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New Copper and Silver Trimethylsilylchalcogenolates

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The synthesis and characterization of the copper and silver trimethylsilylchalcogenolates $(EtPh_2P)_3MESiMe_3$ and $(Et_2PhP)_3MESiMe_3$ ($M = Cu^I$, Ag^I) are reported. These chalcogenolate complexes can be prepared in high yield; however, they are thermally unstable. Low-temperature single-crystal X-ray analysis of $(EtPh_2P)_3CuSSiMe_3$ (**1b**) and $(Et_2PhP)_3CuSeSiMe_3$ (**2a**) confirms the terminal coordination of the chalcogen ligand and the tetrahedral coordination about the metal. Protonolysis of **2a** with EtOH yields the terminal selenol complex $(Et_2PhP)_3CuSeH$ (**6**). Reaction of **1b** with $EtPh_2P$-solubilized AgOAc yields the heterometallic cluster $[Cu_9Ag_3S_6(PEtPh_2)_8]$ (**7**) in good yield.

Introduction

Metal chalcogenolate complexes of the d-block metals containing trialkylsilyl moieties ($MESiR_3$; E = S, Se, Te; R = alkyl) continue to attract the efforts of researchers because of the interesting structures and reactivity of this class of molecule.[1−11] Although less thermally stable than metal silylchalcogenolates containing larger groups, the less sterically demanding methyl substituents on silicon enable $MESiMe_3$ complexes to be used as reagents for the controlled assembly of ternary cluster and nanocluster complexes.[10,12] This is achieved via the selective cleavage of the E−Si bond when $MESiMe_3$ is reacted with a second metal salt, M′−X, to yield M−E−M′ units along with $XSiMe_3$ and form, ultimately, a ternary polynuclear complex.[13] It has been illustrated by Kawaguchi and co-workers that this selective reactivity is optimized with methyl groups about silicon, $-SiMe_3$.[10a] The soluble $XSiMe_3$ does not impede the formation and crystallization of nanocluster complexes. This has been demonstrated with the formation of phosphine-stabilized Cu−Hg−E (E = S, Se) and Cu−In−S ternary clusters from the copper silylchalcogenolates, $(PEt_3)_3CuESiMe_3$ and $(PPr_3)_3CuESiMe_3$. The ancillary phosphine ligands ensure terminal coordination of the $-ESiMe_3$ groups and the formation of mononuclear complexes.

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It has been demonstrated that the steric (i.e., the Tolman cone angle θ of the phosphine ligand[14]) and electronic requirements of the surface PR_2R' molecules play a quintessential role in the final size and shape of binary metal chalcogenide nanocluster cores.[15] Thus, via control of the reaction conditions and the appropriate selection of surface phosphine ligands, a variety of cluster materials may be developed. This has been illustrated by Fenske and coworkers with the assembly of copper chalcogenide clusters with differing tertiary phosphine ligands.[15a,16] By analogy, access to a range of $(R_3P)_3MESiMe_3$ (M = Cu, Ag) is of fundamental importance for the formation of new ternary metal chalcogenide nanocluster architectures. Herein we report the high yield synthesis and spectroscopic characterization of the new copper and silver (trimethylsilyl)chalcogenolates stabilized with (diethylphenyl)- and (diphenylethyl)phosphine ligands: $(Et_2PhP)_3CuSSiMe_3$ (**1a**), $(EtPh_2P)_3CuSSiMe_3$ (**1b**), $(Et_2PhP)_3CuSeSiMe_3$ (**2a**), $(EtPh_2P)_3CuSeSiMe_3$ (**2b**), $(Et_2PhP)_3CuTeSiMe_3$ (**3a**), $(EtPh_2P)_3CuTeSiMe_3$ (**3b**), $(Et_2PhP)_3AgSSiMe_3$ (**4a**), $(EtPh_2P)_3AgSSiMe_3$ (**4b**), $(Et_2PhP)_3AgSeSiMe_3$ (**5a**), and $(EtPh_2P)_3AgSeSiMe_3$ (**5b**). We also describe details of their reactivity, namely, the protonolysis of **2a** to yield the selenolate complex $(Et_2PhP)_3CuSeH$ (**6**) and the formation of the ternary mixed-metal cluster $[Cu_9Ag_3S_6(PEtPh_2)_8]$ (**7**) from the reaction of **1b** with AgOAc.

Experimental Section

All experiments were performed under an inert atmosphere using standard Schlenk-line techniques or a nitrogen-filled glovebox. The starting reagents $E(SiMe_3)_2$,[12e,17] (E = S, Se, Te), PEt_2Ph,[18] $PEtPh_2$,[18] and CuOAc[19] were prepared and purified according to literature preparations. AgOAc was purchased from Strem Chemicals. HPLC-grade solvents, Et_2O, THF, hexane, toluene, and pentane, were dried and collected over activated alumina-packed columns. CH_2Cl_2, CH_3Cl, and CD_3Cl were dried and distilled from P_2O_5, and dry CD_2Cl_2 was used as received.

Low-temperature NMR experiments were performed on a Varian Inova 400 spectrometer using liquid nitrogen and a variable-temperature control unit. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained using operating frequencies of 399.763, 100.522, and 161.96 MHz, respectively. $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra were recorded using operating frequencies of 76.26 and 161.83 MHz, respectively. ^{29}Si NMR chemical shifts were obtained indirectly from resonance magnetization transfer from the corresponding protons of the $-SiMe_3$ groups ($J_{SiH} = 6$ Hz) using a gradient heteronuclear multibond coupling (gHMBC) experiment. ^{29}Si NMR shifts were referenced externally to $SiMe_4$. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual H and C atoms, respectively, in the deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were externally referenced to 85% H_3PO_4. $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra were referenced externally to Me_2Se and Me_2Te using $PhSeSiMe_3$ and $Te(SiMe_3)_2$ as secondary references. Energy-dispersive X-ray (EDX) analyses were carried out by Dr. Brian Hart at Surface Science Western (UWO). A Quartz Xone EDX analysis system coupled to a Leo 440 scanning electron microscope equipped with a Gresham light element detector was used to obtain semiquantitative analysis of Cu and Ag. Analyses were carried out using a 25 kV electron beam rastered over 100 μm × 100 μm areas and repeated to ensure reproducibility. Elemental analysis of **7** was performed by Canadian Microanalytical Service Ltd. Laboratories (British Columbia, Canada). Chemical analyses of **1**−**6** were prohibited by the inherently low melting points, thermal instability, and chemical reactivity of the complexes.

Single-crystal X-ray analyses of complexes were performed using an Enraf-Nonius Kappa CCD X-ray diffractometer. The structures were solved and refined using *SHELXTL 5.01* software. Crystals of **1b**, **2a**, and **6** were mounted from a cold (−78 °C) solvent. All structures were solved by direct methods. For **6**, the Se−H hydrogen atom was located in the difference Fourier map and allowed to refine freely. The Cu−Ag site disorder in **7** was satisfactorily modeled with a 50:50, 75:25, 50:50, and 75:25 occupancy for sites M1, M2, M3, and M4, respectively. Disordered metal sites were refined isotropically.

Melting points were determined by placing crystals in Schlenk tubes and monitoring the temperature and state of the crystals using an acetone/CO_2(s) cold bath.

Synthesis of $(Et_2PhP)_3CuSSiMe_3$ (1a). CuOAc (0.2 g, 1.6 mmol) was placed in a flask with 2 mL of Et_2O and 2.5 mL of hexane. A total of 4 equiv of PEt_2Ph (1.1 mL, 6.5 mmol) was added, resulting in a colorless, clear solution, which was cooled to −60 °C. $S(SiMe_3)_2$ (0.34 mL, 1.6 mmol) was added, and the reaction was stirred for ∼2 h while warming to ∼−10 °C. The flask was placed at −80 °C, where over 2 days colorless low-melting blocklike crystals formed. Yield: 96%, 1.0 g. Mp: −25 °C. ^1H NMR (CD_2Cl_2, −60 °C): δ 7.25 (s, Ph, 15H), 1.65 (s, CH_2, 12H), 0.77 (s, CH_2CH_3, 18H), 0.21 (s, $SiMe_3$, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 136.4 (s, C_{Ph}), 130.2−127.3 (C_{Ph}), 16.7 (s, CH_2), 8.6 (s, CH_2CH_3), 7.7 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ −12.9 (br s, $W_{1/2}$= 453 Hz). ^{29}Si NMR (CD_2Cl_2, −60 °C): δ +5.6.

Synthesis of $(EtPh_2P)_3CuSSiMe_3$ (1b). CuOAc (0.22 g, 1.79 mmol) was dissolved with 4 equiv of PPh_2Et (1.50 mL, 7.28 mmol) in 5 mL of $CHCl_3$ and 4 mL of hexane. The clear colorless solution was cooled to −60 °C, and $S(SiMe_3)_2$ (0.38 mL, 1.81 mmol) was added. The reaction was warmed slowly to ∼−15 °C over 2 h. Storage at −50 °C for 1 week resulted in the formation of colorless, low-melting-point platelike crystals of **1b**. Yield: 86%, 1.25 g. Mp: 5 °C (dec). ^1H NMR (CD_2Cl_2, −70 °C): δ 7.58 (s, Ph, 5H), 7.05 (s, Ph, 14H), 6.75 (s, Ph, 11H), 2.14 (s, CH_2, 6H), 0.62 (s, CH_2CH_3, 9H), 0.36 (s, $SiMe_3$, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70 °C): δ 133.0−128.0 (C_{Ph}), 19.2 (s, CH_2), 7.3 (s, CH_2CH_3), 6.8 (s, $SSiMe_3$). $^{31}P\{^1H)$ NMR (CD_2Cl_2, −70 °C): δ −5.5 (br s, $W_{1/2}$= 768 Hz). ^{29}Si NMR (CD_2Cl_2, −70 °C): δ +7.9.

Synthesis of $(Et_2PhP)_3CuSeSiMe_3$ (2a). CuOAc (0.20 g, 1.63 mmol) was dissolved in 2.5 mL of Et_2O and 3 mL of hexane with the addition of 4 equiv of PEt_2Ph (1.13 mL, 6.49 mmol). At −60 °C, the clear solution was reacted with 1 equiv of $Se(SiMe_3)_2$ (0.35 mL, 1.62 mmol). The solution was warmed slowly to −10 °C with

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stirring. Storage of the product at −80 °C resulted in the formation of low-melting-point crystals. Yield: 86%, 1.0 g. Mp: −28 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.25 (s, Ph, 15H), 1.66 (s, CH_2, 12H), 0.75 (s, CH_2CH_3, 18H), 0.34 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ 136.0 (s, C_{Ph}), 130.2−127.4 (C_{Ph}), 16.7 (s, CH_2), 7.6 (s, CH_2CH_3), 7.3 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −12.8 (br s, $W_{1/2} = 133$ Hz). ^{29}Si NMR (CD_2Cl_2, −60 °C): δ +0.8. $^{77}Se\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −546 (br s, $W_{1/2} = 93$ Hz).

Synthesis of $(EtPh_2P)_3CuSeSiMe_3$ (2b). CuOAc (0.22 g, 1.8 mmol) was dissolved with 4 equiv of PPh_2Et (1.48 mL, 7.2 mmol) in 3 mL of $CHCl_3$ and 1 mL of hexane. The clear, colorless solution was cooled to −60 °C, and $Se(SiMe_3)_2$ (0.40 mL, 1.8 mmol) was added. The solution was gradually warmed to −10 °C and subsequently placed at −80 °C. Colorless, blocklike crystals precipitated after 4 days. Yield: 96%, 1.5 g. Mp: −15 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.28 (s, Ph, 30H), 7.10 (s, Ph, 30H), 6.80 (s, Ph, 30H), 2.19 (br s, CH_2, 6H), 0.68 (br s, CH_2CH_3, 9H), 0.54 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ 138.3 (s, C_{Ph}), 132.8−127.7 (C_{Ph}), 20.0 (s, CH_2), 9.7 (s, CH_2CH_3), 7.3 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −5.6 (br s, $W_{1/2} = 361$ Hz). ^{29}Si NMR (CD_2Cl_2, −60 °C): δ +2.4. $^{77}Se\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −527 (br s, $W_{1/2} = 90$ Hz).

Synthesis of $(Et_2PhP)_3CuTeSiMe_3$ (3a). CuOAc (0.13 g, 1.1 mmol) was dissolved with 4 equiv of PEt_2Ph (0.74 mL, 4.3 mmol) in 5 mL of Et_2O and cooled to −60 °C. $Te(SiMe_3)_2$ was added, and the reaction was stirred for an additional 60 min. Half of the solvent was removed under vacuum, and the resulting white product precipitated with the addition of cold hexane. The isolated solid was washed with hexane and dried under vacuum. Yield: 94.8%, 0.8 g. Mp: −47 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.22 (s, Ph, 15H), 1.65 (s, CH_2, 12H), 0.70 (s, CH_3, 18H), 0.49 (s, $TeSiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ 135.7 (s, C_{Ph}), 130.5 (s, C_{Ph}), 127.8 (s, C_{Ph}), 17.1 (s, CH_2), 7.8 (s, CH_2CH_3), 7.6 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −12.7 (br, $W_{1/2} = 56$ Hz). ^{29}Si NMR (CD_2Cl_2, −60 °C): δ −22.0. $^{125}Te\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −1259 (q, $^{2}J_{TeP} = 92$ Hz).

Synthesis of $(EtPh_2P)_3CuTeSiMe_3$ (3b). CuOAc (0.20 g, 1.6 mmol) was placed in a flask with 2 mL of CH_2Cl_2 and 5 mL of hexane. The suspension was dissolved with the addition of 4 equiv of PPh_2Et (1.35 mL, 6.6 mmol). The clear colorless solution was cooled to −60 °C, and $Te(SiMe_3)_2$ (0.35 mL, 1.6 mmol) was added. The reaction turned a slight orange color as it was warmed to −40 °C and stirred for ∼2 h. Storage at −80 °C for a few days led to cube-shaped crystals of **3b**. Yield: 95.8%, 1.4 g. Mp: −25 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.04 (t, $J_{HH} = 7$ Hz, Ph, 15H), 6.72 (s, Ph, 3H), 6.62 (s, Ph, 12H), 2.16 (s, CH_2, 6H), 0.54 (s, CH_2CH_3, 9H), 0.60 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ 132.1 (s, C_{Ph}), 128.1 (s, C_{Ph}), 127.6 (s, C_{Ph}), 20.5 (s, CH_2), 7.3 (s,CH_2CH_3), 7.6 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −5.2 (br, $W_{1/2} = 131$ Hz). ^{29}Si NMR (CD_2Cl_2, −60 °C): δ −20.6. $^{125}Te\{^{1}H\}$ NMR (CD_2Cl_2, −60 °C): δ −1229 (q, $^{2}J_{TeP} = 94$ Hz).

Synthesis of $(Et_2PhP)_3AgSSiMe_3$ (4a). AgOAc (0.20 g, 1.2 mmol) and 4 equiv of PEt_2Ph (0.83 mL, 4.8 mmol) were placed in 4 mL of dry Et_2O to yield a clear colorless solution. The solution was cooled to ∼−70 °C, and 1 equiv of $S(SiMe_3)_2$ (0.25 mL, 1.2 mmol) was added while the reaction was stirred. The solution remained colorless and was warmed slowly to ∼−25 °C. The pure complex was precipitated out of the solution with cold hexane and isolated as a low-melting-point colorless solid. Yield: 58%, 0.50 g. Mp: −40 °C (dec). ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.46 (s, Ph, 6H), 7.29 (t, $J = 7$ Hz, Ph, 9H), 1.71 (s, CH_2, 12H), 0.82 (s, CH_2CH_3, 18H), 0.10 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ 134.2 (C_{Ph}), 131.2−128.8 (C_{Ph}), 18.0 (s, CH_2), 8.3 (s, CH_2CH_3), 7.0 (s, $SiMe_3$). ^{29}Si NMR (CD_2Cl_2, −70 °C): δ 7.9. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −80 °C): δ −4.3 (br s, $W_{1/2} = 64$ Hz).

Synthesis of $(EtPh_2P)_3AgSSiMe_3$ (4b). AgOAc (0.2 g, 1.2 mmol) was dissolved in 5 mL of Et_2O with the addition of 4 equiv of PPh_2Et (1.00 mL, 4.85 mmol). The resulting solution was cooled to −70 °C, and a white solid appeared. The solid dissolved with the addition of 1 equiv of $S(SiMe_3)_2$ (0.25 mL, 1.2 mmol), and the reaction was stirred for an additional 60 min. **4b** precipitated out as a white solid with the addition of cold hexane at −80 °C. The low-melting-point solid was isolated, washed with hexane, and dried under vacuum. Yield: 92%, 1.0 g. Mp: −25 °C. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.28−7.20 (m, Ph, 30H), 2.02 (s, CH_2, 6H), 0.88 (s, CH_2CH_3, 9H), 0.19 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ 135.3 (s, C_{Ph}), 132.8−128.4 (C_{Ph}), 20.1 (s, CH_2), 9.0 (s, CH_2CH_3), 7.2 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ −0.8 (br s, $W_{1/2} = 136$ Hz). $^{29}Si\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ 8.7.

Synthesis of $(Et_2PhP)_3AgSeSiMe_3$ (5a). AgOAc (0.12 g, 0.719 mmol) and 4 equiv of PEt_2Ph (0.50 mL, 2. 876 mmol) were placed in 5 mL of diethyl ether. The clear colorless solution was cooled to ∼−70 °C, and 1 equiv of $Se(SiMe_3)_2$ was added with stirring. The resulting clear and colorless solution was stirred for an additional 60 min during warming to ∼−40 °C. The product was precipitated with the addition of cold hexane and storage at −80 °C. A white solid was isolated, washed with hexane, and dried under vacuum. Yield: 58%, 0.55 g. Mp: −50 °C. ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.42 (s, Ph, 6H), 7.27 (s, Ph, 9H), 1.65 (s, CH_2, 12H), 0.81 (s, CH_2CH_3, 18H), 0.25 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H)$ NMR (CD_2Cl_2, −70 °C): δ 135.6 (s, C_{Ph}), 130.9−127.5 (C_{Ph}), 18.1 (t, $J_{PC} = 22$ Hz, CH_2), 8.4 (s, CH_2CH_3), 7.4 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ −9.4 (br s, $W_{1/2} = 197$ Hz). ^{29}Si NMR (CD_2Cl_2, −70 °C): δ 0.8. $^{77}Se\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ −559 (br s, $W_{1/2} = 47$ Hz).

Synthesis of $(EtPh_2P)_3AgSeSiMe_3$ (5b). AgOAc (0.2 g, 1.2 mmol) was dissolved in 4 mL of dry Et_2O with the addition of 4 equiv of PPh_2Et (1.0 mL, 4.9 mmol). Upon cooling of the clear colorless solution to −70 °C, a white precipitate formed and was redissolved with the addition of $Se(SiMe_3)_2$ (0.26 mL, 1.2 mmol). After stirring for ∼1 h, a white, low-melting-point solid was precipitated with the addition of cold hexane. The product was isolated, washed with hexane, and dried under vacuum. Yield: 96%, 1.0 g. Mp: −35 °C (dec). ^{1}H NMR (CD_2Cl_2, −70 °C): δ 7.29 (s, Ph, 8H), 7.19 (s, Ph, 22H), 1.98 (s, CH_2, 6H), 0.85 (t, $J_{HH} = 6$ Hz, CH_2CH_3, 9H), 0.34 (s, $SiMe_3$, 9H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ 134.8 (s, C_{Ph}), 132.76−128.32 (C_{Ph}), 20.2 (s, CH_2), 8.9 (s, CH_2CH_3), 7.4 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ −3.1 (br s, $W_{1/2} = 172$ Hz). ^{29}Si NMR (CD_2Cl_2, −70 °C): δ 0.1. $^{77}Se\{^{1}H\}$ NMR (CD_2Cl_2, −70 °C): δ −549 (br s, $W_{1/2} = 54$ Hz).

Synthesis of $(PEt_2Ph)_3CuSeH$ (6). CuOAc (0.24 g, 2.0 mmol) was dissolved with 4 equiv of PEt_2Ph (1.38 mL, 7.9 mmol) in 8 mL of Et_2O. The solution was cooled to −60 °C, and $Se(SiMe_3)_2$ (0.42 mL, 2.0 mmol) was added. The reaction was stirred for 2 h with warming to ∼−10 °C, and a few drops of ethanol was added. The solution was cooled to −80 °C. Colorless blocklike crystals of **6** precipitated over 12 h. Yield: 88%, 1.12 g. ^{1}H NMR (CD_2Cl_2, −30 °C): δ 7.34 (s, Ph, 6H), 7.24 (s, Ph, 9H), 1.62 (q, $J_{HH} = 7$ Hz, CH_2, 12H), 0.74 (t, $J_{HH} = 7$ Hz, CH_3, 18H), −5.26 (s, 1H, $J_{SeH} = 13$ Hz). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, −30 °C): δ 136.4 (s, C_{Ph}), 130.9 (s, C_{Ph}), 128.0 (s, C_{Ph}), 17.2 (d, $J_{PC} = 22$ Hz, CH_2), 7.8 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, −30 °C): δ −11.0 (br s, $W_{1/2} = 327$ Hz). $^{77}Se\{^{1}H\}$ NMR (CD_2Cl_2, −30 °C): δ −507 (br s, $W_{1/2} = 108$ Hz).

Table 1. Selected NMR Data for the $-ESiMe_3$ Groups in **1**−**5**

	^1H	$^{13}C\{^1H\}$	^{29}Si	$^{77}Se\{^1H\}$	$^{125}Te\{^1H\}$
1a	0.21	7.7	5.6		
1b	0.36	6.8	7.9		
2a	0.34	7.3	0.8	−546	
2b	0.54	7.3	2.4	−527	
3a	0.49	7.6	−22.0		−1259
3b	0.60	7.6	−20.6		−1229
4a	0.10	7.0	7.9		
4b	0.19	7.2	8.7		
5a	0.26	7.4	0.8	−559	
5b	0.34	7.4	0.1	−549	

Synthesis of [$Cu_9Ag_3S_6(PPh_2Et)_8$] (7). A solution of $(EtPh_2P)_2\cdot AgOAc$ (1.3 mmol) in 4 mL of THF was cooled to −60 °C and added to a freshly prepared 5 mL THF solution of $(EtPh_2P)_3CuSSiMe_3$ (2.6 mmol) also at −60 °C. An immediate color change to yellow occurred, and further warming to −4 °C over several hours resulted in a brown solution. The volume of the THF solvent was reduced by half, and storage of the reaction at −8 °C for 7 days yielded orange-red blocklike crystals of **7**. Yield: 60%. Anal. Calcd for $C_{112}H_{120}Cu_9Ag_3S_6P_8$: C, 48.0; H, 4.3; S, 6.9; P, 8.8; Ag, 11.6; Cu, 20.4. Found: C, 48.0; H, 4.6; S, 6.42; P, 8.1; Ag, 10.0; Cu, 19.8. EDX anal.: 2.95:1.00 = Cu:Ag. ^1H NMR (CD_2Cl_2, −40 °C): δ 7.28 (br, 10H, Ph), 2.01 (br, 2H, CH_2), 0.94 (br, 3H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C): −12.4 (br s, $W_{1/2}$ = 130 Hz).

Results and Discussion

The copper (trimethylsilyl)chalcogenolates **1**−**3** have been prepared according to eq 1. Because of the differing

$$CuOAc + 4R'R_2P + E(SiMe_3)_2 \rightarrow (PR'R_2)_3CuESiMe_3 + PR'R_2 + AcOSiMe_3 \quad (1)$$

$$E = S\ (\mathbf{1}),\ Se\ (\mathbf{2}),\ Te\ (\mathbf{3});\ R, R' = Et, Ph$$

solubilities of the phosphine-ligated metal complexes, reaction conditions for the synthesis of **1**−**3** were modified as required. Whereas PPh_2Et-ligated complexes were synthesized in $CHCl_3$/hexane or CH_2Cl_2/hexane mixtures, a Et_2O/hexane solvent mixture was used in the synthesis of the PEt_2Ph complexes. In all cases, however, because of the labile nature of the phosphine ligands and to ensure that all additional coordination sites on the Cu^I metal are occupied, CuOAc was dissolved in the presence of 4 equiv of phosphine. Upon the formation of ligated CuOAc, reaction solutions were cooled to −60 °C and treated with 1 equiv of $E(SiMe_3)_2$ (E = S, Se, Te). Reaction solutions were allowed to warm to ∼−15 °C, and products **1**−**3** crystallized by subsequent cooling. Colorless crystals of **1**−**3** were obtained in yields ranging from 85 to 96%.

Generally, the PPh_2Et complexes **1b**, **2b**, and **3b** display lower solubility in hydrocarbon solvents in comparison to those ligated with PEt_2Ph. Similarly, **1**−**3** are less soluble than the previously reported tris(trialkylphosphine)chalcogenolates $(Et_3P)_3CuESiMe_3$ and $(nPr_3P)_3CuESiMe_3$).[12a] In all cases, the selective activation of only one $E-SiMe_3$ bond was achieved to form **1**−**3**, with no evidence for the competitive formation of polynuclear copper chalcogenides. The tendency of chalcogenides (E^{2-}) and chalcogenolates (RE^-) to adopt bridging coordination modes affects the general stability of terminally bonded metal chacolgenolates such that they display a high tendency to form polynuclear species.[20] This is attributed to the high polarizability of the chalcogens and is generally observed to increase from S to Se to Te.[21] The coordination complexes **1**−**3** display higher stability as isolated solids than when dissolved in organic solvents. **1b** displays the highest thermal stability of the metal (arylphosphine)chalcogenolate complexes, melting at 5 °C, followed shortly by its decomposition to an orange-red oil. The copper trimethylselenolates and -tellurolates are less stable, and **1a** melts with decomposition at −47 °C. Because of the instability of **1**−**3** under ambient conditions, it was not possible to obtain elemental analysis. The observed thermal instability is consistent with the previously reported copper *tert*-(alkylphosphine)chalcogenolates.[12a]

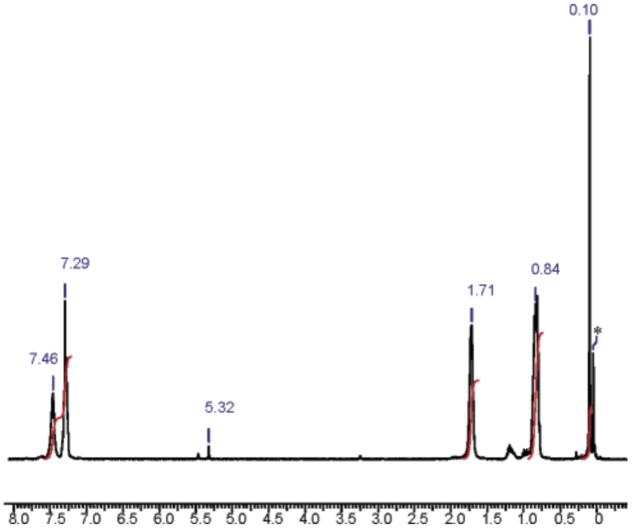

Figure 1. ^1H NMR spectrum of $(Et_2PhP)_3AgSSiMe_3$ in CD_2Cl_2 at −70 °C. The asterisk indicates silicone grease.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **1**−**3** were obtained at −60 °C in a CD_2Cl_2 solvent. There is an evident downfield shift observed in the ^1H NMR spectra for the $SiMe_3$ signals on going from S to Se to Te (Table 1). These signals are themselves shifted from those for $E(SiMe_3)_2$ (E = S, Se, Te).[22] A similar trend is also observed in the $^{13}C\{^1H\}$ NMR spectra. The electronic effects of the PR_2R' ligands are also manifest in the ^1H NMR spectra, with resonances for the $-SiMe_3$ groups in **1b**−**3b** upfield of those for **1a**−**3a**. At temperatures as low as −60 °C, all $^{31}P\{^1H\}$ NMR spectra display only one broad resonance, illustrating the chemical equivalence of the coordinated phosphine ligands on the NMR scale. $^{77}Se\{^1H\}$ NMR spectra for **2a** and **2b** each display a single, broadened peak ($W_{1/2}$ = 93 and 90 Hz, respectively) at −546 (**2a**) and −527 (**2b**). These shifts are at higher field relative to free $Se(SiMe_3)_2$ ($^{77}Se\{^1H\}$ NMR δ −337).[23] $^{125}Te\{^1H\}$ NMR spectra of **3a** and **3b** display resolved quartets ($^2J_{PTe}$ = 92 Hz for **2a** and 94

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Table 2. Summary of the X-ray Crystallographic Data of **1b**, **2a**, **6**, and **7**

	1b	**2a**	**6**	**7**
chemical formula	$C_{45}\ H_{54}CuP_3S\ Si\cdot 4CHCl_3$	$C_{33}H_{54}CuP_3SeSi\cdot Et_2O$	$C_{30}H_{46}CuP_3Se$	$C_{112}H_{120}Ag_3Cu_9P_8S_6\cdot 4OC_4H_8\cdot Et_2O$
fw	1288.95	788.38	642.08	3164.21
space group	$P2(1)/n$	$P2(1)/c$	$P2(1)2(1)2(1)$	$P\bar{1}$
temp (°C)	−73	−73	−73	−73
a (Å)	14.6360(5)	12.2407(2)	13.2461(3)	13.8231(4)
b (Å)	23.7333(3)	16.8474(4)	13.5048(3)	16.1207(7)
c (Å)	17.3278(5)	20.9558(6)	17.4590(5)	16.8049(6)
α (deg)				90.908(2)
β (deg)	97.851(1)	104.764(1)		96.312(2)
γ (deg)				114.197(2)
V (Å^3)	5962.6(3)	4178.9(2)	3123.2(1)	3387.4(2)
μ(Mo Kα_1) (mm^{-1})	1.073	1.563	2.036	2.042
Z	4	4	4	1
ρ (g cm^{-3})	1.436	1.253	1.366	1.551
data/params	7378/610	4593/414	6809/320	10048/678
R1 [$I > 2\sigma(I)$]	0.0619	0.0584	0.0431	0.0637
wR2 (all data)	0.1797	0.1582	0.0933	0.1911

Hz for **2b**) with resonances at δ −1259 and −1229, respectively. These peaks appear upfield from the $Te(SiMe_3)_2$ reagent (δ −842).[24] ^{29}Si NMR experiments were obtained in the form of 2D, ^{29}Si−^{1}H coupled, gHMBC data. The ^{29}Si NMR signals shift upfield with increasing size of the chalcogen atom, from δ +5.6 to +0.8 to −22.0 for **1a**, **2a**, and **3a**, respectively.

The approach for the synthesis of phosphine-stabilized silver (trimethylsilyl)chalcogenolate complexes **4**−**6** parallels the procedure developed for the formation of **1**−**3**. As was observed for $(R_2R'P)_3CuESiMe_3$, it is essential to occupy three additional coordination sites around the Ag metal in order to ensure terminal coordination of the silylchalcogenolate ligand and to avoid further condensation into polynuclear silver chalcogenides. Silver (trimethylsilyl)chalcogenolate complexes are much less thermally stable than those of copper; however, they can be isolated and spectroscopically characterized at low temperatures.

As a result of the ability of chalcogenolates (RE^-) to adopt several bridging coordination modes, as well as the metallophilic[25] effects reported in many Ag clusters,[26] many silver chalcogenolate clusters are known to date.[27] The known reactivity of silver salts toward $ESiMe_3$ reagents in the assembly of Ag_2S megaclusters[28] makes $AgESiMe_3$ extremely attractive targets for the assembly of AgEM nanoclusters.

The low-temperature ^{1}H NMR spectrum for **4a** is illustrated in Figure 1, and a signal at δ 0.10 can be assigned to the $AgSSiMe_3$ moiety. Integration of the ^{1}H NMR signals confirms the coordination of three phosphine ligands to the Ag atom. ^{13}C{^{1}H} NMR spectra also confirm the coordination of $-SSiMe_3$ ligands, with a peak observed at δ 6.7. Similar assignments for the $-ESiMe_3$ signals in ^{1}H and ^{13}C NMR spectra can be made for **4b** and **5b** (Table 1). The ^{29}Si NMR shifts of **4a** and **5b** appear upfield from those observed for the corresponding $E(SiMe_3)_2$ starting reagent.[23] ^{77}Se{^{1}H} NMR spectra of **5a** and **5b** display a single broadened resonance at δ −559 and −549, respectively, slightly upfield from those for the copper complexes **2**.

^{31}P{^{1}H} NMR spectra also display a single peak, even at temperatures as low as −70 °C. Thus, when clear, colorless reaction solutions of $(PR_2R')_3AgOAc$ are cooled to ∼−70 °C and treated with 1 equiv of $E(SiMe_3)_2$ (E = S, Se), NMR spectra of the reaction solutions confirm the formation of $AcOSiMe_3$ at these temperatures and the appearance of an additional signal in the high-field region assigned to $AgESiMe_3$ centers. Concentration of the reaction solutions, in vacuo, and storage of the colorless solutions at −80 °C lead to the formation of low-melting-point crystalline solids. In this manner, the complexes **4a**, **4b**, **5a**, and **5b** can be isolated. As isolated crystals, **4a** decomposes at temperatures as low as −25 °C and the silver selenolates are even more thermally sensitive, decomposing at temperatures above −40 °C. Numerous attempts to isolate (trimethylsilyl)tellurolates of silver were unsuccessful as, even at temperatures as low as −75 °C, highly colored solutions formed from the reactions of R_2RP/AgOAc and $Te(SiMe_3)_2$ together with dark, amorphous precipitates.

Single-crystal X-ray diffraction data on the low-melting-point solids were collected for **1b**·$4CHCl_3$ and **2a**·Et_2O, which crystallize as colorless plates. A summary of the structural parameters for **1b** and **2a** is listed in Table 2, and their molecular structures are given in Figures 2 and 3. Successful solution and refinement of the data illustrate that the Cu centers adopt a distorted tetrahedral coordination geometry, bonded to three phosphine ligands and terminally bonded to the (trimethylsilyl)chalcogenolate. The Cu−P bond distances (Table 3) are slightly longer for $EtPh_2P$ [2.307(2)

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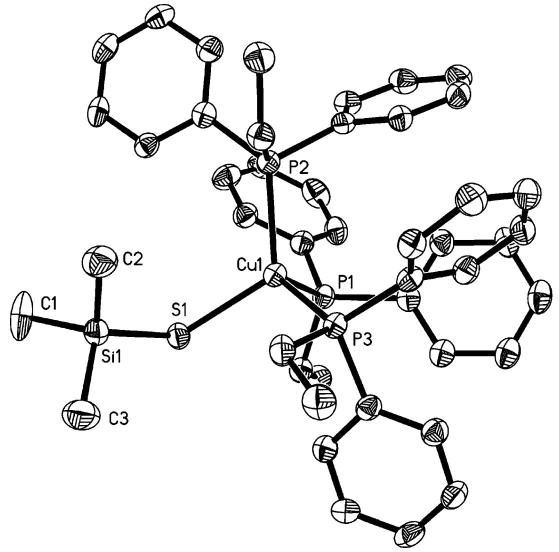

Figure 2. Molecular structure of **1b**. H atoms are omitted for clarity, and thermal ellipsoids are drawn at 40% probability.

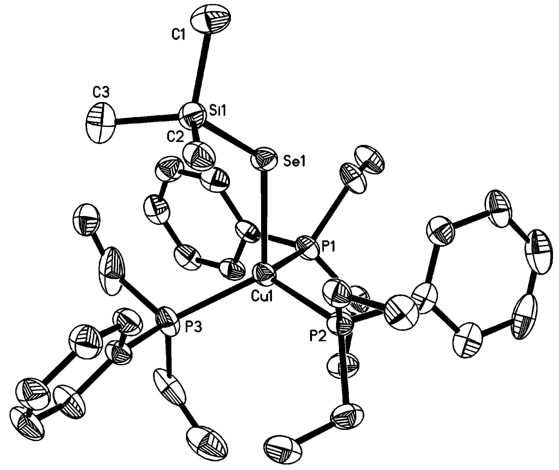

Figure 3. Molecular structure of **2a**. H atoms are omitted for clarity, and thermal ellipsoids are drawn at 40% probability.

Table 3. Selection of Bond Lengths (Å) and Angles (deg) for **1b**, **2a**, and **6**

	1b	2a	6
Si−E	2.105(2)	2.226(2)	
Cu−E	2.371(1)	2.5026(8)	2.4594(5)
Cu−P1	2.317(2)	2.306(1)	2.2766(8)
Cu−P2	2.307(1)	2.281(1)	2.2805(8)
Cu−P3	2.298(1)	2.276(2)	2.2787(9)
∠Si−E−Cu	120.39(7)	124.55(4)	
∠E−Cu−P1	99.38(5)	95.35(4)	101.89(2)
∠E−Cu−P2	119.71(5)	99.76(4)	102.54(2)
∠E−Cu−P3	106.89(5)	117.58(5)	112.05(3)

Å av] versus Et_2PhP [2.288(2) Å av]. The Cu−E bond distances are typical of such systems where the Cu−S bond length [2.371(1) Å] is shorter than the bond length for Cu−Se in **2a** [2.5026(8) Å]. These bond distances are shorter than those observed for $(R_3P)_3Cu{-}ESiMe_3$ [R = Et, Pr; E = S, 2.400(1) Å av; E = Se, 2.5142(7) Å av] complexes.[12a] The angles P−Cu−S vary from 99.38(5) to 119.71(5)° in **1b** and those for P−Cu−Se between 95.35(4) and 117.58(5)° in **2a**.

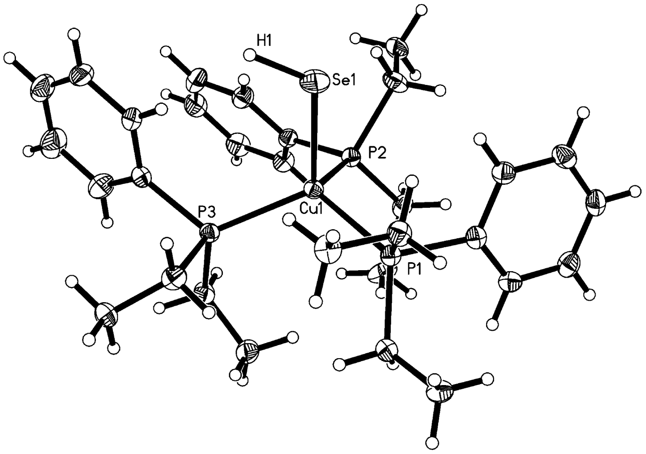

Figure 4. Molecular structure of **6**. Thermal ellipsoids are drawn at 40% probability.

The reactivity of the E−Si bond is demonstrated with the formation of **6** (Figure 4) when solutions of **2a** are treated with small amounts of protic (EtOH) solvents. Solution ^1H NMR spectra of **6** display, in addition to signals assigned to the $EtPh_2P$ ligands, a singlet at δ −5.26 assigned to the −SeH group. J_{SeH} is evident in the ^1H NMR spectra with well-resolved satellites and a value of 13 Hz. $^{77}Se\{^1H\}$ NMR spectra display a single resonance at δ −507. **6** represents a rare report of a structurally characterized MSeH complex,[29] and the first example reported for Cu. The Cu atom in **6** adopts a less distorted tetrahedral coordination geometry [∠P−Cu−Se = 101.89(2)−112.05(3)°] than is observed in $P_3CuESiMe_3$ complexes, and there is little variation observed in the Cu−P bond lengths [2.2766(8)−2.2805(8) Å]. The Cu−Se bond length is 2.4594(5) Å, which is also shorter than that observed for the (trimethylsilyl)selenolates $P_3CuSeSiMe_3$.

The new chalcogenolates **1**−**5** described above offer entry points for the formation of polyheterometallic complexes. Thus, the reaction of **1b** with 0.5 equiv of $PEtPh_2$-solubilized AgOAc results in the gradual darkening of the reaction solutions when they are warmed slowly from −60 °C. A reduction in the volume of the solvent and storage of the reaction solutions at −8 °C lead to the formation of orange-red crystals of **7**. X-ray analysis indicates that **7** is composed of 12 metal atoms and 6 sulfide ligands, and this core is stabilized with 8 PPh_2Et ligands (Figure 5). The molecule resides about a crystallographic inversion center, and the overall structure is similar to that reported for the homometallic sulfide $Cu_{12}S_6(PR'_2R)_8$ clusters.[30] The four central atom positions in **7** (Cu5/5A/6/6A) were satisfactorily refined as Cu atoms; however, the phosphine ligated atoms M1−M4

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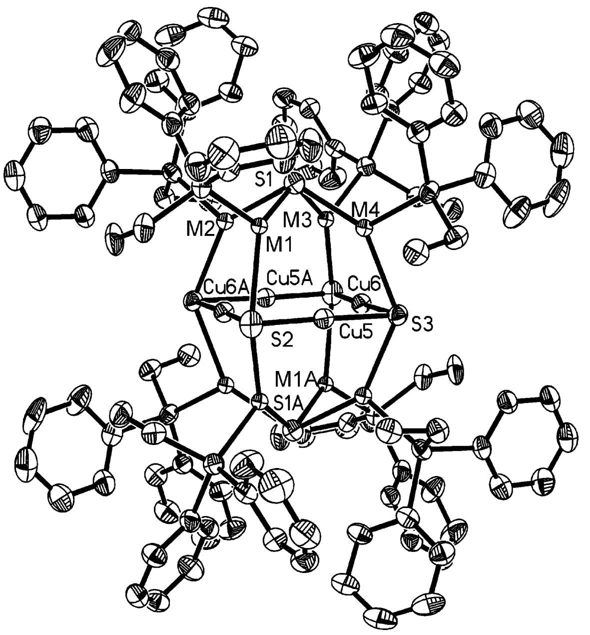

Figure 5. Molecular structure of **7**. The positions labeled "M" are those occupied by Ag and Cu. H atoms are omitted for clarity, and thermal ellipsoids are drawn at 40% probability.

Table 4. Selection of Bond Lengths (Å) in **7**

Cu1−S1	2.302(3)	Cu1−P1	2.400(3)
Cu1−S2	2.642(3)	Cu1−Cu6	2.807(3)
Cu1−Cu2	2.846(3)	Cu1−Cu5	2.974(3)
Cu1−Cu4	3.016(3)	Ag1−S2	2.418(3)
Ag1−P1	2.425(3)	Ag1−S1	2.488(2)
Ag1−Cu6	2.690(2)	Ag1−Cu5	2.825(2)
Cu5−S2	2.154(2)	Cu5−S3	2.173(2)
Cu5−Ag2	2.620(4)	Cu5−Cu3	2.772(3)
Cu5−C2	2.780(2)	Cu5−Ag3	2.816(2)

and their symmetry equivalents were refined as a disordered distribution of three Ag atoms and five Cu atoms. Figure S1 in the Supporting Information illustrates the different positions refined for the Ag and Cu sites. In cluster **7**, the six sulfide ligands are arranged to form a distorted octahedron, with the Cu_9Ag_3 centers arranged around its edges. The sulfide ligands are μ_4-bonded to the metals, with Cu−S bond lengths ranging from 2.144(2) to 2.642(3) Å and the Ag−S bond distances ranging from 2.299(4) to 2.576(3) Å (Table 4). The four central Cu atoms are each bonded to two sulfide ligands, leading to an almost linear S−Cu−S arrangement. The additional Cu atom and all Ag atoms are bonded to two sulfide and one phosphine ligands in a (distorted) trigonal-planar fashion. $^{31}P\{^1H\}$ NMR spectra of solutions of **7** display only one broad ($W_{1/2} = 118$ Hz) peak at δ −10.3. EDX analysis on single crystals of **7** confirmed the X-ray crystallographic model, with a measured ratio Cu:Ag = 2.95:1.00. Elemental analysis of single crystals also verified the composition of three Ag and nine Cu atoms. Found: Ag, 10.0; Cu, 19.8. Calcd: Ag, 11.6; Cu, 20.4.

Crystals of **7** are stable under an inert atmosphere at room temperature; however, solutions of **7** decompose over ∼2 h, as evidenced by the formation of a silver-colored mirror on the reaction glassware. Absorption spectra of freshly prepared solutions of **7** were compared to those of the previously reported and structurally related cluster $[Cu_{12}S_6(PPh_2Et)_8]$.[30a] There is an intense absorption peak observed at 255 nm for both samples arising from the PPh_2Et ligands.[31] For **7**, a discrete, lower-energy absorption maximum is also observed at 420 nm ($\epsilon = 22\,000$ L·mol^{-1}·cm^{-1}), which is not observed for $[Cu_{12}S_6(PPh_2Et)_8]$. This absorption is in keeping with previous reports of ligand-to-metal charge-transfer transitions in polynuclear silver sulfide complexes.[32]

In summary, $PEtPh_2$- and PEt_2Ph-ligated copper and silver (trimethylsilyl)chalcogenolate coordination complexes have been synthesized and characterized. Complexes **4** ($AgSSiMe_3$) and **5** ($AgSeSiMe_3$) represent the first (trimethylsilyl)-chalcogenolates reported for Ag^I; however, the corresponding tellurolate complexes were not able to be isolated. Although **1**−**5** are thermally unstable with respect to the formation of binary metal chalcogenides, they are, nonetheless, potentially powerful synthons for the formation of heterometallic clusters.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1b**, **2a**, **6**, and **7**, a representation of cluster **7** (Figure S1), and ^1H NMR spectra (Figures S2−S14). This material is available free of charge via the Internet at http://pubs.acs.org.

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