Synthesis and Characterization of Tris(trialkylphosphine)copper(I)trimethylsilylchalcogenolates

Diem T. T. Tran and John F. Corrigan*

Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 5B7 Canada

Received July 18, 2000

The copper−chalogenolates $(R_3P)_3Cu-ESiMe_3$ (E = S, **1**; Se, **2**; Te, **3**; R = Et, **a**; ^{n}Pr, **b**) have been prepared in high yield from $(R_3P)_3CuOAc$ and $E(SiMe_3)_2$ at low temperatures. Complexes **1**−**3** contain a pendant $-SiMe_3$ moiety bonded to a chalcogen center. These copper−chalcogenolates are clear, colorless, low-melting-point solids and have been characterized by single-crystal crystallographic and spectroscopic methods.

Introduction

The chemistry of selenolate (−SeR) and tellurolate (−TeR) complexes has received broad interest in recent years[1] and has been augmented by the discovery that they may be used as single-source precursors to semiconducting metal chalcogenides.[2] Many of the complexes synthesized involve bulky substituents bonded to the chalcogen centers. Examples include $Si(SiMe_3)_3$,[3] $C(SiMe_3)_3$,[4] mesityl,[5] or supermesityl[6] groups stabilizing the E^{2-} center. A variety of anionic salts[7] and transition[8] and main group metal[9] derived chalcogenolates have been reported, and access to these metal chalcogenides can be achieved by different approaches, including cleavage of the E−H bond via chalcogenolysis[10] (eq 1) or direct insertion into transition metal M−C bonds[11] (eq 2).

$$L_nM-X + HER \rightarrow L_nM-ER + HX \quad (1)$$

$$L_nM-R + E \rightarrow L_nM-ER \quad (2)$$

$$L_nM + RE-ER \rightarrow L_nM(ER)_2 \quad (3)$$

Other strategies include oxidative addition of dichalcogenides[12] (eq 3) where the R groups should not be so bulky that they hinder attack. The method of interest to our research can be depicted by eq 4, where use of

$$L_nM-X + RE-SiMe_3 \rightarrow L_nM-ER + X-SiMe_3 \quad (4)$$

the trimethylsilyl moiety allows for favorable thermodynamic release of $X-SiMe_3$[13] (X can be a halide,

(1) For reviews see: (a) Arnold, J. *Prog. Inorg. Chem.* **1995**, *43*, 353−415. (b) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133−244. (c) Janssen, M. D.; Grove, D. M.; van Koten, G. *Prog. Inorg. Chem.* **1997**, *46*, 97−149. (d) Dilworth, J. R.; Hu, J. *Adv. Inorg. Chem.* **1993**, *40*, 411−459.

(2) (a) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200−7201. (b) O'Brien, P. *Chemtronics* **1991**, *5*, 61−70. (c) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245−246. (d) Singh, H. K; Sudha, N. *Polyhedron*, **1996**, *15*, 745−763. (e) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 2256−2257. (f) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141−4143. (g) Strzelecki, A. R.; Timinski, P. A.; Helsel, B. A.; Bianconi, P. A. *J. Am. Chem. Soc.* **1992**, *114*, 3159−3160. (h) Strzelecki, A. R.; Likar, C. L.; Helsel, B. A.; Utz, T.; Lin, M. C.; Bianconi, P. A. *Inorg. Chem.* **1994**, *33*, 5188−5194. (i) O'Brien, P.; Nomura, R. *J. Mater. Chem.* **1995**, *5*, 1761−1773. (j) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228−4231.

(3) (a) Christou, V.; Wuller, S. P.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 10545−10552. (b) Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791−1796. (c) Cary, D. R.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 2520−2521. (d) Cary, D. R.; Ball, G. E.; Arnold, J. *J. Am. Chem. Soc.* **1995**, *117*, 3492−3501. (e) Gerlach. C. P.; Wuller, S. P.; Arnold, J. *Chem. Commun.* **1996**, 2565−2566.

(4) (a) Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800−1801. (b) Giselbrecht, K.; Bildstein, B.; Sladky, F. *Chem. Ber.* **1989**, *122*, 1255−1256. (c) Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854−4861. (d) Lee, H. K.; Luo, B.; Mak, T. C. W.; Leung, W. *J. Organomet. Chem.* **1995**, *489*, C71−C73. (e) Ostrowski, M.; Jeske, J.; Jones, P. G.; du Mont, W. W. *Chem. Ber.* **1993**, *126*, 1355−1359. (f) Wagner, I.; du Mont, W. W.; Pohl, S.; Saak, W. *Chem. Ber.* **1990**, *123*, 2325−2327. (g) Bonasia, P. J.; Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1993**, *32*, 5126−5131.

(5) (a) Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973−975. (b) Bonasia, P. J.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1299−1301. (c) Recknagel, A.; Noltemeyer, M.; Stallke, D.; Pieper, U.; Schmidt, H.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *411*, 347−356. (d) Buchholz, D.; Huttner, G.; Zsolnai, L.; Imhof *J. Organomet. Chem.* **1989**, *377*, 25−41. (e) Keller, H.; Daran, J. C.; Lang, H. *J. Organomet. Chem.* **1994,** *482*, 63−66. (f) Wedler, M.; Recknagel, A.; Gilje, J. W.; Nottenmeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1992**, *426*, 295−306. (g) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430−442. (h) Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995,** *14*, 3869−3875. (i) Nakamoto, M.; Hiller, W.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 605−610. (j) Schneider, J. J.; Kuhnigkh, J.; Krüger, C. *Inorg. Chim. Acta* **1997**, *266*, 109−112. (k) Hamor, T. A.; Hussain, W.; Jones, C. J.; McCleverty, J. A.; Rothin, A. S. *Inorg. Chim. Acta* **1988**, *146*, 181−185. (l) Geissinger, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 755−761. (m) Jeske, J.; Salzen, A. M.; du Mont, W. W.; Jones, P. G. *Acta Crystallogr.* **1998**, *C54*, 1873−1875. (n) Ball, J. M.; Boorman, M.; Fait, J. F.; Hinman, S.; Lundmark, P. J. *Can. J. Chem.* **1989**, *67*, 751−758. (o) Kersting, B.; Krebs, B. *Inorg. Chem.* **1994**, *33*, 3886−3892.

(6) (a) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638−639. (b) Lange, L.; du Mont, W. W. *J. Organomet. Chem.* **1985**, *286*, C1−C2. (c) du Mont, W. W.; Lange, L.; Karsch, H. H.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 11−14. (d) Jin, X.; Tang, K.; Xia, T.; Tang, Y. *J. Coord. Chem.* **1995**, *34*, 187−194. (e) Wieber, M.; Habersack, R. *Phosphorus, Sulfur, Silicon* **1995**, *106*, 233−241. (f) Bochmann, M.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2317−2323. (g) Yasui, M.; Taka, H.; Shimizu, T.; Kamigata, N.; Twasaki, F. *Acta Crystallogr.* **1999** *C55*, 1861−1862. (h) Bochmann, M.; Webb, K. J.; Powell, A. K. *Polyhedron* **1992**, *11*, 513−516. (i) Ruhlandt-Senge, K.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1724−1728. (j) Atwood, D. A.; Cowley, A. H.; Hernandez, R. D.; Jones. R. A.; Rand, L. L.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1993**, *32*, 2972−2974. (k) Ruhlandt-Senge, K.; Davis, K.; Dalal, S.; Englich, U.; Senge, M. O. *Inorg. Chem.* **1995**, *34*, 2587−2592.

10.1021/om000624d CCC: $19.00
Publication on Web 10/31/2000

acetate, amide, or any other adequate leaving group). In this case the substituent "R" is typically an alkyl (butyl)[14] or aryl (phenyl, mesityl)[15] moiety. Tanaka and co-workers have illustrated recently that a terminal trimethylsilytellurolate ligand can be accessed via the oxidative addition of $Te(SiMe_3)_2$ to a Pt(0) center.[16] We have recently communicated that copper−trimethylsilylthiolate complexes can be used as precursors to ternary nanocluster materials.[17] Herein we describe the complete synthesis and structural and spectroscopic characterization of a series of complexes $(R_3P)_3Cu-ESiMe_3$ (E = S, **1**; Se, **2**; Te, **3**; R = Et, **a**; ^{n}Pr, **b**), the first examples of structurally characterized chalcogenolate complexes containing a terminally bonded $ESiMe_3$ moiety.

Results and Discussions

The growing interest in nanoparticles and their possible uses in materials applications[18] has led to great many efforts to access these particles in a size-controlled manner.[19] Silylchalcogen reagents offer excellent routes into these materials. Fenske et al. have been successful in isolating a large number of metal−chalcogenide nanoclusters via the reaction of metal salts, stabilized by phosphine ligands, and $E(SiMe_3)_2$ (E = S, Se, Te).[20] More recently, it has also been shown that trimethylsilylseleno and telluro ethers[21] can lead to the generation of other series of novel high-nuclearity clusters. To date, exploration of binary nanoclusters has been much more extensive in contrast with ternary phase nanoparticles,[22] and this may be attributed, in part, to a lack of suitable "binary" silyl reagents that can be employed to yield ternary clusters.

The facile synthetic route to **1**−**3** involves dissolving CuOAc with 4 equiv of trialkylphosphine in hexane/ether solvents (eq 5). The low $Cu:PR_3$ ratio is critical, as it is essential to occupy three coordination sites

(7) (a) Bonasia, P. J.; Gindelberger, D. E.; Dabbousi, B. O.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 5209−5214. (b) Liesk, J.; Schulz, P.; Klar, G. *Z. Anorg. Allg. Chem.* **1977**, *435*, 98−102. (c) Becker, G.; Klinkhammer, K. W.; Lartiges, S.; Bottcher, P.; Poll, W. *Z. Anorg. Allg. Chem.* **1992**, *613*, 7−18. (d) Gornitzka, H.; Besser, S.; Herbst-Irmer, R.; Kilimann, U.; Edelmann T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1260−1261. (e) Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Sigel, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1674−1675. (f) Gindelberger, D. E.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6242−6243. (g) du Mont, W. W.; Wagner, I. *Chem. Ber.* **1988**, *121*, 2109−2110. (h) du Mont, W. W.; Kubiniok, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem. Ber.* **1991**, *124*, 1315−1320. (i) Bonasia, P. J.; Arnold, J. *J. Organomet. Chem.* **1993**, *449*, 147−157. (j) Flick, K. E.; Bonasia, P. J.; Gindelberger, D. E.; Katari, J. E. B.; Schwartz, D. *Acta Crystallogr.* **1994,** *C50*, 674−675. (k) Sigel, G. A.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2819−2822.

(8) (a) Herberfold, M.; Schrepfermann, M.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *394*, 113−120. (b) Lau, P.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1992**, *440*, 41−46. (c) Millar, M. M.; O'Sullivan, T.; de Vries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714−3715. (d) Huttner, G.; Schuler, S.; Zsolnai, L.; Gottlieb, M.; Braunwarth, H.; Minelli, M. *J. Organomet. Chem.* **1986**, *299*, C4−C6. (e) Braunwarth, H.; Ettel, F.; Huttner, G. *J. Organomet. Chem.* **1988**, *355*, 281−288. (f) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770−5780. (g) Gindelberger, D. E.; Arnold, J. *Organometallics* **1994**, *13*, 4462−4468. (h) Zhang, J.; Leong, W. K. *J. Chem. Soc., Dalton Trans.* **2000,** 1249−1253. (i) Sato, M.; Yoshida, T. *J. Organomet. Chem.* **1975**, *94*, 403−408. (j) Bonasia, P. J.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508−2514. (k) Gruff, E. S.; Koch, S. A.; *J. Am. Chem. Soc.* **1990**, *112*, 1245−1247.

(9) (a) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M., Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116−2120. (b) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8214−8220. (c) Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854−4861. (d) Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547−1551. (e) Wuller, S. P.; Seligson, A. L.; Mitchell, G. P.; Arnold, J. *Inorg. Chem.* **1995**, *34*, 4854−4861. (f) Huttner, F. E.; Zsolnai, L.; Emmerich, C. *J. Organomet. Chem.* **1991**, *414*, 71−87. (g) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478−3481.

(10) (a) Bochmann, M.; Webb, K. J. *J. Chem. Soc., Dalton Trans.* **1991**, 2325−2329. (b) Dabbousi, B. O.; Bonasia, P. J.; Arnold, J. *J. Am. Chem. Soc.* **1991**, *113*, 3186−3188. (c) Chisholm, M. H.; Huffman, J. C.; Parkin, I. P.; Streib, W. E. *Polyhedron* **1990**, *9*, 2941−2952. (d) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683−3686. (e) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240−6242.

(11) (a) Piers, W. E.; Macgillivray, L. R.; Zaworotko, M. *Organometallics* **1993**, *12*, 4723−4725. (b) Piers, W. E.; Parks, D. J.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1994**, *13*, 4547−4558.

(12) (a) Cotton, F. A.; Dunbar, K. R. *Inorg, Chem.* **1987**, *26*, 1305−1309. (b) Andreu, P. L.; Cabeza, J. A.; Miguelm, D.; Riera, V.; Villa, M. A.; García-Granda, S. *J. Chem. Soc., Dalton Trans* **1991**, 533−536. (c) Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5327−5334. (d) Brewer, M.; Lee, J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5919−5924. (e) Mirzaei, F.; Han, L.; Tanaka, M. *Chem. Commun.* **2000**, 657−658. (f) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *J. Chem. Soc., Dalton Trans.* **2000**, 1663−1668.

(13) (a) Jones, P. G.; Thöne, C. *Chem. Ber.* **1990**, *123*, 1975−1978. (b) Ball, J. M.; Boorman, P. M.; Fait, J. F.; Kraatz, H. B.; Richardson, J. F.; Collison, D.; Mabbs, F. E. *Inorg. Chem.* **1990**, *29*, 3290−3293. (c) Hänisch, C.; Fenske, D.; Kattannek, M.; Ahlrichs, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 2736−2738. (d) Dehnen, S.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2287−2289.

(14) (a) Fenske, D.; Bettenhausen, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1291−1294. (b) Zhu, N.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1999**, 1067−1075. (c) Corrigan, J. F.; Fenske, D. *Chem. Commun.* **1996**, 943−944. (d) Fenske, D.; Zhu, N. *J. Clust. Sci.* **2000**, *11*, 135−151.

(15) (a) Corrigan, J. F.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1981−1983. (b) Bettenhausen, M.; Fenske, D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1245−1246. (c) Corrigan, J. F.; Fenske, D.; Power, W. P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1176−1179. (d) Behrens, S.; Bettenhausen, M.; Deveson, A. C.; Eichhöfer, A.; Fenske, D.; Lohde, A.; Woggon, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2215−2218. (e) DeGroot, M. W.; Corrigan, J. F.; *J. Chem. Soc., Dalton Trans.* **2000**, 1235−1236.

(16) Han, L.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1997**, *119*, 8133−8134.

(17) Tran, D. T. T.; Taylor, N. J.; Corrigan, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 935−937.

(18) (a) Schmid, G. *J. Chem. Soc., Dalton Trans.* **1998**, 1077−1082. (b) Weller H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1658−1659. (c) Schmid G.; Bäumle M.; Geerkens M.; Heim I.; Osemann C.; Sawitowski T. *Chem. Soc. Rev.* **1999**, *28*, 179−185. (d) Gebauer, T.; Schmid, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1124−1128. (e) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226−13239. (f) Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* **1997**, *389*, 699−701. (g) Alivisatos, A. P. *Science* **1996**, *271*, 933−937.

(19) (a) Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589−595. (b) Schmid, G.; Peschel, S. *New J. Chem.* **1998**, 669−675. (c) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690−1693. (d) Adair, J. H.; Li, T.; Kido, T.; Havey, K.; Moon, J.; Mecholsky, J.; Morrone, A.; Talham, D. R.; Ludwig, M. H.; Wang, L. *Mater. Sci. Eng.* **1998**, *R23*, 139−242. (e) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046−3050. (f) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322−1326. (g) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(20) (a) Dehnen, S.; Fenske, D. *Chem. Eur. J.* **1996**, *2*, 1407−1416. (b) Eichhöfer, A.. ; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1998**, 2969−2972. (c) Dehnen, S.; Schäfer, A.; Ahlrichs, R.; Fenske, D. *Chem. Eur. J.* **1996**, *2*, 429−435. (d) Deveson, A.; Dehnen, S.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1997**, 4491−4497. (e) Fenske, D.; Krautscheid, H.; Balter, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 796−799. (f) Fenske, D.; Ohmer, J.; Hachgenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993−995.

(21) (a) Eichhöfer, A.; Fenske, D.; Pfistner, H.; Wunder, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1909−1914. (b) Fenske, D.; Zhu, N.; Langetepe, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 2639−2644. (c) Hope, E. G.; Levason, W. *Coord. Chem. Rev.* **1993**, *122*, 109−170. (d) Corrigan, J. F.; Fenske, D. *Chem. Commun.* **1997**, 1837−1838.

(22) (a) Schneider, J. J.; Hagen, J.; Spickermann, D.; Bläser, D.; Boese, R.; de Biani, F. F.; Laschi, F.; Zanello, P. *Chem. Eur. J.* **2000**, *6*, 237−246. (b) Stephan, H.; Henkel, G.; Kanatzidis, G. *Chem. Commun.* **2000**, 67−68. (c) Carmalt, C. J.; Morrison, D. E.; Parkin, I. P. *J. Mater. Chem.* **1998**, *8*, 2209−2211. (d) Eichhöfer, A.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **2000**, 941−944. (e) Hirpo, W.; Dhingra, S.; Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 1597−1599. (f) Hirpo, W.; Dhingra, S.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1992**, 557−559. (g) Harvey, P. D.; Eichhöfer, A.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1998**, 3901−3903.

$$CuOAc + 4\ PR_3 + E(SiMe_3)_2 \xrightarrow[\substack{\text{hexanes/diethyl ether}\\ R = Et, Pr\\ E = S, Se, Te}]{-45\ ^\circ C} (R_3P)_3CuESiMe_3 + AcOSiMe_3 + PR_3 \quad (5)$$

around the metal in order to force terminal coordination of the formed silylchalcogenolate and to avoid the generation of polynuclear copper−chalcogenide complexes.[23] This can be attributed to the retention of the reactive E−$SiMe_3$ moiety on the formed target molecules with general formulas $(R_3P)_3Cu-ESiMe_3$. A related, lighter congener, $(Me_3P)_3Cu-OSiMe_3$, has been reported and characterized spectroscopically.[24]

When cooled to −45 °C, the copper−trialkylphosphine adducts precipitate from solution, and 1 equiv of bis(trimethylsilyl)chalcogen is added. After 1 h of stirring at −15 °C or lower, a new white solid appears. This solid (**1**−**3**) is then recrystallized by first raising the temperature of the reaction mixture (ca. −10 °C), allowing the white solid to dissolve, and immediately cooling to −70 °C. The solvent ratios were very critical to the product yield, which were often quantitative. Alternatively, the solvent could be removed, in vacuo at ∼0 °C, after an hour of stirring, to give solid **1**−**3**. The yields, however, were not optimal via this latter method. As expected, the Et_3P derivatives are less soluble in hydrocarbon solvents than their $^nPr_3P$ counterparts. When 3 equiv of phosphine was used in attempting to access **1**−**3**, the reaction mixtures produced either dark, viscous oils or higher nuclearity copper−chalcogenide complexes.[23] Presumably, an excess of phosphine is required to force terminal coordination of the chalcogenolate ligand by sequestering all remaining coordination sites about copper. Complexes **1**−**3** are all clear, colorless solids with low melting points (3−11 °C for **1a** and **2b**, respectively) and high air sensitivity. Compounds **1a**, **2a**, and **3a** are in general less stable than their P^nPr_3 analogues (**1b**−**3b**), as they could not remain at room temperature for extended amounts of time without forming copper−chalcogenide clusters.[25] Similarly, complexes **1**−**3** are unstable in solution above ∼0 °C, forming copper−chalcogenide polynuclear complexes. **3a** and **3b** (E = Te) decompose upon melting with the formation of elemental tellurium.

Complete structural information was obtained for **1**−**3** from single-crystal X-ray crystallographic analyses (see Supplementary Information Tables S1−S30). Compounds **1a**−**3a** crystallized in space group $P2_1/n$, whereas complexes **1b**−**3b** were satisfactorily solved and refined in the space group $P\bar{1}$. Table 1 provides a summary of the crystallographic data for all six structures, and Table 2 lists selected bond lengths and angles. The molecular structures of $(Et_3P)_3Cu-SSiMe_3$ (**1a)** and $(Pr_3P)_3Cu-TeSiMe_3$ (**3b)** are illustrated in Figures 1 and 2, respectively.

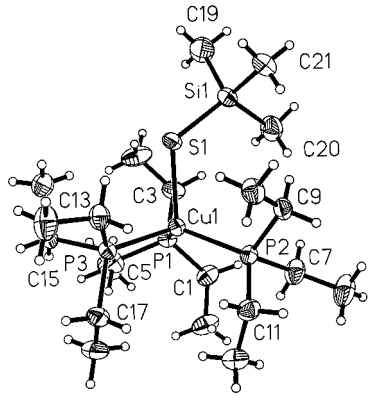


Figure 1. Molecular structure of $(Et_3P)_3CuSSiMe_3$, **1a**. Thermal elipsoids are drawn at the 50% probability level.

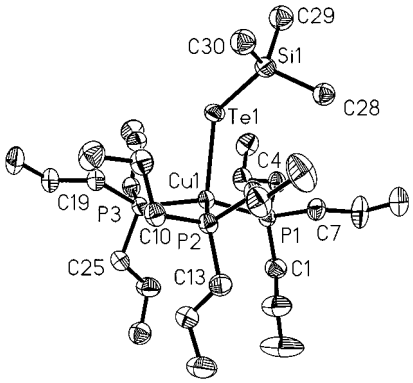


Figure 2. Molecular structure of $(Pr_3P)_3CuTeSiMe_3$, **3b**. Hydrogen atoms have been omitted for clarity. Thermal elipsoids are drawn at the 50% probability level.

Both the pendant trimethylsilyl moieties and the copper centers in **1**−**3** display tetrahedral coordination geometry. The Si−E bond lengths range from 2.0776(13) to 2.4692(9) Å, increasing in length with increasing size of the chalcogen center. Accordingly, the Cu−E bond lengths follow the same pattern, varying from 2.3970(10) (E = S) to 2.7126(4) Å (E = Te). The Te−Si [2.4692(9) and 2.4467(7) Å for **3a** and **3b**, respectively] bond lengths are shorter than that observed in $(Me_3P)_3$-Co−$TeSi(SiMe_3)_3$ (2.494(2) Å). This related tetrahedral complex has been synthesized by Arnold et al. using a much larger silyl group.[26] This Co d^8 complex displays incredible thermal stability with a melting point of 154 °C. There are surprisingly few reports detailing terminally bonded selenolate and tellurolate complexes on copper centers. Indeed, a search of the Cambridge Structural Database (version 5.19 April 2000) yielded only two examples.[27] Other copper-bonded selenolate and tellurolate ligands most often adopt a bridging coordination mode.[28]

For their part, the Cu−P lengths range from 2.2843(10) to 2.3116(11) Å, and in each case (with the exception of **1a**) the bond lengths Cu−P2 are the shortest observed in these molecules. The angles ∠E−Cu−P span a wide range, between 96.69(3)° and 114.16(2)°. The smallest angles are invariably displayed by ∠E−Cu−P3, the phosphorus center trans to the E−Si vector.

(23) (a) Eichhöfer, A.; Corrigan, J. F.; Fenske, D.; Tröster, E. *Z. Anorg. Allg. Chem.* **2000**, *626*, 338−348. (b) Fenske, D.; Krautscheid, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1452−1454. (c) Dehnen, S.; Schäfer, A.; Fenske, D.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 746−749. (d) Krautscheid, H.; Fenske, D.; Baum, G.; Semmelmann, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1303−1305. (e) Corrigan, J. F.; Balter, S.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1996**, 729−738. (f) Dehnen, S.; Fenske, D.; Deveson, A. C. *J. Clust. Sci.* **1996**, *7*, 351−369.

(24) Schmidbaur, H.; Adlkofer, J.; Shiotani, A. *Chem. Ber.* **1972,** *105*, 3389−3396.

(25) Tran, D. T. T., Corrigan, J. F. To be published.

(26) Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1993**, *32*, 2, 5813−5820.

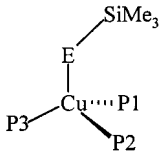
(27) Semmelmann, M.; Fenske, D.; Corrigan, J. F. *J. Chem. Soc., Dalton Trans.* **1998**, 2541−2545.

Published on October 31, 2000 on http://pubs.acs.org | doi: 10.1021/om000624d

Table 1. Crystal Data for 1−3

	$(Et_3P)_3CuSSiMe_3$, **1a**	$(Et_3P)_3CuSeSiMe_3$, **2a**	$(Et_3P)_3CuTeSiMe_3$, **3a**	$(Pr_3P)_3CuSSiMe_3$, **1b**	$(Pr_3P)_3CuSeSiMe_3$, **2b**	$(Pr_3P)_3CuTeSiMe_3$, **3b**
empirical formula	$C_{21}H_{54}CuP_3SSi$	$C_{21}H_{54}CuP_3SeSi$	$C_{21}H_{54}CuP_3TeSi$	$C_{30}H_{72}CuP_3SSi$	$C_{30}H_{72}CuP_3SeSi$	$C_{30}H_{72}CuP_3TeSi$
source and habit	colorless blocks from cold diethyl ether					
wavelength	0.71073 Å					
temp (K)	200(2)	200(2)	190(2)	200(2)	200(2)	200(2)
radiation type	Mo $K\alpha_1$					
monochromator	graphite					
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.9276(4)	16.7522(7)	16.5294(3)	10.9010(8)	10.8887(4)	10.9124(2)
b (Å)	13.9813(5)	11.6163(3)	12.0854(2)	11.1233(7)	11.1231(5)	11.1359(2)
c (Å)	18.2051(5)	17.4349(7)	16.9309(3)	17.3734(11)	17.3991(8)	17.5397(2)
α (deg)	90	90	90	92.8890(34)	94.0153(24)	95.0140(11)
β (deg)	97.5700(19)	117.2780(14)	115.6712(11)	97.3160(38)	97.0699(24)	97.0804(11)
γ (deg)	90	90	90	105.1135(26)	103.9299(29)	102.2238(7)
μ (mm^{-1})	1.000	2.136	1.877	0.761	1.607	1.390
diffractometer	Enraf Nonius KappaCCD single crystals					
F(000)	1136	1208	1280	712	748	784
θ range (deg)	1.93 to 25.98	2.63 to 24.45	2.67 to 26.36	3.46 to 20.79	2.67 to 27.14	2.99 to 27.16
index ranges	$-14 \le h \le 14$	$0 \le h \le 19$	$0 \le h \le 20$	$0 \le h \le 10$	$0 \le h \le 13$	$0 \le h \le 14$
	$-17 \le h \le 15$	$0 \le k \le 13$	$0 \le k \le 15$	$-11 \le k \le 10$	$-14 \le k \le 13$	$-14 \le k \le 13$
	$-22 \le h \le 22$	$-20 \le l \le 18$	$-21 \le l \le 19$	$-17 \le l \le 17$	$-22 \le l \le 22$	$-22 \le l \ge 22$
no. of reflns collected	17 868	23 637	21 083	11 440	19 905	23 130
no. of ind reflns	5870 [R(int) = 0.032]	4981 [R(int) = 0.068]	6200 [R(int) = 0.059]	4058 [R(int) = 0.037]	8759 [R(int) = 0.053]	9029 [R(int) = 0.036]
R indices [$(I)>2\sigma(I)$]	R1 = 0.0267	R1 = 0.0393	R1 = 0.0334	R1 = 0.0357	R1 = 0.0406	R1= 0.0342
	wR2 = 0.0691	wR2 = 0.0786	wR2 = 0.0830	wR2 = 0.0851	wR2 = 0.0993	wR2 = 0.0857
R indices (all data)	R1 = 0.0358	R1 = 0.0921	R1 = 0.0384	R1 = 0.0412	R1 = 0.0576	R1 = 0.0401
	wR2 = 0.0716	wR2 = 0.0886	wR2 = 0.0865	wR2 = 0.0886	wR2 = 0.1096	wR2 = 0.0899
refinement method	full-matrix least-squares on F^2					
refinement software	Bruker SHELXTL Version 5.1					

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−3



	1a E = S, R = Et	**1b** E = S, R = Pr^n	**2a** E = Se, R = Et	**2b** E = Se, R = Pr^n	**3a** E = Te, R = Et	**3b** E = Te, R = Pr^n
Si−E	2.0812(6)	2.0776(13)	2.2241(11)	2.2185(8)	2.4692(9)	2.4467(7)
E−Cu	2.4022(5)	2.3970(10)	2.5124(6)	2.5160(4)	2.7126(4)	2.6812(3)
Cu−P1	2.3031(5)	2.2971(10)	2.2956(13)	2.2953(7)	2.2991(8)	2.2956(6)
Cu−P2	2.3046(5)	2.2843(10)	2.2923(14)	2.2858(7)	2.2878(8)	2.2874(6)
Cu−P3	2.3029(5)	2.3011(9)	2.3116(11)	2.2946(7)	2.3007(8)	2.2945(6)
∠Si−E-Cu	120.64(3)	129.20(5)	124.51(4)	127.28(3)	123.31(2)	124.492(19)
∠E−Cu−P1	107.541(18)	101.22(4)	112.03(4)	99.94(2)	98.08(3)	99.358(18)
∠E−Cu−P2	108.245(18)	109.77(4)	108.34(4)	108.58(2)	114.16(2)	107.484(19)
∠E-Cu−P3	97.774(17)	100.06(3)	96.69(3)	99.86(2)	97.77(2)	100.129(17)

Table 3. Summary of NMR Data (δ, ppm) for 1−3 at −90 °C in C_7D_8 (^{1}H and ^{13}C, only the −SiMe$_3$ signals are listed)

	^{1}H	^{13}C{^{1}H}	^{31}P{^{1}H}	^{29}Si{^{1}H}	^{77}Se{^{1}H}	^{125}Te{^{1}H}
1a	0.82	8.5	−13.5	5.3		
1b	0.82	8.5	−22.0	4.9		
2a	0.94	8.6	−13.5	0.6	−570.4	
					$^2J_{SeP}$ = 43 Hz	
2b	0.92	8.6	−21.0	0.7	−565.8	
				$^3J_{SiP}$ = 6 Hz	$^2J_{SeP}$ = 41 Hz	
3a	1.09	9.0	−14.0	−23.9		−1300.6
						$^2J_{TeP}$ = 96 Hz
3b	1.01	9.0	−21.6	−24.3		−1293.7
				$^3J_{SiP}$ = 5 Hz		$^2J_{TeP}$ = 96 Hz

Despite the chemical inequivalence of phosphorus centers P1 and P2 versus P3 in the solid state, we were able to observe only one signal in the ^{31}P{^{1}H} NMR spectrum, even at the lowest temperatures accessible (−90 °C). A summary of the NMR spectroscopic data is listed in Table 3. Shifts in the ^{31}P{^{1}H} NMR spectra for **1**−**3** are downfield from those observed for the free phosphine and relatively independent of the chalcogen bonded to the copper center: ca. −14 ppm for **1a**−**3a** (compared to PEt_3, −19 ppm[29]) and ca. −22 ppm for **1b**−**3b** (free P^{n}Pr$_3$, −33 ppm[30]). The phosphorus signals were all broad due to scalar relaxation of the second kind,[31] as a result of the neighboring copper center. ^{77}Se{^{1}H} NMR spectra for **2a** and **2b** each display a quartet ($^2J_{PSe}$ = 43 Hz for **2a**, 41 Hz for **2b**) with resonances at −570.4 and −565.8 ppm, respectively. These shifts lie between those reported for the salt $(thf)_2LiSeSi(SiMe_3)_3$[32] (−825 ppm) and $Se(SiMe_3)_2$ (−334 ppm).[33] For **3a** and **3b**, the expected quartet in the ^{125}Te{^{1}H} spectrum is observed at −1300.6 ppm ($^2J_{PTe}$ = 96 Hz) and −1293.7 ($^2J_{PTe}$ = 96 Hz), comparable to Arnold's $(CO)_2(Me_3P)_2$-$CoTeSi(SiMe_3)_3$[25] (−1417 ppm) and upfield of $Te(SiMe_3)_2$ (−858.3 ppm).[34] J-coupling is also observed in the ^{29}Si-{^{1}H} NMR spectra between the silicon and the phosphorus centers. In the case of **2b** and **3b** the $^3J_{PSi}$ coupling was large enough to resolve the expected quartets (6 and 5 Hz, respectively). It is also worth noting that the shift of the silicon signal moves upfield with increasing chalcogen size, from 5.3 ppm for **1a** to −23.9 ppm for **3a**. In contrast, the chemical shifts of the carbon and proton centers of the trimethylsilyl groups displayed downfield shifts on going from **1** to **2** to **3**. In the series **1a**−**3a**, the proton signals of the −SiMe$_3$ groups shift from 0.82 to 0.94 to 1.09 ppm, on going from sulfur to selenium to tellurium. This change in chemical shift with increasing chalcogen size was also observed in the ^{13}C{^{1}H} NMR spectra of **1**−**3**, shifting slightly from 8.5 ppm for **1a** to 9.0 ppm for **3a**. These variations can be attributed to the inductive effect and have been noted by Drake et al.[35] in the ^{1}H and ^{13}C-{^{1}H} NMR spectra of $E(SiMe_3)_2$ (E = S, Se, Te). A similar trend is also observed for $E(Ph)SiMe_3$, as the −SiMe$_3$ signal in the ^{1}H NMR spectrum varies from 0.30 ppm[36] to 0.37 ppm[37] to 0.47 ppm[38] on going from S → Se → Te.

The facile, high-yield synthesis of the copper−chalcogenolate complexes prompts investigations probing their use in nanocluster synthesis. We have recently communicated that the reaction of **1b** with $Hg(OAc)_2$ yields the cluster $[Hg_{15}Cu_{20}S_{25}(PPr_3)_{18}]$ in good yield,[17] and ongoing research using this general strategy will be published elsewhere.

Conclusions

We have demonstrated that a series of terminal tris-(trialkylphosphine)copper(I) (trimethylsilyl)chalcogenolates (E = S, Se, Te) can be prepared readily and in good yield from the reaction of $E(SiMe_3)_2$ and $(R_3P)_3CuOAc$.

(28) (a) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 7339−7344. (b) Bonasia, P. J.; Mitchell, G. P.; Hollander, F. J.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1797−1802. (c) Kampf, J.; Kumar, R.; Oliver, J. P. *Inorg. Chem.* **1992**, *31*, 3626−3629. (d) Jin, X.; Tang, K.; Long, Y.; Tang, Y. *Acta Crystallogr.* **1999**, *C55*, 1799−1800. (e) Lackmann, J.; Hauptmann, R.; Weissgräber, S.; Henkel, G. *Chem. Commun.* **1999**, 1995−1996. (f) Ohlmann, D.; Marchand, C. M.; Schönberg, H.; Grützmacher, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1349−1357. (g) Ohlmann, D.; Pritzkow, H.; Grützmacher, H.; Anthamatten, M.; Glaser, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1011−1012.

(29) R. Kirss, *J. Organomet. Chem.* **1995**, *498*, 171−176.

(30) Henderson, W. A.; Buckler, S. *J. Am. Chem. Soc.* **1960**, *82*, 5794−5800.

(31) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*; Longman Scientific & Technical: New York, 1986; pp 90.

(32) Bonasia, P. J.; Christou, V.; Arnold J. *J. Am. Chem. Soc.* **1993**, *115*, 6777−6781.

(33) Semmelmann, M. Doctoral Dissertation, Universität Karlsruhe, 1997; Germany.

(34) Jones, C. H. W.; Sharma, R. D. *J. Organomet. Chem.* **1984**, *268*, 113−118.

(35) Drake, J. E.; Glanvincevski, B. M.; Humphries R.; Majid, A. *Can. J. Chem.* **1979**, *57*, 3253−56.

(36) Mathieu-Pelta, I.; Evans, S. A. *J. Org. Chem.* **1992**, *57*, 3409−3413.

(37) Detty, M. R. *J. Org. Chem.* **1979**, *44*, 4528−4531.

(38) Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879−1883.

To ensure that reactions proceed smoothly and that terminal coordinate of the chalcogenolate ligand is ensured, it is imperative that an excess of phosphine is used during the preparation of these novel molecules. Although these solids display melting points below room temperature, they can be stored for indefinite periods of time in the solid state at low (−40 °C) temperatures. This synthetic approach is a general one and should lead to a large number of metal−(trimethylsilyl)chalcogenolate complexes.

Experimental Section

Experiments were all performed in an inert nitrogen atmosphere with the use of Schlenk line techniques and gloveboxes. The starting materials, PEt_3,[39] P^nPr_3,[40] $E(SiMe_3)_2$ (E = Te,[41] Se,[42] S[43]), and CuOAc[44] were prepared and purified as reported in the literature. Solvents were dried and distilled over sodium/benzophenone. ^1H (399.763 MHz), $^{13}C\{^1H\}$ (100.522 MHz), $^{31}P\{^1H\}$ (161.832 MHz), $^{29}Si\{^1H\}$ (79.423 MHz), $^{77}Se\{^1H\}$ (76.217 MHz), and $^{125}Te\{^1H\}$ (126.033 MHz) NMR spectra were measured on a Varian Inova 400 spectrometer. Chemical shifts were reported in ppm and externally referenced to $SiMe_4$ (using the residual proton signal from the deuterated solvent, ^1H), 85% phosphoric acid (^{31}P), Me_2Se (with $PhSeSiMe_3$ as a secondary reference, ^{77}Se), and Me_2Te (with $PhTeSiMe_3$ as a secondary reference, ^{125}Te). Chemisar Laboratories Inc. (Guelph, Ontario) performed chemical analyses. The solvent-to-reagent ratio was critical to the formation of product in high yield, and solids **1**−**3** were stored at −40 °C to prevent decomposition.

$(Et_3P)_3CuSSiMe_3$, 1a. CuOAc (0.96 g, 7.8 mmol) was dissolved in 5 mL hexanes/4 mL diethyl ether with 4 equiv of PEt_3 (4.60 mL, 31.1 mmol) to give a clear colorless solution. The solution was cooled to −45 °C, and a white flocculent solid appeared. Bis(trimethylsilyl)sulfide (1.64 mL, 7.8 mmol) was added to give a clear, pale yellow solution after the white solid dissolved. The reaction mixture was allowed to warm slowly, with stirring, to −15 °C. After an hour another white solid (**1a**) appeared, and the temperature of the flask was raised sufficiently to dissolve the solid and form a clear yellow solution. The solution was then immediately cooled to −70 °C. After sitting for 2 h undisturbed **1a** crystallized at the bottom of the flask. The mother liquor was removed by pipet, and the crystals were dried under vacuum at 0 °C for 2 h. Complex **1a** melts at 3 °C to give a clear, colorless oil, which was stable at room temperature for a short period of time. The solid was recrystallized from 5 mL of cold ether at −30 °C to yield clear colorless crystals of **1a** within 4 h suitable for X-ray crystallography. Yield: 3.57 g (87.1%). Anal. Calcd: C, 44.71; H, 9.42. Found: C, 44.24; H, 9.55. ^1H NMR (C_7D_8, 183 K, δ): 1.34(br, CH_2), 0.95(br, CH_3), 0.82(s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −13.5(s, br). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 16.7(s, CH_2), 8.5 (s, $SiMe_3$), 8.1 (s, CH_3). $^{29}Si\{^1H\}$ NMR (C_7D_8, 183 K, δ): 5.3(s).

$(Pr_3P)_3CuSSiMe_3$, **1b**, was prepared as for **1a** using CuOAc (1.17 g, 9.5 mmol) dissolved in 8 mL hexanes/4 mL diethyl ether and 4 equiv of PPr^n_3 and reacted with $S(SiMe_3)_2$ (1.94 mL, 9.3 mmol) at −45 °C. The solid white product was recrystallized from cold diethyl ether to give clear, colorless blocks suitable for analysis by X-ray crystallography. Yield: 6.00 g (96.8%). Mp: 8.5 °C Anal. Calcd: C, 55.48; H, 11.17. Found: C, 55.42; H, 11.13. ^1H NMR (C_7D_8, 183 K, δ): 1.34(br, CH_2), 1.02(br, CH_3), 0.82 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −23.0(s, br). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 27.4 (s, CH_2), 17.4(s, CH_2), 16.7(s, CH_3), 8.5(s, $SiMe_3$). $^{29}Si\{^1H\}$NMR (C_7D_8, 183 K, δ): 4.9(s).

$(Et_3P)_3CuSeSiMe_3$, **2a**, was prepared as for **1a** using CuOAc (1.27 g, 10.4 mmol) dissolved in 5 mL hexanes/7 mL diethyl ether and 4 equiv of PEt_3 and reacted with $Se(SiMe_3)_2$ (2.33 mL, 10.8 mmol) at −45 °C. The solid off-white product was recrystallized from cold diethyl ether to give clear, colorless blocks suitable for analysis by X-ray crystallography. **2a** melted at 6 °C to give a yellow/orange oil. Yield: 4.96 g (84%). Anal. Calcd: C, 48.2; H, 10.4. Found: C, 48.36; H, 10.7. ^1H NMR (C_7D_8, 183 K, δ): 1.36(br, CH_2), 0.94(br, CH_3 & $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −13.5(s, br).$^{77}Se\{^1H\}$ NMR (C_7D_8, 183 K, δ): −570.4 (q, $^2J_{SeP} = 43.3$). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 16.9(s, CH_2), 8.6(s, $SiMe_3$), 8.1(s, CH_3). $^{29}Si\{^1H\}$ NMR (C_7D_8, 183 K, δ): 0.7(s).

$(Pr_3P)_3CuSeSiMe_3$, **2b**, was prepared by the same method as **1a** using CuOAc (0.94 g, 7.7 mmol) dissolved in 7 mL hexanes/3 mL diethyl ether and 4 equiv of tri-*n*-propylphosphine and reacted with $Se(SiMe_3)_2$ (1.7 mL, 7.8 mmol) at −45 °C. This compound crystallized from the minimal amount of cold diethyl ether to give clear, colorless blocks. At room temperature **2b** was a stable, viscous orange oil. X-ray analysis, chemical analysis, and NMR spectroscopy were performed on the light yellow product. Yield: 5.33 g (97%). Mp: 11 °C Anal. Calcd: C, 51.74; H, 10.42. Found: C, 51.90; H, 10.36. ^1H NMR (C_7D_8, 183 K, δ): 1.33(br, CH_2), 1.2(br, CH_3), 0.92(s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −22.5(s, br). $^{77}Se\{^1H\}$ NMR (C_7D_8, 183 K, δ): −565.8 (q, $^2J_{SeP} = 41.4$). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 27.6(s, CH_2), 17.6(s, CH_2), 16.7(s, CH_3), 8.6(s, $SiMe_3$). $^{29}Si\{^1H\}$NMR (C_7D_8, 183 K, δ): 0.7(q, $^3J_{SiP} = 6$ Hz).

$(Et_3P)_3CuTeSiMe_3$, **3a**, was prepared as for **1a** using CuOAc (1.38 g, 11.3 mmol) dissolved in 10 mL hexanes/15 mL diethyl ether and 4 equiv of PEt_3 and reacted with $Te(SiMe_3)_2$ (2.5 mL, 11 mmol) at −45 °C. The solid white product was recrystallized from cold diethyl ether to give clear, colorless blocks suitable for analysis by X-ray crystallography. **3a** decomposed upon melting at 3.5 °C, and as such chemical analysis could not be performed. Yield: 6.89 g (99%). ^1H NMR (C_7D_8, 183 K, δ): 1.36(br, CH_2), 1.09(s, $SiMe_3$), 0.72(br, CH_3). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −14.0(s, br). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 17.2(s, CH_2), 9.0(s, $SiMe_3$), 8.3(s, CH_3). $^{125}Te\{^1H\}$ NMR (C_7D_8, 183 K, δ): −1300.6(q, $^2J_{TeP} = 96$ Hz). $^{29}Si\{^1H\}$ NMR (C_7D_8, 183 K, δ): −23.9(s).

$(Pr_3P)_3CuTeSiMe_3$, **3b**, was prepared by the same method as **1a** using CuOAc (0.49 g, 4 mmol) dissolved in 10 mL hexanes/5 mL diethyl ether and 4 equiv of PPr^n_3 and reacted with $Te(SiMe_3)_2$ (0.9 mL, 4 mmol) at −45 °C. The white solid product was characterized by X-ray crystallography and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Chemical analysis was not possible due to its low melting point and instability at room temperature. Yield: 2.31(77.6%). Mp: 8 °C (decomp). ^1H NMR (C_7D_8, 183 K, δ): 1.32(br, CH_2), 1.04(br, CH_3), 1.01(s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K, δ): −23.0(s, br). $^{13}C\{^1H\}$ NMR (C_7D_8, 183 K, δ): 27.9(s, CH_2), 17.7(s, CH_2), 16.6(s, CH_3), 9.0(s, $SiMe_3$). $^{125}Te\{^1H\}$ NMR (C_7D_8, 183 K, δ): −1293.7(q, $^2J_{TeP} = 96$ Hz). $^{29}Si\{^1H\}$ NMR (C_7D_8, 183 K, δ): −24.3(q, $^3J_{SiP} = 5$ Hz).

X-ray Analyses. Crystals were mounted immersed in cold mineral oil and placed in a cold stream of N_2 during data collection. A single crystal suitable for X-ray analysis was mounted on a glass fiber. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALE-PACK (Nonius, 1998), and

(39) Kaesz, H. D.; Stone, F. G. A. *J. Org. Chem.* **1959**, *24*, 635−637.
(40) Cumper, C. W. N.; Foxton, A. A.; Read, J.; Vogel, A. I. *J. Chem. Soc.* **1964**, 430−434.
(41) Drake, J. E.; Glavincevski, B. M.; Hemmings, R. T.; Henderson, H. E. *Inorg. Synth.* **1980**, *20*, 171−176.
(42) Schmidt, V. H.; Ruf, H. *Z. Anorg. Allg. Chem.* **1963**, *321*, 270−273.
(43) So, J.; Boudjouk, P. *Synthesis* **1989**, 306−307.
(44) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2463−2468.

no other absorption corrections were applied. The SHELXTL (G. M. Sheldrick, Madison, WI) program package was used to solve (direct methods) and refine the structure. All non-hydrogen atoms, with the exception of disordered carbon centers (see Supporting Information), were refined with anisotropic thermal parameters. Hydrogen atoms were included as riding on their respective carbon atoms. A summary of the X-ray determinations is given in Table 1.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Western Ontario's ADF program for supporting this research. D.T.T. thanks the Government of Ontario for an OGSST scholarship. We also acknowledge the Canada Foundation for Innovation and the Ontario Research and Development Challenge Fund for equipment funding.

Supporting Information Available: Complete X-ray crystallographic data, including atomic coordinates, hydrogen coordinates, anisotropic displacement parameters, bond lengths, and bond angles for **1a** (Tables S1-S5, Figure S1), **2a** (Tables S6-S10, Figures S2 & S3), **3a** (Table S11-S15, Figure S4), **1b** (Tables S16-S20, Figures S5 & S6), **2b** (Tables S21−S25, Figures S7 & S8), and **3b** (Tables S26-S30, Figures S9 & S10). This material is available free of charge via the Internet at http://pubs.acs.org.

OM000624D