solution. Although crystals of **6** are unstable in solution, ¹H and ¹³C{¹H} NMR spectra can be obtained by dissolving the crystals in cold CDCl₃ (-30° C; NMR spectra of **6** display only one set of resonances for the ligated carbenes.

Conclusion

Exploiting the stabilizing effect of ligated N-heterocyclic carbenes to metal-chalcogenolate M-ESiMe₃ moieties, we have isolated [(IPr)Ag-ESiMe₃] and [(*i*Pr₂-bimy)Cu-ESiMe₃]₂ (E=S, Se) complexes. The reaction of [(IPr)Ag-SSiMe₃] with mercuric(II) acetate afforded the heterometallic complex [{(IPr)AgS}₂Hg], which is the first example of a mixed silver-mercury-sulfide complex. The smaller NHC *i*Pr₂-bimy)Cu-SeSiMe₃]₂ was marked-ly less thermally stable. Using [(*i*Pr₂-bimy)Cu-SSiMe₃]₂ as a precursor for ternary cluster formation led to the high nuclearity [(*i*Pr₂-bimy)₆Cu₁₀S₈Hg₃], thus demonstrating the dramatic effect of changing surface ligands in this system. The strategy outlined above for the synthesis of NHC stabilized metal chalcogenolate complexes offers a powerful new route into a variety of binary and ternary metal-chalcogen clusters.

Experimental Section

All of the syntheses were carried out under an atmosphere of high-purity dried nitrogen using standard double-manifold Schlenk line techniques and nitrogen-filled glove boxes unless otherwise stated. Solvents were dried and collected using an MBraun MB-SP Series solvent purification system with tandem activated alumina (tetrahydrofuran) and an activated alumina/copper redox catalyst (pentane). Chlorinated solvents ([D]chloroform, [D₂]dichloromethane) were dried and distilled over P₂O₅. Other chemicals were used as received from commercial sources (Alfa Aesar and Aldrich). [(IPr)AgOAc],^[15] (ⁱPr₂-bimy)·HI,^[16] and E(SiMe₃)₂ (E = S, Se)^[5d,17] were synthesized according to previously reported procedures.

NMR spectra were recorded on Varian Mercury 400, Inova 400, and Inova 600 NMR spectrometers. ¹H and ¹³C{¹H} chemical shifts are referenced to SiMe₄, using solvent peaks as a secondary reference. Elemental analysis was performed by Laboratoire d'Analyze Élementaire de l'Université de Montréal, Montréal, Canada. Samples were dried for about twelve hours prior to send for analysis. Experimentally obtained values of elemental analysis and NMR spectra suggests some residual lattice solvent remained for **4** (ca. 0.75 THF molecule per molecular formula).

Single-crystal X-ray diffraction measurements were completed on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. Single crystals of the complexes were carefully selected, immersed in paraffin oil, and mounted on MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL.^[18] All non-hydrogen atoms, with the exception of disordered carbon centers, were refined with anisotropic thermal parameters. For **3**, the TWIN command in SHELXTL was used to refine the structure. In **6**, some of the disordered THF solvents in the crystal packing were removed by the SQUEEZE program. CCDC 1418107–1418112 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

UV/Vis diffuse reflectance spectra of the solid samples were recorded using a Shimadzu UV-VIS-NIR spectrophotometer UV-3600 with an integrating sphere attachment ISR-3100. Barium sulfate was used as reflectance standard and as the diluting matrix for the finely ground samples (5-10% in mixture). Spectra were converted using the Kubelka-Munk function and normalized. Solid-state PL spectra were obtained at room temperature using the experimental setup shown in the Supporting Information, Figure S4. An excitation beam from laser diode (US-Lasers, Inc.) with wavelength 405 ± 10 nm and power output of 120 mW was filtered using a low-pass (405 nm) filter. The emitted fluorescence was filtered using a long-pass filter and analyzed using a HRS-BD1 Mightex Spectrometer equipped with CCD multichannel detector with entrance slit size 10 µm and wavelength range 300-1050 nm. Calibration and data processing were performed with custom-made code using Matlab (version 2014) software. To prepare samples for solid state PL measurements, a small amount of solid material was suspended in 1-2 mL of pentane. One drop of such a suspension was placed on a cleaned Si wafer and allowed to evaporate; procedure was repeated until desired density of coverage was achieved, and then the substrate with a thin film of a sample was thoroughly dried, finally under vacuum.

Synthesis of [(IPr)Ag-SSiMe₃] (1): $S(SiMe_3)_2$ (38 µL, 0.18 mmol) was added to the cold (-70 °C) solution of one equivalent of [(IPr)-AgOAc] (100 mg, 0.18 mmol) in tetrahydrofuran (10 mL), followed by storing the solution at -25 °C overnight. The reaction was layered with pentane (30 mL) at this temperature. Colorless, block-like single crystals formed after 3–4 days. The crystals were washed with 3×10 mL cold pentane (-70 °C) and dried under dynamic vacuum (75 % yield); m.p. 175–179 °C.

Performing the reaction in CDCl₃ at -40 °C and maintaining the solution at -25 °C confirmed the concomitant formation of [(IPr)Ag–SSiMe₃] and the side product AcOSiMe₃ by ¹H NMR spectroscopy. ¹H NMR for 1 (CDCl₃, 599.36 MHz, 25 °C): δ 7.46 (t, J = 7.6 Hz, 2H, *para*-CH), 7.28 (d, J = 7.6 Hz, 4H, *meta*-CH), 7.18 (s, 2H, NCH), 2.56 (sept., J = 7.0 Hz, 4H, $CH(CH_3)_2$), 1.29 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.20 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), -0.13 ppm (s, 9H, -Si(CH₃)₃); ¹³C{¹H} NMR (CDCl₃, 100.53 MHz, -30 °C): 145.3 (*ortho*-C), 134.5 (*ipso*-C), 130.3 (*para*-C), 124.0 (*meta*-C), 123.1 (NCH), 28.5 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 7.0 ppm (-Si(CH₃)₃). Anal. calcd (%) for C₃₀H₄₅AgN₂SSi: C 59.88, H 7.45, N 4.66, S 5.33; found: C 60.02, H 7.56, N 4.63, S 4.32.

Synthesis of [(IPr)Ag-SeSiMe₃] (2): Se(SiMe₃)₂ (35 μ L, 0.14 mmol) was reacted with one equivalent of [(IPr)AgOAc] (78 mg, 0.14 mmol) in tetrahydrofuran (10 mL) as described for the preparation of **1**. Colorless block single crystals suitable for X-ray diffraction were obtained after five to six days by layering the mother liquor with 30 mL of pentane at -25 °C (55% yield); m.p. 170–175 °C.

Monitoring this reaction by ¹H NMR spectroscopy in CDCl₃ showed the formation of **2** and trimethylsilylacetate. ¹H NMR for **2** (CDCl₃, 399.76 MHz, -30° C): δ 7.47 (t, J = 7.8 Hz, 2H, *para*-CH), 7.28 (d, J = 7.8 Hz, 4H, *meta*-CH), 7.21 (s, 2H, NCH), 2.51 (sept., J = 7.0 Hz, 4H, *CH*(CH₃)₂), 1.30 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), 1.20 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), -0.02 ppm (s, 9H, -Si(CH₃)₃); ¹³C{¹H} NMR (CDCl₃, 100.53 MHz, -30° C): 145.3 (*ortho*-C), 134.5 (*ipso*-C), 130.3 (*para*-C), 124.0 (*meta*-C), 123.1 (NCH), 28.5 (CH(CH₃)₂), 25.0 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 7.6 ppm (-Si(CH₃)₃). Anal. calcd (%) for C₃₀H₄₅AgN₂SeSi: C 55.55, H 6.99, N 4.32; found: C 55.59, H 7.10, N 4.25.

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Synthesis of [{(IPr)AgS}2Hg] (3): S(SiMe3)2 (53 µL, 0.251 mmol) was added to the cold ($-70\,^\circ\text{C}$) solution of one equivalent of [(IPr)-AgOAc] (140 mg, 0.251 mmol) in tetrahydrofuran (10 mL), followed by storage at $-25\,^{\circ}C$ overnight. The reaction solution was cooled down to -70° C again to mix with a 5 mL solution of Hg(OAc)₂ (40 mg, 125 mmol) at this temperature. After warming and keeping the solution to -25 °C for 6 h, the solvent was layered with cold pentane (-70 °C). Colorless block single crystals suitable for X-ray diffraction were obtained after five to six days (ca. 30% yield); m.p. 190 $-195 \,^{\circ}$ C (decom.). ¹H NMR (CDCl₃, 399.76 MHz, $-30 \,^{\circ}$ C): δ 7.44 (t, J=7.8 Hz, 4 H, para-CH), 7.23 (d, J=7.8 Hz, 8 H, meta-CH), 7.14 (s, 4H, NCH), 2.45 (sept., J=7.0 Hz, 8H, CH(CH₃)₂), 1.24 (d, J= 7.0 Hz, 24 H, CH(CH₃)₂), 1.14 ppm (d, J = 7.0 Hz, 24 H, CH(CH₃)₂); $^{13}C{^{1}H}$ NMR (CDCl₃, 100.53 MHz, $-30^{\circ}C$): δ 145.2 (ortho-C), 134.4 (ipso-C), 130.4 (para-C), 124.0 (meta-C), 122.9 (NCH), 28.5 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 23.7 ppm (CH(CH₃)₂). Anal. calcd (%) for C₃₀H₄₅AgN₂SeSi: C 51.57, H 5.77, N 4.45, S 5.10; found: C 51.77, H 5.89, N 4.45, S 5.05.

Synthesis of [(iPr₂-bimy)CuOAc]: A 100 mL Schlenk flask was charged with copper(I) acetate (0.67 g, 5.49 mmol) and an equivalent molar amount of *i*Pr₂-bimy. THF (25 mL) was added using a syringe. The resulting cloudy yellow solution was stirred for 12 h, and then filtered through Celite. The clear, gold-colored filtrate was dried in vacuo, affording [(*i*Pr₂-bimy)CuOAc] as an off-white powder, 1.62 g (90.8%); m.p. 145–148 °C. ¹H NMR (CDCl₃, 399.76 MHz, 25 °C): δ 7.55 (m, 2H), 7.33 (m, 2H), 5.09 (sept., *J*= 7.0 Hz, 2H, CH(CH₃)₂), 2.15 (br, 3H, CH₃C(O)₂) 1.77 ppm (d, *J*= 7.0 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (CD₂Cl₂, 100.53 MHz, 25 °C): 133.2, 123.3,112.0 (Ar-C), 52.6 (CH(CH₃)₂), 22.9 ppm (CH(CH₃)₂). Anal. calcd (%) for C₁₅H₂₁CuN₂O₂: C 55.45, H 6.52, N 8.62; found: C 55.25, H 6.56, N 8.56.

Synthesis of $[(iPr_2-bimy)Cu-SSiMe_3]_2$ (4): $S(SiMe_3)_2$ (83 µL, 0.33 mmol) was added to a cold (-70°C) solution of [(iPr₂-bimy)-CuOAc] (108 mg, 0.33 mmol) in tetrahydrofuran (10 mL), followed by storing the solution at -25 °C overnight. The reaction was layered with 30 mL of pentane at low temperature. Three to four days later, colorless block-like single crystals were obtained. The crystals were washed with $3 \times 10 \text{ mL}$ cold pentane (-70 °C) and dried under dynamic vacuum for further analysis (45% yield); m.p. 91–93 °C. ¹H NMR (CD₂Cl₂, 399.76 MHz, -60 °C): δ 7.58 (m, 2 H), 7.32 (m, 2 H), 5.08 (sept., J = 7.0 Hz, 2 H, $CH(CH_3)_2$), 1.69 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), 0.25 ppm (s, 9H, -Si(CH₃)₃); ¹³C{¹H} NMR (CD₂Cl₂, 100.53 MHz, -60 °C): 132.7, 122.9,112.2 (Ar-C), 52.7 (CH(CH₃)₂), 22.5 6.9 ppm (-Si(CH₃)₃). Anal. calcd (%) $(CH(CH_2)_2)$ for C₁₆H₂₇CuN₂SSi·0.75 THF: C 53.67, H 7.82, N 6.59, S 7.54;found: C 53.15, H 8.06, N 6.93, S 7.38.

Synthesis of $[(iPr_2-bimy)Cu-SeSiMe_3]_2$ (5): Se(SiMe_3)_2 (74 µL, 0.296 mmol) was added to the cold (-70 °C) solution of one equivalent of $[(iPr_2-bimy)CuOAc]$ (96 mg, 0.296 mmol) in tetrahydrofuran (10 mL), followed by storing the solution at -40 °C overnight. The reaction was layered with pentane (30 mL) at low temperature. Three to four days later, colorless needle-like single crystals formed. The crystals were washed with 3×10 mL cold pentane (-70 °C) and dried under dynamic vacuum for further analysis (ca. 10% yield).

¹H NMR (CDCl₃, 399.76 MHz, -35 °C): δ 7.57 (m, 2H), 7.33 (m, 2H), 5.14 (sept., J = 7.0 Hz, 2H, $CH(CH_3)_2$), 1.72 (d, J = 7.0 Hz, 12H, $CH(CH_3)_2$), 0.45 ppm (s, 9H, $-Si(CH_3)_3$); ¹³C{¹H} NMR (CDCl₃, 100.53 MHz, -35 °C): 132.6, 123.1,112.2 (Ar-C), 52.6 (CH(CH₃)₂), 22.7 (CH(CH₃)₂), 7.6 ppm (-Si(CH₃)₃).

Synthesis of $[(iPr_2-bimy)_6Cu_{10}S_8Hg_3]$ (6): A solution of $[(iPr_2-bimy)Cu-SSiMe_3]_2$ (0.18 mmol) in THF (10 mL), prepared as described above and cooled to -70 °C, was added to a 5 mL solution

of Hg(OAc)₂ (57 mg, 0.18 mmol) in THF at this temperature. The yellow solution was warmed to -25 °C. and maintained at this temperature. Yellow, block-like single crystals suitable for X-ray diffraction were obtained after six days (50% yield); m.p. (decomp.) ca. 100 °C. ¹H NMR (CDCl₃, 399.76 MHz, -30 °C): δ 7.78 (m, 2H), 7.52 (m, 2H), 5.33 (sept., J=7.0 Hz, 2H, $CH(CH_3)_2$), 1.74 ppm (d, J=7.0 Hz, 12H, $CH(CH_3)_2$); ¹³C(¹H) NMR (CDCl₃, 100.53 MHz, -30 °C): 129.2, 125.6,114.8 (Ar-C), 52.1 ($CH(CH_3)_2$), 21.0 ppm ($CH(CH_3)_2$). Anal. calcd (%) for $C_{78}H_{108}Cu_{10}Hg_3S_8N_{12}$: C 34.60, H 4.02, N 6.21, S 9.47; found: C 35.07, H 4.29, N 5.89, S 9.54.

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