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Synthesis and Characterization of Group 13 and 15 Selenolates and Tellurolates and the X-ray Crystal Structures of $Ga[TeSi(SiMe_3)_3]_3$, $In[SeC(SiMe_3)_3]_3$, $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$, and $P[SeSi(SiMe_3)_3]_3$

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A broad range of chalcogenolate complexes of group 13 and 15 elements have been isolated and studied. Metathesis of $AlEt_2Cl$ with $(THF)LiSeSi(SiMe_3)_3$ gave $(THF)AlEt_2[SeSi(SiMe_3)_3]$ in good yield. Chalcogenolysis of $Al[N(SiMe_3)_2]_3$ with 3 equiv of $HESi(SiMe_3)_3$ (E = Se, Te) afforded $Al[ESi(SiMe_3)_3]_3$ (E = Se, Te). Treatment of $GaCl_3$ with 3 equiv of $(THF)_2LiTeSi(SiMe_3)_3$ produced the homoleptic species $Ga[TeSi(SiMe_3)_3]_3$; likewise, addition of 3 equiv of $(DME)LiSeC(SiMe_3)_3$ to $InCl_3$ yielded $In[SeC(SiMe_3)_3]_3$. Reaction of $InCl_3$ with 3 equiv of $(THF)_2LiSeSi(SiMe_3)_3$ produced $(THF)In[SeSi(SiMe_3)_3]_3$ in low yield. Homoleptic chalcogenolates, $In[ESi(SiMe_3)_3]_3$ (E = Se, Te) were prepared by chalcogenolysis of $InCp_3$ (Cp = η^5-C_5H_5). Addition of THF, pyridine, or TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) to $In[SeSi(SiMe_3)_3]_3$ gave 1:1 adducts, $(L)In[SeSi(SiMe_3)_3]_3$ (L = THF, pyridine, TMEDA). Addition of DMPE (1,2-bis(dimethylphosphino)ethane) to $In[SeSi(SiMe_3)_3]_3$ produced a 1:1 complex $In[SeSi(SiMe_3)_3]_3(DMPE)$ that was characterized in solution by NMR spectroscopy; attempts to isolate the complex yielded instead the crystalline 2:1 adduct $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$, whose X-ray structure was determined. Indium(I) complexes $InESi(SiMe_3)_3$ (E = Se, Te) were isolated from either the metathesis of InCl with $(THF)_2LiESi(SiMe_3)_3$ or chalcogenolysis with InCp. Likewise, chalcogenolysis with TlCp produced $TlESi(SiMe_3)_3$ (E = Se, Te). Reaction of PCl_3 with $(THF)_2LiSeSi(SiMe_3)_3$ produced $P[SeSi(SiMe_3)_3]_3$ in good yield. The arsenic derivative $As[SeSi(SiMe_3)_3]_3$ was isolated from the reaction of $As(NMe_2)_3$ and 3 equiv of selenol. Similarly, the antimony and bismuth complexes $M[ESi(SiMe_3)_3]_3$ (M = Sb, E = Se, Te; M = Bi, E = Se, Te) were prepared in good yields by chalcogenolysis with $Sb(NMe_2)_3$ or $Bi[N(SiMe_3)_2]_3$. Crystallographic data are as follows. $Ga[TeSi(SiMe_3)_3]_3$: monoclinic, $P2_1/c$, $Z = 4$, $a = 24.235(4)$ Å, $b = 13.808(3)$ Å, $c = 18.689(4)$ Å, $\beta = 106.424(16)°$, $R = 0.0926$, $R_w = 0.0731$. $In[SeC(SiMe_3)_3]_3$: triclinic, $P\bar{1}$, $Z = 2$, $a = 13.772(4)$ Å, $b = 13.778(4)$ Å, $c = 16.026(4)$ Å, $\alpha = 74.75(2)°$, $\beta = 75.27(2)°$, $\gamma = 62.12(2)°$, $R = 0.0424$, $R_w = 0.0476$. $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$: triclinic, $P\bar{1}$, $Z = 2$, $a = 13.655(3)$ Å, $b = 13.8323(20)$ Å, $c = 18.442(3)$ Å, $\alpha = 97.874(13)°$, $\beta = 104.066(16)°$, $\gamma = 113.708(15)°$, $R = 0.0323$, $R_w = 0.0332$. $P[SeSi(SiMe_3)_3]_3$: monoclinic, $P2_1/c$, $Z = 6$, $a = 22.706(4)$ Å, $b = 13.959(5)$ Å, $c = 17.619(3)$ Å, $\beta = 93.851(14)°$, $R = 0.0554$, $R_w = 0.0463$.

Introduction

We are exploring the chemistry of selenolate and tellurolate derivatives involving a wide range of metal and metalloid elements. These efforts have been greatly assisted by the incorporation of sterically demanding tris(trimethylsilyl)silyl-substituted ligands, which are useful for the preparation of transition metal,[1−6] lanthanide,[7,8] and main group selenolates and tellurolates.[9−13] This paper describes an extension of this work to derivatives of the heavier group 13 and 15 elements, in particular Al, Ga, In, Tl, P, As, Sb, and Bi.

Part of the resurgence of interest in main group chalcogenolates is due to their potential use as single-source precursors to binary[14,15] and ternary[16] metal chalcogenides. There are few selenium and tellurium analogs of the well-known aluminum alkoxides and phosphites,[17,18] and complexes with the heavier group 13 and 15 metals are even more uncommon.[19−24] Although the aluminum and phosphorus benzeneselenolates, Al-

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$(\mathrm{SePh})_3$[25] and $\mathrm{P(SePh)_3}$,[26,27] have been known for some time, the field appears to have been dormant until quite recently when related species began to appear. For example, the aluminum tellurolate $[\mathrm{Al}\text{-}t\text{-}\mathrm{Bu}_2(\mu\text{-}\mathrm{Te}\text{-}t\text{-}\mathrm{Bu})]_2$, prepared from the reaction of $\mathrm{Al}\text{-}t\text{-}\mathrm{Bu}_3$ with Te, was isolated and structurally characterized by Cowley and co-workers.[17] Metathetical reactions were used by Beachley, Gysling, and co-workers to prepare $[\mathrm{M}(\mu\text{-}\mathrm{TePh})(\mathrm{CH_2CMe_3})_2]_2$ (M = Ga,[28] In[29]) whereas Ruhlandt-Senge and Power synthesized the sterically hindered areneselenolates $\mathrm{M[Se(2,4,6\text{-}}t\text{-}\mathrm{Bu_3C_6H_2)]_3}$ (M = Ga,[30] In[31]) by selenolysis. Tellurium and selenium were found to insert into Ga−C bonds in $\mathrm{Ga}(t\text{-}\mathrm{Bu})_3$ to form $[(t\text{-}\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{E}\text{-}t\text{-}\mathrm{Bu})]_2$ (E = Se, Te).[32] Becker and co-workers have used a bulky silanetellurolate ligand to prepare the mono(tellurolate) species $[(\mathrm{Me_3Si})_2\mathrm{CH}]_2\mathrm{Ga[TeSi(SiMe_3)_3]}$[13b] and Oliver *et al.* reported the tellurolate dimers $[\mathrm{Mes_2In}(\mu\text{-}\mathrm{TeR})]_2$ (Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$; R = *n*-Pr, Ph).[33] A complex with bridging selenolates, $\{(\mathrm{PPh_3})_2\mathrm{Cu[In}(\mu\text{-}\mathrm{SeEt})_2(\mathrm{SeEt})_2]\}$, was recently described by Kanatzidis *et al.*[16]

Experimental Section

All operations were carried out under a dry nitrogen atmosphere using standard Schlenk-line techniques with dry, $\mathrm{O_2}$-free solvents.[34] Hexamethyldisiloxane (HMDSO) was distilled from sodium under nitrogen before use. Metal amides,[35] InCp, $\mathrm{InCp_3}$,[36] $\mathrm{(THF)_2LiSeSi(SiMe_3)_3}$,[11] $\mathrm{(DME)LiSeC(SiMe_3)_3}$,[11] $\mathrm{(THF)_2LiTeSi(SiMe_3)_3}$,[10] $\mathrm{HTeSi(SiMe_3)_3}$,[37] and $\mathrm{HSeSi(SiMe_3)_3}$[11] were prepared by literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300 and 75.469 MHz in benzene-d_6 at ambient temperature unless stated otherwise. ^{31}P{^{1}H} NMR spectra were recorded at 121.497 MHz, with chemical shifts relative to external 85% $\mathrm{H_3PO_4}$ at 0 ppm. ^{77}Se{^{1}H} samples were recorded at 57.239 MHz and were indirectly referenced to $\mathrm{SeMe_2}$ at 0 ppm by direct reference to KSeCN at −322 ppm. The ^{125}Te{^{1}H} spectra were recorded at 94.580 MHz, referenced indirectly to neat $\mathrm{Me_2Te}$ at 0 ppm by direct reference to external $\mathrm{Te(OH)_6}$ (1.74 M in $\mathrm{D_2O}$, 20 °C) at 712 ppm. IR spectra were recorded as Nujol mulls between either CsI or KBr plates. UV−vis samples were approximately 10^{-5} M solutions in hexanes. Elemental analyses were performed by the microanalytical laboratory in the College of Chemistry, University of California, Berkeley.

AlEt$_2$[SeSi(SiMe$_3$)$_3$](THF). Neat $\mathrm{Et_2AlCl}$ (250 μL, 2.0 mmol) was added to a stirring hexanes (25 mL) solution of $\mathrm{(THF)LiSeSi(SiMe_3)_3}$ (0.81 g, 2.0 mmol) at 0 °C. A white precipitate immediately formed. The mixture was stirred for 30 min, at which time the precipitate was allowed to settle. Filtration, followed by concentration and cooling to −40 °C, afforded the product as colorless crystals (0.68 g, 70%). Mp: 52−55 °C. ^{1}H NMR: δ 3.5 (m, 4H), 1.35 (t, 6H, 8.1 Hz), 0.96 (m, 4H), 0.46 (s, 27H), 0.37 (q, 4H, 8.1 Hz). ^{13}C{^{1}H} NMR: δ 71.2, 24.9, 10.0, 9.2, 1.1. IR: 1308 w, 1242 s, 1188 w, 1040 w, 1006 m, 982 w, 950 w, 920 w, 837 vs, 744 w, 688 m, 623 m, 541 w cm^{-1}. UV−vis: 218, 232, 290 nm. Anal. Calcd for $\mathrm{C_{17}H_{45}AlOSeSi_4}$: C, 42.20; H, 9.37. Found: C, 41.99; H, 9.25.

Al[SeSi(SiMe$_3$)$_3$]$_3$. $\mathrm{Al[N(SiMe_3)_2]_3}$ (0.20 g, 0.39 mmol) and $\mathrm{HSeSi(SiMe_3)_3}$ (0.52 g, 1.6 mmol) were combined in a Schlenk flask. The flask was cooled to 0 °C in an ice bath, and hexanes (50 mL) was added. The resultant mixture was allowed to warm to room temperature and stirred for an additional 3 h. The volatile materials were removed under reduced pressure, and the colorless solid was extracted with HMDSO. Concentration of the solution and cooling to −40 °C for 18 h afforded 0.20 g (40%) of colorless crystals. Mp: 242−245 °C. IR: 2361 w, 1244 m, 1155 w, 837 s, 722 m, 688 w, 668 w, 623 w cm^{-1}. UV−vis: 218, 246, 284 nm. ^{1}H NMR ($\mathrm{C_7D_8}$): δ 0.35. ^{13}C{^{1}H} NMR: δ 1.5. Anal. Calcd for $\mathrm{C_{27}H_{81}AlSe_3Si_{12}}$: C, 32.21; H, 8.11. Found: C, 32.41; H, 8.44.

Al[TeSi(SiMe$_3$)$_3$]$_3$. $\mathrm{Al[N(SiMe_3)_2]_3}$ (0.90 g, 1.77 mmol) and $\mathrm{HTeSi(SiMe_3)_3}$ (2.00 g, 5.32 mmol) were reacted as above, yielding 0.90 g (44%) of pale yellow crystals. Mp: 289−291 °C (dec). IR: 1307 w, 1241 s, 835 vs, 741 w, 687 m, 622 m cm^{-1}. UV−vis: 218, 300 nm. ^{1}H NMR ($\mathrm{C_7D_8}$): δ 0.48. ^{13}C{^{1}H} NMR($\mathrm{C_7D_8}$): δ 1.9. Anal. Calcd for $\mathrm{C_{27}H_{81}AlSi_{12}Te_3}$: C, 28.13; H, 7.08. Found: C, 28.05; H, 7.28.

Reactions of Al[SeSi(SiMe$_3$)$_3$]$_3$ and Al[TeSi(SiMe$_3$)$_3$]$_3$ with Cp$_2$TiCl$_2$. To a benzene-d_6 solution of $\mathrm{Cp_2TiCl_2}$ (5 mg, 20 μmol) was added a solution of an equivalent amount of the aluminum complex in the same solvent. An immediate color change took place upon addition to give blue-green and black solutions for the selenolate and tellurolate, respectively. $\mathrm{Cp_2Ti[SeSi(SiMe_3)_3]_2}$: ^{1}H NMR δ 6.02 (s, 10H), 0.44 (s, 54H); ^{13}C{^{1}H} NMR δ 114, 2.3. $\mathrm{Cp_2Ti[TeSi(SiMe_3)_3]_2}$: ^{1}H NMR δ 6.07 (s, 10H), 0.47 (s, 54H); ^{13}C{^{1}H} NMR δ 110, 2.8.

Ga[TeSi(SiMe$_3$)$_3$]$_3$. Pentane (40 mL) was added to a mixture of $\mathrm{GaCl_3}$ (0.11 g, 0.63 mmol) and $\mathrm{(THF)_2LiTeSi(SiMe_3)_3}$ (1.00 g, 1.90 mmol), and the cloudy solution was stirred overnight. The volatile components were removed under vacuum, and the orange solid remaining was extracted into HMDSO (40 mL). The filtered extract was concentrated and cooled to −20 °C for 8 h. Filtration afforded 0.74 g of orange crystals (67%). Analytically pure material was obtained by recrystallization from the same solvent. Mp: 195−198 °C. ^{1}H NMR: δ 0.45 (s). IR: 1257 m, 1243 s, 837 s, 737 w, 687 m, 623 m cm^{-1}. EI MS (*m/z*): 1196 ($\mathrm{M^+}$), 1181, 949, 821. Anal. Calcd for $\mathrm{C_{27}H_{81}InTe_3Si_{12}}$: C, 27.1; H, 6.83. Found: C, 27.3; H, 6.82.

In[SeC(SiMe$_3$)$_3$]$_3$. $\mathrm{InCl_3}$ (0.18 g, 0.82 mmol) and $\mathrm{(DME)LiSeC(SiMe_3)_3}$ (1.00 g, 2.5 mmol) were combined in a Schlenk flask. Hexanes (50 mL) was added, and the resultant mixture was stirred overnight. The volatile materials were removed under reduced pressure, and the residue was extracted with hexanes. The solution was concentrated and cooled to −40 °C. The yellow powder obtained was recrystallized from HMDSO, yielding 0.26 g (31%) of orange crystals. Mp: 195 °C. ^{1}H NMR: δ 0.41 (s). IR: 1256, 841, 770 cm^{-1}. Anal. Calcd for $\mathrm{C_{30}H_{81}InSe_3Si_9}$: C, 34.43; H, 7.80. Found: C, 34.31; H, 7.67.

In[SeSi(SiMe$_3$)$_3$]$_3$. Hexanes (50 mL) was added to a mixture of $\mathrm{InCp_3}$ (0.48 g, 1.6 mmol) and $\mathrm{HSeSi(SiMe_3)_3}$ (1.53 g, 4.7 mmol). The homogeneous golden solution was stirred for 2 h. The volatile components were removed under reduced pressure, and the residue was dissolved in hexanes. Concentration of the solution followed by crystallization at −40 °C afforded 1.02 g (60%) of yellow crystals. Mp: 173−176 °C. IR: 1244 m, 838 s, 722 w, 688 w, 622 w cm^{-1}. UV−vis: 218, 234, 296 nm. ^{1}H NMR: δ 0.40. ^{13}C{^{1}H} NMR: δ 1.1. Anal. Calcd for $\mathrm{C_{27}H_{81}InSe_3Si_{12}}$: C, 29.63; H, 7.46. Found: C, 30.08; H, 7.72.

In[SeSi(SiMe$_3$)$_3$]$_3$(THF). $\mathrm{InCl_3}$ (0.10 g, 0.45 mmol) and $\mathrm{(THF)LiSeSi(SiMe_3)_3}$ (0.55 g, 1.35 mmol) were combined in a Schlenk flask to which 60 mL of hexanes was added. The reaction mixture became golden with a white precipitate. The solution was stirred for 12 h. Filtration of the mixture, evaporation under reduced pressure, and extraction of the yellow solid with HMDSO gave a golden solution. Concentration of the solution and crystallization at −40 °C afforded

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0.20 g (23%) of product. ^{1}H NMR (C_7D_8): δ 3.8 (m, 4H), 1.4 (m, 4H), 0.44 (s, 81H).

In[SeSi(SiMe$_3$)$_3$]$_3$(L). To a hexanes solution of In[SeSi(SiMe$_3$)$_3$]$_3$ (0.20 g, 0.18 mmol) was added an excess (ca. 2.1 equiv) of base. The volatile materials were removed under reduced pressure, and the resulting solid was extracted with hexanes. Concentration and cooling at −40 °C afforded the product. The adducts may be recrystallized from toluene or HMDSO as colorless or pale yellow crystals.

In[SeSi(SiMe$_3$)$_3$]$_3$(py). Yield: 0.19 g (86%). Mp: 147−165 °C (dec). IR: 1604 w, 1307 w, 1255 m, 1241 s, 1216 m, 1154 w, 1068 w, 1036 w, 1011 w, 836 s, 742 m, 685 s, 620 s, 459 w cm^{-1}. UV−vis: 216, 244, 296 nm. ^{1}H NMR (C_7D_8, −60 °C): δ 9.15 (m, br, 2H), 6.64 (m, br, 1H), 6.55 (m, br, 2H), 0.44 (s, 81H). Anal. Calcd for $C_{32}H_{86}InNSe_3Si_{12}$: C, 32.75; H, 7.38; N, 1.19. Found: C, 32.19; H, 6.98; N, 1.22.

In[SeSi(SiMe$_3$)$_3$]$_3$(TMEDA). Yield: 0.20 g (72%). Mp: 210−214 °C (dec). IR: 1242 m, 1032 w, 890 w, 860 sh, 836 s, 722 w, 688 w, 622 w cm^{-1}. UV−vis: 216, 246, 298 nm. ^{1}H NMR (C_7D_8): δ 2.44 (s, 4H), 2.15 (s, 12H), 0.44 (s, 81H). Anal. Calcd for $C_{33}H_{97}InN_2Si_{12}Te_3$: C, 32.73; H, 8.07; N, 2.31. Found: C, 31.95; H, 7.77; N, 2.25.

In[SeSi(SiMe$_3$)$_3$]$_3$(DMPE). ^{1}H NMR (C_7D_8, −60 °C): δ 1.84 (m, br, 4H), 1.13 (d, 6H, $|J| = 7.9$ Hz), 0.92 (d, 6H, $|J| = 2.8$ Hz), 0.47 (s, 81H). ^{31}P{^{1}H} NMR (C_7D_8, −60 °C): δ −41.9 (d, 1P, $|^3J_{PP}| = 21$ Hz, $|^2J_{PSe}| = 53$ Hz), 44.9 (d, 1P, $|^3J_{PP}| = 21$ Hz).

{In[SeSi(SiMe$_3$)$_3$]$_3$}(μ-DMPE). To a stirred hexanes solution of In[SeSi(SiMe$_3$)$_3$]$_3$ (0.25 g, 0.23 mmol) was added DMPE (45 μL, 0.27 mmol). The reaction mixture was stirred for 30 min, the volatile materials were removed, and the yellow powder was extracted with warm hexanes. The solution was concentrated and cooled to −40 °C. Isolation and recrystallization from toluene afforded 0.24 g (90%) of small, pale yellow needles. Mp: 150−163 °C (dec). IR: 1241 m, 907 w, 836 s, 722 w, 688 w, 622 w cm^{-1}. UV−vis: 216, 242, 298 nm. ^{1}H NMR (C_7D_8, −50 °C): δ 2.3 (br, 4H), 1.6 (br, 12H), 0.44 (s, 162H). ^{31}P{^{1}H} NMR (C_7D_8): δ −45.7 (s). Anal. Calcd for $C_{60}H_{178}In_2P_2Se_6Si_{24}$: C, 30.80; H, 7.67. Found C, 30.62; H, 7.85.

In[TeSi(SiMe$_3$)$_3$]$_3$. InCp$_3$ (0.31 g, 1.0 mmol) and HTeSi(SiMe$_3$)$_3$ (1.20 g, 3.1 mmol) were combined in a Schlenk flask. Hexane (25 mL) was added, yielding an orange solution, which was stirred for 30 min. Removal of the volatile components, dissolving the residue with hexanes, concentration of the solution, and cooling to −40 °C yielded 1.02 g (60%) of orange crystals. Mp: 162−164 °C. IR: 1256 sh, 1243 m, 858 sh, 836 s, 722 w, 688 w, 622 w, 469 w cm^{-1}. UV−vis: 216, 246, 418 nm. ^{1}H NMR: δ 0.42. ^{13}C{^{1}H} NMR: δ 2.0. Anal. Calcd for $C_{27}H_{81}InSi_{12}Te_3$: C, 26.14; H, 6.59. Found: C, 26.41; H, 6.58.

InSeSi(SiMe$_3$)$_3$. Method A. Hexane (20 mL) was added to a mixture of InCl (0.10 g, 0.67 mmol) and (THF)LiSeSi(SiMe$_3$)$_3$ (0.27 g, 0.67 mmol). After 2 h of stirring, the solvent was stripped off under reduced pressure and the residue extracted with hexanes (40 mL), affording an orange solution. The solution was concentrated and cooled to −40 °C to afford 0.15 g (51%) of orange-brown product.

Method B. Freshly sublimed InCp (0.68 g, 3.8 mmol) and HSeSi(SiMe$_3$)$_3$ (1.24 g, 3.8 mmol) were combined in a Schlenk flask. Hexane (60 mL) was added, and the reaction mixture was stirred for 30 min. The volatile material was removed under reduced pressure, and the remaining solid was extracted with hexanes (40 mL). The golden solution was reduced and placed at −40 °C to induce crystallization. The light-sensitive product was isolated in 84% yield (1.40 g). Mp: >300 °C (dec). IR: 1307 w, 1255 sh, 1242 m, 859 sh, 835 s, 743 w, 688 w, 622 w cm $^{-1}$. UV−vis: 218, 248, 282, 368 nm. ^{1}H NMR: δ 0.41. ^{13}C{^{1}H} NMR: δ 1.8. Anal. Calcd for $C_9H_{27}InSeSi_4$: C, 24.49; H, 6.16. Found: C, 24.90; H, 6.18.

InTeSi(SiMe$_3$)$_3$. Method A. InCl (0.086 g, 0.57 mmol) and (THF)$_2$LiTeSi(SiMe$_3$)$_3$ (0.30 g, 0.57 mmol) were combined, and hexane (50 mL) was added. After 2 h, the volatile materials were removed under reduced pressure and the residue was extracted with HMDSO. The solution was concentrated and placed at −40 °C. Orange-red crystals 0.18 g (65 %) were isolated by filtration.

Method B. Freshly sublimed InCp (0.36 g, 2.0 mmol) and HTeSi(SiMe$_3$)$_3$ (0.76 g, 2.0 mmol) were combined in a Schlenk flask. Addition of hexane (25 mL) gave an orange solution, which was stirred for 30 min. Removal of the volatile components and extraction into hexanes followed by concentration and cooling to −40 °C yielded orange-red crystals. Recrystallization from HMDSO gave 0.41 g (43%) of light-sensitive product. Mp: 140−143 °C (dec). IR: 1256 sh, 1243 m, 836 s, 742 w, 688 m, 622 m. UV−vis: 216, 248, 296. ^{1}H NMR: δ 0.43. ^{13}C{^{1}H} NMR: δ 2.0.

Tl[SeSi(SiMe$_3$)$_3$](C$_6$H$_{14}$)$_{0.25}$. Hexane (25 mL) was added to a mixture of HSeSi(SiMe$_3$)$_3$ (0.69 g, 2.1 mmol) and TlCp (0.57 g, 2.1 mmol), resulting in the formation of a yellow-orange solution. The mixture was stirred for 16 h, and the solvent was removed under reduced pressure. The dry residue was extracted with hexane (30 mL), and the solution was filtered, concentrated to 10 mL, and cooled to −40 °C for 24 h. Yellow-orange crystals (0.99 g, 88%) were isolated by filtration in two crops. The compound is air stable, but photosensitive. Mp: 280−300 °C (dec). ^{1}H NMR (400 MHz): δ 0.38 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 2.8 (s, br). IR: 1254 w, 1240 s, 834 s, 742 w, 722 w, 687 m, 622 m cm^{-1}. UV−vis: 202, 210, 216, 222 nm. Anal. Calcd for $C_{10.25}H_{30.50}SeSi_4Tl$: C, 22.83; H, 5.56 Found: C, 22.62; H, 5.52.

Tl[TeSi(SiMe$_3$)$_3$](C$_6$H$_{14}$)$_{0.125}$. The tellurolate was prepared as above using HTeSi(SiMe$_3$)$_3$ (0.70 g, 1.9 mmol) and TlCp (0.50 g, 1.9 mmol) to afford red-orange crystals of the hexane solvate (0.86 g, 80%). The compound is air stable, but is photosensitive and should be stored in the dark. Mp: 240−255°C (dec). ^{1}H NMR (400 MHz): δ 0.43 (s, br). ^{13}C{^{1}H} NMR (100 MHz): δ 2.9 (s, br). IR: 1256 w, 1239 s, 858 sh, 833 s, 741 w, 686 m, 621 m cm^{-1}. UV−vis: 216, 232, 242 nm. Anal. Calcd for $C_{9.75}H_{28.75}Si_4TeTl$: C, 19.84; H, 4.91 Found: C, 19.71; H, 4.71.

P[SeSi(SiMe$_3$)$_3$]$_3$. A solution of PCl$_3$ (0.12 mL, 1.38 mmol) in Et$_2$O (20 mL) was combined with a solution of (THF)$_2$LiSeSi(SiMe$_3$)$_3$ (2.00 g, 4.19 mmol) in the same solvent (40 mL) to give a yellow solution along with a fine white precipitate. After 2 h of stirring, the volatile material was removed under reduced pressure, yielding a sticky yellow solid. Extraction with HMDSO (40 mL), followed by filtration through a plug of Celite on fritted glass, yielded a yellow solution, which was concentrated and cooled to −40 °C for 24 h. Yellow crystals (0.67 g, 63%) were isolated by filtration. Mp: 228−229 °C. ^{1}H NMR (400 MHz): δ 0.42 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 1.91 (s). ^{31}P{^{1}H} NMR: δ 133.6 (s, $|J_{PSe}| = 237$ Hz). ^{77}Se{^{1}H} NMR: δ 51.2 (d, $|J_{SeP}| = 237$ Hz, $\Delta\nu_{1/2} = 4$ Hz). IR: 1258 w, 1243 m, 837 s, 734 w, 687 w, 622 m cm^{-1}. UV−vis: 220, 250, 268 nm. Anal. Calcd for $C_{27}H_{81}PSe_3Si_{12}$: C, 32.08; H, 8.08 Found: C, 32.48; H, 8.23. EI-MS (70 eV): 1010 (M$^+$), 937, 786, 685.

As[SeSi(SiMe$_3$)$_3$]$_3$. A solution of HSeSi(SiMe$_3$)$_3$ (0.80 g, 2.44 mmol) in hexane (10 mL) was added to a solution of As(NMe$_2$)$_3$ (0.17 g, 0.82 mmol) in the same solvent (10 mL) at −78 °C, and the mixture was stirred for 30 min, resulting in the formation of an white precipitate. The mixture was stirred for 45 min at 0 °C and then for 30 min room temperature, whereupon all solid precipitate redissolved, yielding a yellow solution. The volatile material was removed under reduced pressure, the dry yellow residue was extracted with HMDSO (30 mL), and the solution was filtered, concentrated to 5 mL, and cooled to −40 °C for 24 h. Yellow crystals (0.55 g, 64%) were isolated by filtration. Mp: 222−223 °C. ^{1}H NMR (400 MHz): δ 0.41 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 1.81 (s). ^{77}Se{^{1}H} NMR: δ 9.1 (s, $\Delta\nu_{1/2} = 3$ Hz). IR: 1257 w, 1242 m, 837 s, 742 w, 687 m, 622 m cm^{-1}. UV−vis: 223, 232, 274 nm. Anal. Calcd for $C_{27}H_{81}AsSe_3Si_{12}$: C, 30.75; H, 7.74. Found: C, 30.31; H, 7.61.

Sb[SeSi(SiMe$_3$)$_3$]$_3$. A solution of HSeSi(SiMe$_3$)$_3$ (1.26 g, 3.9 mmol) in hexane (20 mL) was added to a solution of Sb(NMe$_2$)$_3$ (0.33 g, 1.3 mmol) in the same solvent (10 mL) at −78 °C, resulting in the formation of a yellow orange solution. The mixture was stirred for 10 min at this temperature, then warmed to room temperature, and stirred an additional 2 h. The volatile material was removed under reduced pressure, the dry orange residue was extracted with HMDSO (30 mL), and the solution was filtered, concentrated to 8 mL, and cooled to −40 °C for several days. Orange crystals (1.25 g, 87%) were isolated by filtration in two crops. Mp: 237–239 °C . ^{1}H NMR (400 MHz): δ 0.38 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 1.66. ^{77}Se{^{1}H} NMR: δ −207 (s, $\Delta\nu_{1/2}$ = 4 Hz). IR: 1243 s, 837 s, 742 w, 687 m, 621 m cm^{-1}. UV–vis: 220, 228, 234, 286 nm. Anal. Calcd for $C_{27}H_{81}SbSe_3Si_{12}$: C, 29.44; H, 7.41. Found: C, 29.74; H, 7.28.

Sb[TeSi(SiMe$_3$)$_3$]$_3$. A solution of HTeSi(SiMe$_3$)$_3$ (2.00 g, 5.3 mmol) in hexane (15 mL) at −78 °C was added to a solution of Sb(NMe$_2$)$_3$ (0.45 g, 1.8 mmol) at −78 °C in the same solvent (10 mL), resulting in the formation of an orange solution. The reaction solution was stirred at this temperature for 15 min, the cold bath was removed, and the solution was stirred at room temperature for an additional 60 min. Workup as above, followed by crystallization from HMDSO (5 mL) at −40 °C for 24 h, yielded orange crystalline product (1.66 g, 75%). Mp: 214–216 °C (dec). ^{1}H NMR (400 MHz): δ 0.40 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 2.14 (s). ^{125}Te{^{1}H} NMR: δ −584 (s, $\Delta\nu_{1/2}$ = 10 Hz). IR: 1257 w, 1244 m, 835 s, 744 w, 689 m, 622 m cm^{-1}. UV–vis: 250, 295, 350, 460 nm. Anal. Calcd for $C_{27}H_{81}SbSi_{12}Te_3$: C, 26.00; H, 6.54. Found: C, 25.97; H, 6.48.

Bi[SeSi(SiMe$_3$)$_3$]$_3$. A solution of HSeSi(SiMe$_3$)$_3$ (0.57 g, 1.7 mmol) in hexane (10 mL) was added to a solution of Bi[N(SiMe$_3$)$_2$]$_3$ (0.40 g, 0.58 mmol). The reaction mixture was stirred in the absence of light at room temperature for 12 h, and the solvent was removed under reduced pressure. The orange residue was extracted with HMDSO (20 mL), the extract filtered, and the filtrate concentrated to 5 mL and cooled to −40 °C for several days. Orange crystals (0.44 g, 66%) were isolated by filtration. Mp: 217–219 °C (dec). ^{1}H NMR (400 MHz): δ 0.39 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 1.68 (s). ^{77}Se{^{1}H} NMR: δ −222 (s, $\Delta\nu_{1/2}$ = 10 Hz). IR: 1244 m, 837 s, 744 w, 689 m, 623 m cm^{-1}. UV–vis: 246, 276, 302, 432 nm. Anal. Calcd for $C_{27}H_{81}BiSe_3Si_{12}$: C, 27.28; H, 6.87. Found: C, 27.46; H, 6.84.

Bi[TeSi(SiMe$_3$)$_3$]$_3$. A solution of HTeSi(SiMe$_3$)$_3$ (0.67 g, 1.8 mmol) in hexane (15 mL) was added to a solution of Bi[N(SiMe$_3$)$_2$]$_3$ (0.41 g, 0.59 mmol) at −78 °C in the same solvent (15 mL), resulting in the formation of a dark purple solution. The mixture was stirred at this temperature for 30 min and then warmed to 0 °C and stirred an additional 30 min. The solvent was removed under reduced pressure at the same temperature, yielding a red-purple residue. The dry powder was extracted with HMDSO (25 mL, 0 °C), and the solution was filtered, concentrated to 4 mL, and cooled to −40 °C for 24 h. Red-purple crystals (0.52 g, 68%) were isolated by filtration in two crops. The compound is extremely light and thermally sensitive and must be stored at low temperature in the absence of light. Mp: 195–197 °C (dec). ^{1}H NMR (400 MHz): δ 0.39 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 2.12 (s). ^{125}Te{^{1}H} NMR: δ −627 (s, $\Delta\nu_{1/2}$ = 200 Hz). IR: 1244 m, 837 s, 689 w, 623 w cm^{-1}. UV–vis: 248, 286, 504 nm. Anal. Calcd for $C_{27}H_{81}BiSi_{12}Te_3$: C, 24.30; H, 6.12. Found: C, 24.16; H, 6.04.

X-ray Crystallographic Studies. The X-ray studies were carried out at the CHEXRAY Facility of the University of California, Berkeley, using an Enraf-Nonius CAD-4 diffractometer. The structures of Ga[TeSi(SiMe$_3$)$_3$]$_3$ and In[SeC(SiMe$_3$)$_3$]$_3$ were solved by direct methods (SHELXS) while those of {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE) and P[SeSi(SiMe$_3$)$_3$]$_3$ were solved via Patterson methods. The structures were all refined via standard least-squares and Fourier techniques.

Ga[TeSi(SiMe$_3$)$_3$]$_3$. Crystals were obtained from slow crystallization from hexanes at −40 °C. Fragments cleaved from some of these crystals were mounted in thin-walled glass capillaries in an inert-atmosphere glovebox, and the capillaries were flame-sealed. Attempts to cool the crystal resulted in fracturing, so the data set was collected at room temperature. Automatic peak search and indexing procedures yielded a monoclinic reduced cell of higher symmetry. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 7616 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the systematic absences indicated uniquely space group $P2_1/c$. Systematic removal of the data left 7264 unique data in the final data set. A slight disorder ($^1/_6$ occupancy) was resolved in the position of Te3. The disorder was only seen at this position. The bond angles and lengths from Te3′ are otherwise unaffected.

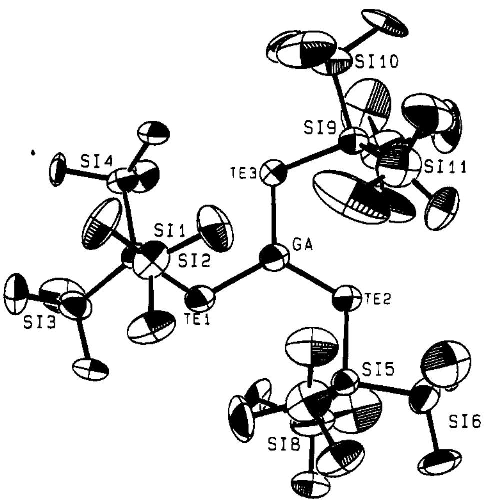

Figure 1. ORTEP diagram of Ga[TeSi(SiMe$_3$)$_3$]$_3$ with thermal ellipsoids drawn at 50% probability. Hydrogen atoms have been removed for clarity. A slight disorder at Te3 is not shown (see Experimental Section for details).

Table 1. Metrical Parameters of Ga[TeSi(SiMe$_3$)$_3$]$_3$

	Selected Bond Lengths, Å		
Ga−Te1	2.493(4)	Te2−Si5	2.526(8)
Ga−Te2	2.488(4)	Te3−Si9	2.543(9)
Ga−Te3	2.507(4)	Te3′−Si9	2.545(16)
Ga−Te3′	2.656(13)	Si−Si(av)	2.34 (1)
Te1−Si1	2.538(8)		
	Selected Bond Angles, deg		
Te1−Ga−Te2	120.79(14)	Te2−Si5−Si6	98.9(4)
Te1−Ga−Te3	118.28(15)	Te2−Si5−Si7	115.9(4)
Te1−Ga−Te3′	121.6(3)	Te2−Si5−Si8	107.2(4)
Te2−Ga−Te3	119.25(15)	Si6−Si5−Si7	109.4(5)
Te2−Ga−Te3′	113.9(3)	Si6−Si5−Si8	112.2(6)
Ga−Te1−Si1	111.41(20)	Si7−Si5−Si8	112.5(5)
Ga−Te2−Si5	113.00(21)	Te3−Si9−Si10	96.3(4)
Ga−Te3−Si9	110.13(21)	Te3−Si9−Si11	116.5(5)
Ga−Te3′−Si9	105.5(5)	Te3−Si9−Si12	105.1(5)
Te1−Si1−Si2	107.9(4)	Te3′−Si9−Si10	95.8(5)
Te1−Si1−Si3	97.2(4)	Te3′−Si9−Si11	85.7(6)
Te1−Si1−Si4	115.2(4)	Te3′−Si9−Si12	134.9(6)
Si2−Si1−Si3	110.9(5)	Si10−Si9−Si11	110.6(5)
Si2−Si1−Si4	113.9(4)	Si10−Si9−Si12	110.1(5)
Si3−Si1−Si4	110.5(4)	Si11−Si9−Si12	116.3(6)

In[SeC(SiMe$_3$)$_3$]$_3$. Pale yellow bladelike crystals were obtained by slow crystallization from HMDSO at −40 °C. A fragment of one of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. It was cooled to −103 °C by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the same position. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The 6648 unique raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards revealed a reduction of 5.8% of the original intensity. The data were corrected for this decay. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.2 times the B_{eqv} values of the atoms to which they were attached. These were included in the structure factor calculations but not refined.

{In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE). Small clear prismatic crystals were obtained by slow crystallization from toluene at −40 °C. A fragment cut from one of these crystals was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal was cooled to −155 °C, and the crystal quality was evaluated via measurement of intensities and inspection of peak scans. Automatic search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values

Table 2. Metrical Parameters of In[SeC(SiMe$_3$)$_3$]$_3$ and {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE)

	Selected Bond Lengths, Å		
	In[SeC(SiMe$_3$)$_3$]$_3$		
In−Se1	2.544(1)	In−C8	3.465(9)
In−Se2	2.512(1)	In−C17	3.671(9)
In−Se3	2.526(1)	In−C28	3.344(10)
Se1−C1	2.013(7)	In−H8B	2.744(1)
Se2−C11	2.018(7)	In−H17B	2.970(1)
Se3−C21	2.028(7)	In−H28B	2.454(1)
C−Si(av)	1.912(8)		
	{In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE)		
In−Se1	2.560(1)	Se3−Si9	2.315(2)
In−Se2	2.531(1)	P1−C28	1.837(6)
In−Se3	2.544(1)	P1−C29	1.809(6)
In−P1	2.683(2)	P1−C30	1.815(6)
Se1−Si1	2.325(2)	C28−C28′	1.522(11)
Se2−Si5	2.304(2)	Si−Si (avg)	2.349(2)
	Selected Bond Angles, deg		
	In[SeC(SiMe$_3$)$_3$]$_3$		
Se1−In−Se2	103.86(3)	Se2−C11−Si4	108.3(4)
Se1−In−Se3	127.37(4)	Se2−C11−Si5	108.8(4)
Se2−In−Se3	128.60(3)	Se2−C11−Si6	99.6(3)
In−Se1−C1	115.56(21)	Si4−C11−Si5	114.7(4)
In−Se2−C11	121.26(21)	Si4−C11−Si6	112.2(4)
In−Se3−C21	114.96(20)	Si5−C11−Si6	112.1(4)
Se1−C1−Si1	98.9(3)	Se3−C21−Si7	103.3(3)
Se1−C1−Si2	112.2(4)	Se3−C21−Si8	100.6(3)
Se1−C1−Si3	107.9(4)	Se3−C21−Si9	113.9(4)
Si1−C1−Si2	111.0(4)	Si7−C21−Si8	113.4(4)
Si1−C1−Si3	112.9(4)	Si7−C21−Si9	112.7(4)
Si2−C1−Si3	113.1(4)	Si8−C21−Si9	112.0(4)
	{In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE)		
Se1−In−Se2	107.53(2)	Se3−Si9−Si12	104.20(8)
Se1−In−Se3	120.37(2)	Si2−Si1−Si3	110.05(8)
Se1−In−P1	100.14(4)	Si2−Si1−Si4	108.76(9)
Se2−In−Se3	125.69(3)	Si3−Si1−Si4	109.19(9)
Se2−In−P1	104.16(4)	Si6−Si5−Si7	110.79(9)
Se3−In−P1	91.76(4)	Si6−Si5−Si8	109.96(9)
In−Se1−Si1	114.90(5)	Si7−Si5−Si8	110.75(9)
In−Se2−Si5	119.55(5)	Si10−Si9−Si11	111.94(9)
In−Se3−Si9	119.50(5)	Si10−Si9−Si12	108.59(8)
Se1−Si1−Si2	96.40(7)	Si11−Si10−Si12	108.98(8)
Se1−Si1−Si3	114.11(8)	In−P1−C28	111.03(18)
Se1−Si1−Si4	117.42(8)	In−P1−C29	117.31(20)
Se2−Si5−Si6	100.21(7)	In−P1−C30	115.82(20)
Se2−Si5−Si7	107.60(8)	C28−P1−C29	103.5(3)
Se2−Si5−Si8	117.06(8)	C28−P1−C30	103.8(3)
Se3−Si9−Si10	117.55(8)	C29−P1−C30	103.8(3)
Se3−Si9−Si11	105.09(7)	P1−C28−C28′	118.5(5)

revealed no conventional cell of higher symmetry. The data were corrected for a 5.4% loss in intensity as determined by inspection of the intensity standards. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.25 times the B_{eqv} values of the atoms to which they were attached. These were included in the structure factor calculation but not refined. In the final cycles of least-squares, six data with abnormally large weighted differences were given zero weight.

P[SeSi(SiMe$_3$)$_3$]$_3$. Clear yellow platelike crystals were obtained by slow cooling of an HMDSO solution. Fragments cleaved from some of these crystals were mounted on glass fibers using Paratone N hydrocarbon oil. Preliminary rotation photographs on the diffractometer were used to determine crystal quality. The crystal used was transferred to the diffractometer, centered in the beam, and cooled to −105 °C. Automatic peak search and indexing yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. Data collection was terminated by serious loss of orientation of the crystal shortly after collection of the l = 13 layer. Examination of the crystal showed that it had developed a large crack, presumably at the time of loss of orientation. The 6911 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standard revealed a nonlinear reduction of 17% of the original intensity. The data were corrected for the decay. An empirical correction was applied to the data based on the combined differences in the F_o and F_c values following the refinement of all atoms with isotropic thermal parameters (Corr$_{max}$ = 1.15, Corr$_{min}$ = 0.88).[38] Removal of the systematically absent and redundant data left 6430 unique data in the final data set. Inspection of the region near the disordered selenolate revealed independent locations for all silicons and carbons except for C23/C19′. These two atoms were refined as an isotropic carbon atom, "C23", while the silicons and all other carbon atoms in this ligand were refined as half-occupancy atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.25 times the B_{eqv} values of the atoms to which they were attached. These were included in the structure factor calculations but not refined.

Results and Discussion

In general, the new compounds described here were prepared by following well-established general synthetic routes to complexes of the heavier chalcogenolates. This involved, for example, either metathesis (eq 1) or chalcogenolysis of cyclopentadienyl (Cp) (eq 2) or amide complexes (eq 3).

$$\mathrm{MCl}_x + x(\mathrm{THF})_2\mathrm{LiEY(SiMe_3)_3} \rightarrow \mathrm{M[EY(SiMe_3)_3]}_x + x\mathrm{LiCl} \quad (1)$$

$$\mathrm{MCp}_x + x\mathrm{HEY(SiMe_3)_3} \rightarrow \mathrm{M[EY(SiMe_3)_3]}_x + x\mathrm{HCp} \quad (2)$$

$$\mathrm{M[N(SiMe_3)_2]_3} + 3\mathrm{HEY(SiMe_3)_3} \rightarrow \mathrm{M[EY(SiMe_3)_3]_3} \quad (3)$$

$\mathrm{M = Al}, x = 3; \mathrm{E = Se, Te; Y = Si}$

$\mathrm{M = Ga}, x = 3; \mathrm{E = Te; Y = Si}$

$\mathrm{M = In}, x = 1, 3; \mathrm{E = Se, Te; Y = C, Si}$

$\mathrm{M = Tl}, x = 1; \mathrm{E = Se, Te; Y = Si}$

$\mathrm{M = P}, x = 3; \mathrm{E = Se; Y = Si}$

$\mathrm{M = As}, x = 3; \mathrm{E = Se; Y = Si}$

$\mathrm{M = Sb}, x = 3; \mathrm{E = Se, Te; Y = Si}$

$\mathrm{M = Bi}, x = 3; \mathrm{E = Se, Te; Y = Si}$

Group 13. Reaction of Al[N(SiMe$_3$)$_2$]$_3$ with the corresponding chalcogenol resulted in isolation of Al[ESi(SiMe$_3$)$_3$]$_3$ (E = Se (colorless), Te (pale yellow)) in moderate yields. The complexes are extremely soluble in hydrocarbon solvents and are air-sensitive in both solution and the solid state. Metathesis reactions of AlCl$_3$ with the lithium selenolate afforded mixtures of THF adducts, (THF)Al[SeSi(SiMe$_3$)$_3$]$_3$ and (THF)AlCl[SeSi(SiMe$_3$)$_3$]$_2$, which proved impossible to obtain in pure form. A mono(selenolate), (THF)AlEt$_2$[SeSi(SiMe$_3$)$_3$], was isolated as thin colorless plates from reaction of AlEt$_2$Cl and the lithium selenolate, but all attempts at metathetical reactions with lithium tellurolates failed. In common with Al(SePh)$_3$,[25] the homoleptic derivatives are useful chalcogenolate transfer reagents. Thus, reactions of Al[ESi(SiMe$_3$)$_3$]$_3$ with Cp$_2$TiCl$_2$ afforded the known titanocene bis(chalcogenolates), Cp$_2$Ti[ESi(SiMe$_3$)$_3$]$_2$ (E = Se,[39] Te[2]). In related work, Vyazankin et al. found that chalcogenolysis of AlR$_3$ (R = Me, Et) or AlEt$_2$Cl with Et$_3$SiEH gave

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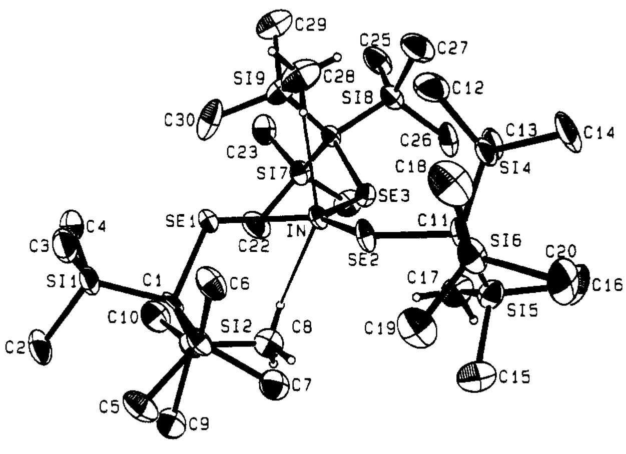

Figure 2. ORTEP diagram of In[SeC(SiMe$_3$)$_3$]$_3$ with thermal ellipsoids drawn at 50% probability. The close In−H nonbonded distances are shown; remaining hydrogen atoms have been removed for clarity.

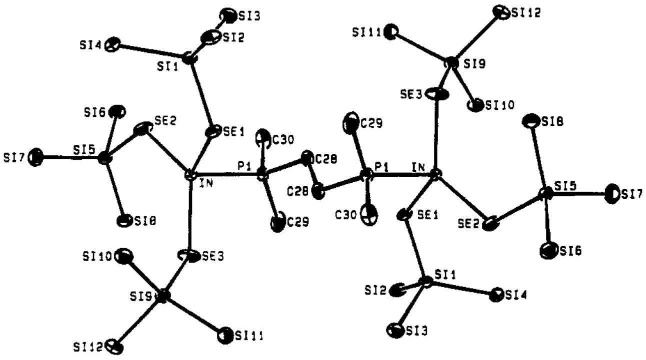

Figure 3. ORTEP diagram of {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE) with thermal ellipsoids drawn at 50% probability. Selected carbon and hydrogen atoms have been removed for clarity.

Table 3. Torsion Angles (deg) in {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE)

Se2−In−Se1−Si1	−5.80(0.05)
Se3−In−Se1−Si1	−159.21(0.05)
Se1−In−Se2−Si5	−163.72(0.05)
Se3−In−Se2−Si5	−12.12(0.06)
Se1−In−Se3−Si9	39.56(0.06)
Se2−In−Se3−Si9	−108.73(0.05)
P1−In−Se1−Si1	102.69(0.05)
P1−In−Se2−Si5	90.60(0.06)
P1−In−Se3−Si9	142.40(0.06)
Se1−In−P1−C28	14.68(0.19)
Se2−In−P1−C28	125.82(0.19)
Se3−In−P1−C28	−106.61(0.19)
In−P1−C28−C28′	65.25(0.41)
P1−C28−C28′−P1′	−180.00(0.48)

complex mixtures from which only chalcogenide species, such as (EtAlS)$_n$, were isolated.[40]

The metathesis reaction between GaCl$_3$ and 3 equiv of the lithium tellurolate gave yellow crystals of the homoleptic gallium tellurolate Ga[TeSi(SiMe$_3$)$_3$]$_3$. The results of an X-ray diffraction study are shown as an ORTEP view in Figure 1. There is a slight disorder in the position of Te3 which was modeled by a $^1/_6$ occupancy at Te3′. The average non-disordered gallium−tellurium bond length of the 2.491(4) Å in the compound is shorter than the same parameter in [(Me$_3$Si)$_2$CH]$_2$Ga[TeSi(SiMe$_3$)$_3$] of 2.535(1) Å.[13b] The average Ga−Te distance to the disordered tellurium is 2.531(6) Å but should be given less weight as this position is less well defined. As expected, the Ga−Te bond length in the tris(tellurolate) is much shorter than that found in the bridging tellurolate complex [(Me$_3$CCH$_2$)$_2$Ga(μ-TePh)]$_2$ (2.755 Å).[28]

Table 4. Metrical Parameters for P[SeSi(SiMe$_3$)$_3$]$_3$

	Selected Bond Lengths, Å		
P−Se1	2.272(4)	Se2−Si5	2.331(4)
P−Se2	2.269(4)	Se3−Si9	2.324(11)
P−Se3	2.426(8)	Se3′−Si9	2.334(12)
P−Se3′	2.142(8)	Si−Si(av)	2.35(1)
Se1−Si1	2.330(4)		
	Selected Bond Angles, deg		
Se1−P−Se2	96.78(15)	Se2−Si5−Si8	111.1(2)
Se1−P−Se3	101.5(2)	Si6−Si5−Si7	113.4(2)
Se1−P−Se3′	94.2(2)	Si6−Si5−Si8	109.9(2)
Se2−P−Se3	104.1(2)	Si7−Si5−Si8	112.4(2)
Se2−P−Se3′	89.3(2)	Se3−Si9−Si10	114.9(5)
P−Se1−Si1	107.38(15)	Se3−Si9−Si11	112.1(5)
P−Se2−Si5	107.34(14)	Se3−Si9−Si12	98.8(4)
P−Se3−Si9	110.5(3)	Si10−Si9−Si11	110.9(5)
P−Se3′−Si9	105.3(3)	Si10−Si9−Si12	110.0(5)
Se1−Si1−Si2	115.5(2)	Si11−Si9−Si12	109.5(5)
Se1−Si1−Si3	111.7(2)	Se3′−Si9′−Si10′	117.8(4)
Se1−Si1−Si4	95.8(2)	Se3′−Si9′−Si11′	102.8(5)
Si2−Si1−Si3	108.8(2)	Se3′−Si9′−Si12′	100.6(5)
Si2−Si1−Si4	112.8(2)	Si10′−Si9′−Si11′	111.1(5)
Si3−Si1−Si4	111.8(2)	Si10′−Si9′−Si12′	111.3(5)
Se2−Si5−Si6	95.4(2)	Si11′−Si9′−Si12′	112.6(5)
Se2−Si5−Si7	113.5(2)		

Indium(III) derivatives were prepared from InCl$_3$ and 3 equiv of the alkaneselenolate, which gave the homoleptic derivative In[SeC(SiMe$_3$)$_3$]$_3$. In contrast, an attempt to prepare the corresponding *silane*selenolate instead led to the THF adduct In[SeSi(SiMe$_3$)$_3$]$_3$(THF) under similar reaction conditions. An ORTEP view of In[SeC(SiMe$_3$)$_3$]$_3$ showing the numbering scheme is depicted in Figure 2. The compound crystallizes as a monomer with no close intermolecular contacts. The In−Se bond lengths (2.512−2.544 Å) are comparable to those seen in In[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$ (average 2.505(3) Å)[31] and are significantly shorter than the corresponding parameters in the bridging selenolates [In(μ-SePh)$_3$]$_n$ (average 2.77 Å)[41] and [(Me$_3$CCH$_2$)$_2$In(μ-SePh)]$_2$ (average 2.75 Å).[29] The average Se−In−Se bond angle in In[SeC(SiMe$_3$)$_3$]$_3$ is again comparable to that found in In[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$; however, one angle (Se1−In−Se2) shows a marked deviation (103.86°) from the expected trigonal geometry seen in the other angles. The indium atom is positioned 0.06 Å out of the plane formed by the three seleniums, comparable to the value noted for In[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$, where the displacement was 0.054 Å. One of the central carbon atoms lies in the plane of the selenium atoms while the other two are located one above and one below the plane, thus helping to alleviate steric repulsions. Interestingly, several methyl groups bend back over the indium: C8 and C28 are positioned within 3.5 Å while C17 is located 3.67 Å from the indium. These atoms are in good positions for their hydrogens (H8B, H17B, and H28B) to interact with the metal (In−H distances of 2.74, 2.97, and 2.45 Å).

As expected, the homoleptic tris(selenolates) are Lewis acidic, forming stable 1:1 adducts In[SeSi(SiMe$_3$)$_3$]$_3$L with various bases such as THF, pyridine, and TMEDA. The latter is fluxional on the NMR time scale as only three singlets (one each for the selenolate, the methyls, and the methylenes) are observed by ^{1}H NMR spectroscopy from −60 to +60 °C. In contrast, In(SePh)$_3$ is reported to form 1:2 adducts such as In(SePh)$_3$(PPh$_3$)$_2$.[42] In solution, DMPE also appears to form a 1:1 complex with In[SeSi(SiMe$_3$)$_3$]$_3$, although attempts to isolate this material instead resulted in the exclusive isolation of the

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Table 5. Crystallographic Parameters

	$Ga[TeSi(SiMe_3)_3]_3$	$In[SeC(SiMe_3)_3]_3$	$\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$	$P[SeSi(SiMe_3)_3]_3$
formula	$GaTe_3Si_{12}C_{27}H_{81}$	$InSe_3Si_9C_{30}H_{81}$	$InSe_3Si_{12}PC_{30}H_{89}$	$PSe_3Si_{12}C_{27}H_{81}$
mol wt	1195.5	1046.5	1169.7	1010.8
cryst size, mm	0.20 × 0.20 ×0.30	0.13 × 0.15 × 0.40	0.27 × 0.13 × 0.39	0.25 × 0.35 × 0.07
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	24.235(4)	13.722(4)	13.655(3)	22.706(1)
b, Å	13.808(3)	13.778(4)	13.8323(20)	13.959(5)
c, Å	18.689(4)	16.026(4)	18.442(3)	17.619(3)
α, deg	90	74.75(2)	97.874(13)	90
β, deg	106.424(16)	75.27(2)	104.066(16)	93.851(14)
γ, deg	90	62.12(2)	113.708(15)	90
V, Å^3	5999(4)	2553(1)	2983.9(25)	5572(4)
Z	4	2	2	6
d_{calcd}, g cm^{-3}	1.32	1.36	1.30	1.95
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
scan mode	ω	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
2θ range, deg	3−45	3−45	3−45	3−45
collection range	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$	$\pm h,k,l$ (0−13 only)
abs coeff (μ), cm^{-1}	21.4	28.0	24.8	36.6
no. of reflns collcd	7616	6648	7775	6911
no. of unique reflns	7264	6648	7775	6430
reflns with $F^2 > n\sigma(F^2)$	2823 ($>2\sigma(F^2)$)	4711 ($>3\sigma(F^2)$)	5479 ($>3\sigma(F^2)$)	2923 ($>2.5\sigma(F^2)$)
final R, R_w	9.26, 7.31	4.24, 4.76	3.23, 3.32	5.54, 4.63
T, °C	293	−103	−155	−105

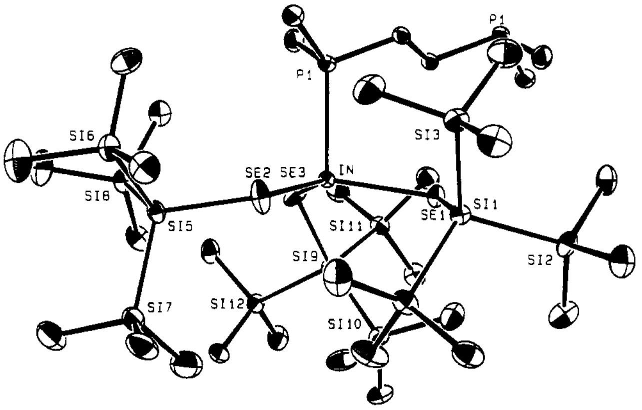

Figure 4. View of $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$ showing the flattened tetrahedral environment of the indium. The symmetry-related half of the dimer has been removed for clarity.

Table 6. Fractional Atomic Coordinates and B_{eqv} Values for Selected Atoms of $Ga[TeSi(SiMe_3)_3]_3$, $In[SeC(SiMe_3)_3]_3$, $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$, and $P[SeSi(SiMe_3)_3]_3$

atom	x	y	z	B, Å^2	occ
		$Ga[TeSi(SiMe_3)_3]_3$			
Te1	0.17972(7)	−0.0167(1)	−0.0043(1)	6.53(6)	1.00
Te2	0.21077(9)	0.2702(2)	−0.0782(1)	9.28(7)	1.00
Te3	0.3436(1)	0.1201(2)	0.0870(1)	8.29(8)	0.83
Te3′	0.3589(5)	0.0915(9)	0.0191(6)	6.6(3)	0.17
Ga	0.2465(1)	0.1197(2)	0.0070(2)	6.6(1)	1.00
Si1	0.2331(3)	−0.1767(6)	0.0234(4)	4.9(2)	1.00
Si5	0.1253(3)	0.2412(6)	−0.1902(4)	5.4(2)	1.00
Si9	0.4051(3)	0.2558(6)	0.0584(4)	5.5(2)	1.00
		$In[SeC(SiMe_3)_3]_3$			
In	0.40670(1)	0.07044(1)	0.24753(1)	1.96(1)	1.0
Se1	0.43221(6)	−0.11868(1)	0.23009(1)	2.76(2)	1.0
Se2	0.20406(1)	0.19393(1)	0.23776(1)	2.51(2)	1.0
Se3	0.55566(1)	0.12281(1)	0.25927(1)	2.27(2)	1.0
C1	0.3631(5)	−0.1984(5)	0.3330(4)	2.0(2)	1.0
C11	0.1379(5)	0.3583(5)	0.2413(5)	2.3(2)	1.0
C21	0.7015(5)	0.0585(5)	0.1780(4)	2.0(2)	1.0
		$\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$			
In	0.01502(1)	−0.09609(1)	0.18669(1)	1.074(8)	1.0
Se1	−0.11888(1)	−0.00781(1)	0.16967(1)	1.43(1)	1.0
Se2	−0.09112(1)	−0.28378(1)	0.20491(1)	2.35(1)	1.0
Se3	0.22842(1)	0.02253(1)	0.24088(1)	2.14(1)	1.0
P1	0.0207(1)	−0.1371(1)	0.04169(8)	1.33(3)	1.0
Si1	−0.3030(1)	−0.1213(1)	0.16238(8)	1.37(4)	1.0
Si5	0.0079(1)	−0.3744(1)	0.25431(9)	1.53(4)	1.0
Si9	0.3034(1)	0.1787(1)	0.34146(8)	1.37(4)	1.0
C28	−0.0367(4)	−0.0616(4)	−0.0155(3)	1.5(1)	1.0
C29	0.1581(4)	−0.0995(4)	0.0302(3)	2.4(1)	1.0
C30	−0.0629(5)	−0.2785(4)	−0.0155(3)	2.2(1)	1.0
		$P[SeSi(SiMe_3)_3]_3$			
P	0.2477(2)	0.1341(2)	0.3982(2)	2.81(9)	1.0
Se1	0.19291(1)	0.26344(8)	0.35927(8)	2.49(3)	1.0
Se2	0.20888(1)	0.3054(9)	0.30899(8)	2.43(3)	1.0
Se3′	0.3268(1)	0.1693(2)	0.3166(2)	2.65(7)	0.5
Se3	0.3322(1)	0.1706(2)	0.3592(2)	2.10(6)	0.5
Si1	0.1056(1)	0.2581(2)	0.4214(2)	2.17(8)	1.0
Si5	0.2502(2)	−0.1195(2)	0.3362(2)	2.45(9)	1.0
Si9	0.3825(3)	0.2731(5)	0.4449(4)	2.4(2)	0.5
Si9′	0.3882(3)	0.2774(5)	0.3852(4)	2.6(2)	0.5

2:1 derivative $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$. Thus, in solution at −60 °C, the $^{31}P\{^1H\}$ NMR spectrum of a sample prepared *in situ* from $In[SeSi(SiMe_3)_3]_3$ and excess DMPE shows two inequivalent phosphorus signals. These couple to give two doublets ($|^3J_{PP}| = 21$ Hz[43]) with one of these (the lower-field signal) displaying ^{77}Se coupling ($|^2J_{PSe}| = 53$ Hz). We assign these data to the mono-DMPE adduct $In[SeSi(SiMe_3)_3]_3DMPE$. In contrast, dissolution of the yellow crystals obtained from preparative-scale reactions showed only a singlet in the $^{31}P\{^1H\}$ NMR spectrum from room temperature to −60 °C. Analytical data suggested the formulation $\{In[SeSi(SiMe_3)_3]_3\}_2(\mu\text{-DMPE})$, which was confirmed by a single-crystal X-ray diffraction study. These data show that the phosphorus atom occupies the fourth position in the distorted tetrahedral environment about the indium center. The significant bond angles and distances are summarized in Table 2, and an ORTEP view is shown in Figure 3. The indium atoms are roughly tetrahedrally coordinated, but the tetrahedron is flattened (Figure 4). The angles around the indium are also quite irregular (92−126°), probably reflecting van der Waals repulsive forces between the interacting ligands. The indium−selenium distances, despite the different environments, are quite regular. The complex possesses an inversion center located between C28 and C28′, causing the plane P1/C28/C28′/P1′ to be precisely planar. The indium bonds are not, however, staggered with respect to the C28−C28′ bond but have a torsion angle of about 65° (Table 3). From a comparison of the average Se−In−Se angles and

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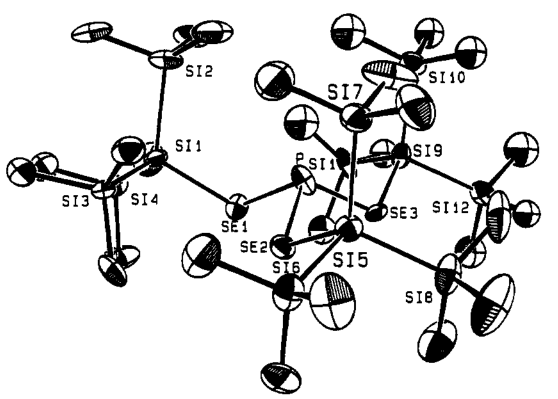

Figure 5. ORTEP diagram of P[SeSi(SiMe$_3$)$_3$]$_3$ with thermal ellipsoids drawn at 50% probability. Hydrogen atoms have been removed for clarity. Disorder in the selenolate ligands is not shown (see Experimental Section for details).

In−Se bond lengths in the two selenolates, it is evident that the change in geometry causes a slight change from 119.9° and 2.527 Å in In[SeC(SiMe$_3$)$_3$]$_3$ to 117.8° and 2.545 Å in {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE). The most dramatic change is the displacement of the indium from the plane of the selenium atoms. The indium in the DMPE adduct is located 0.37 Å above this plane whereas in the homoleptic complex it lies only 0.06 Å above the plane, a result that can be attributed to the change from tetrahedral to trigonal geometry.

The indium(III) tellurolate In[TeSi(SiMe$_3$)$_3$]$_3$ reacted with various Lewis bases, but in all cases these reactions led to considerable decomposition to Te[Si(SiMe$_3$)$_3$]$_2$ and [TeSi(SiMe$_3$)$_3$]$_2$, as evidenced by ^{1}H and ^{13}C{^{1}H} NMR spectra. Light-sensitive indium(I) derivatives were isolated from metathesis reactions of the lithium chalcogenolates with InCl. In all cases, chalcogenolysis of the indium cyclopentadienyl compounds, InCp$_3$ and InCp, gave cleaner products and higher yields of the base-free complexes. Attempts to prepare Tl(III) derivatives were unsuccessful, leading in all cases to oxidation of the ligands to dichalcogenide. Although we were unable to isolate the (presumed) Tl(I) byproducts in these reactions, these could be prepared instead by chalcogenolysis of TlCp, which yielded TlESi(SiMe$_3$)$_3$ (E = Se, Te) in reasonable yields. The Tl(I) and In(I) complexes always crystallized along with variable amounts of solvent (evident from NMR and analytical data), which could not be removed even on gentle heating under vacuum.

Group 15. The phosphorus selenolate P[SeSi(SiMe$_3$)$_3$]$_3$ was prepared in good yield by the metathesis reaction between PCl$_3$ and (THF)LiSeSi(SiMe$_3$)$_3$; in contrast, chalcogenolysis provided the best routes to the heavier derivatives. The brightly colored, moderately air-sensitive products are highly soluble in nonpolar solvents but could be crystallized from concentrated hexamethyldisiloxane (HMDSO). The antimony and bismuth tellurolates are light sensitive, especially the latter, which must be handled under subdued light to prevent decomposition. Attempts to prepare phosphorus and arsenic tellurolates were unsuccessful. In both cases, the only well-characterized product was the ditelluride [TeSi(SiMe$_3$)$_3$]$_2$, presumably resulting from reductive elimination from the putative M[TeSi(SiMe$_3$)$_3$]$_3$ species.

The phosphorus selenolate is thermally stable, giving rise to a strong molecular ion in the EI mass spectrum and allowing it to be purified by sublimation. In contrast to the case of group 13 chalcogenolates, informative ^{77}Se and ^{125}Te NMR data were obtained for all the group 15 complexes, with the resonances shifting to higher field on going from P to Bi, in accord with the decreased electronegativity of the pnictide element as the group is descended. A similar trend was reported for tellurolate derivatives of the group 4 transition metals Ti, Zr, and Hf.[2]

An ORTEP view of the crystal structure of P[SeSi(SiMe$_3$)$_3$]$_3$ (Figure 5) shows the central phosphorus atom to be remarkably hindered as a result of steric shielding by the three bulky selenolates. Two of the ligands are well-ordered and a disorder in the remaining ligand was almost entirely resolved with half-occupancies in both Se3 and Se3′ as well as the remaining ligand (see Supporting Information for a figure displaying the disorder). Within each ligand, distances and angles are quite similar to those of other −SeSi(SiMe$_3$)$_3$ derivatives. The P−Se bond lengths to the two ordered ligands (2.272, 2.269 Å) are slightly longer than values calculated on the basis of covalent radii (2.22 Å).[44] The average P−Se distance to the disordered ligand (2.284 Å) is even longer but should be given less weight due to its relative uncertainty. The Se1−P−Se2 angle (96.78(15)°) is identical, within experimental error, to those in P(SePh)$_3$ (average 96.97°).[27] Taken together, these data show that intraligand repulsions have a significant influence on the structure of the molecule.

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Supporting Information Available: Tables of crystal data, details of the structure determinations, temperature factor expressions, positional parameters, intramolecular distances and angles, torsion angles, and least-squares planes, an ORTEP figure of Ga[TeSi(SiMe$_3$)$_3$]$_3$ showing the disorder at Te3′ and the labeling scheme, an ORTEP figure of {In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-DMPE) showing the full labeling scheme, and an ORTEP figure of P[SeSi(SiMe$_3$)$_3$]$_3$ showing the disordered selenolate and labeling scheme (41 pages). Ordering information is given on any current masthead page.

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