Synthesis of Low-Coordinate Chalcogenolato Complexes of Zinc with O, N, S, and P Donor Ligands. Molecular and Crystal Structures of $Zn(S\text{-}t\text{-}Bu_3C_6H_2\text{-}2,4,6)_2(L)$ ($L = NC_5H_3Me_2\text{-}2,6$, $PMePh_2$), $Zn(Se\text{-}t\text{-}Bu_3C_6H_2\text{-}2,4,6)_2(OSC_4H_8)$, and $Zn(S\text{-}t\text{-}Bu_3C_6H_2\text{-}2,4,6)_2(N\text{-methylimidazole})_2$

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The dimeric complexes $[Zn(EAr'')_2]_2$ (**1a**, E = S; **1b**, E = Se) ($Ar'' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) reacted with N, S, or P donor ligands to give three-coordinate monomeric complexes, $Zn(EAr'')_2(L)$ (L = 2,6-lutidine, tetrahydrothiophene, PMe_3, $PMePh_2$). From the reaction of $[Zn(SeAr'')_2]_2$ (**1b**) with excess tetrahydrothiophene the *S*-oxide complex $Zn(SeAr'')_2(OSC_4H_8)$ (**12b**) was also isolated and identified by X-ray diffraction. The solid-state structures of these three-coordinate complexes are characterized by a surprisingly wide variation of the E–Zn–E angles, ranging from 129.0(2)° ($L = OSC_4H_8$) to 156.26(4)° (L = 2,6-lutidine). The Zn–E bond distances are bond angle dependent and decrease with increasing E–Zn–E angles, in agreement with changes in the hybridization of zinc from approximately sp^2 in **12b** to sp in **2a**. A semiquantitative theoretical interpretation of these observations is proposed. With excess *N*-methylimidazole (imid) tetracoordinate complexes were obtained, $Zn(EAr'')_2(imid)_2$ (**4a,b**) which readily lost one donor ligand on recrystallization from toluene to give $Zn(EAr'')_2(imid)$ (**5a,b**). The structures of these three- and four-coordinate complexes illustrate that the metal–ligand bond lengths even in zinc chalcogenolato complexes with a high degree of steric hindrance are determined by electronic rather than steric factors. Crystal data are as follows. $Zn(SAr'')_2(NC_5H_3Me_2\text{-}2,6)$ (**2a**): monoclinic space group $C2/c$; $Z = 4$; $a = 18.475(2)$, $b = 20.352(9)$, $c = 11.835(1)$ Å; $\beta = 95.03(2)°$; $V = 4432.86$ Å^3; $R = 0.0458$, $R_w = 0.0492$; 2572 reflections with $F_o > 3\sigma(F_o)$. $Zn(SAr'')_2(imid)_2$ (**4a**): monoclinic space group $P2_1/c$; $Z = 4$; $a = 17.438(5)$, $b = 15.894(5)$, $c = 17.964(5)$ Å; $\beta = 109.58(2)°$; $V = 4691.0$ Å^3; $R = 0.0665$, $R_w = 0.0933$; 2768 reflections with $F_o > 6\sigma(F_o)$. $Zn(SAr'')_2(PMePh_2)$ (**8a**): monoclinic space group $P2_1/c$; $Z = 4$; $a = 16.971(2)$, $b = 15.887(1)$, $c = 19.509(5)$ Å; $\beta = 117.87(1)°$; $V = 4649.88$ Å^3; $R = 0.055$, $R_w = 0.059$; 6788 reflections with $F_o > 2\sigma(F_o)$. $Zn(SeAr'')_2(OSC_4H_8)$ (**12b**): monoclinic space group $C2/c$; $Z = 4$; $a = 17.706(6)$, $b = 9.141(2)$, $c = 27.338(8)$ Å; $\beta = 104.64(3)°$; $V = 4281.21$ Å^3; $R = 0.068$, $R_w = 0.073$; 2047 reflections with $F_o > 2\sigma(F_o)$.

Chalcogenolato complexes of group 12 metals consist, in general, of infinite lattices with bridging ligands and tetrahedrally coordinated metal ions.[1,2] The degree of association in these compounds is however sensitive to the steric requirements of the chalcogenolato ligands, and we recently showed that with suitably bulky substituents nonpolymeric complexes $[M(EAr'')_2]_2$ ($Ar'' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$; M = Zn, Cd; E = S, Se) result whose solid-state structures confirm the existence of dimeric units with trigonal-planar three-coordinate metal centers.[3-5] These complexes dissociate appreciably in solution to two-coordinate monomers and are sufficiently volatile to be of interest as single-source precursors for the deposition of II–VI semiconductor films from the gas phase by low-pressure MOCVD techniques.[6] In contrast to complexes with smaller thiolato ligands which tend to dissolve only in strongly-coordinating solvents and react with donor ligands such as pyridine to give four-coordinate complexes $M(SR)_2L_2$, the bulky Ar″ derivatives are soluble in hydrocarbons and react with electron-pair donors to give three-coordinate monomeric adducts. Three-coordinate chalcogenolato complexes of zinc are rare, and besides the mentioned dimers $[Zn(EAr'')_2]_2$,[3,4] examples include $[Zn\{TeSi(SiMe_3)_3\}_2]_2$,[7] $Zn(SAr'')_2(Et_2O)$,[8] $Zn(SeAr'')_2(THF)$,[4] the di- and trinuclear alkyl derivatives $[ZnR(SR')]n$ ($R' = CPh_3$, $n = 2$; $R' = Ar''$, $n = 3$),[9] and the anion $[Zn(SC_6HMe_4)_3]^-$.[10] We report here the synthesis and structures of a series of three- and four-coordinate zinc chalcogenolato complexes with N, O, S, and P donor ligands.

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Experimental Section

General Procedures. All reactions were carried out under argon using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium–benzophenone [diethyl ether, THF, petroleum ether (bp 40–60 °C)] or sodium (toluene). NMR solvents were stored over 4A molecular sieves and degassed by freeze–thaw cycles. NMR spectra were recorded using a JEOL EX90Q instrument. Molecular weight determinations were carried out cryoscopically in benzene. [Zn(SAr″)$_2$]$_2$ (**1a**) and [Zn(SeAr″)$_2$]$_2$ (**1b**) were prepared as described previously.[4] Glassware was decontaminated with bleach solution. PMe$_3$, PMePh$_2$, (Me$_2$PCH$_2$)$_2$ (dmpe), pyridine, and 2,6-lutidine were stored over solid KOH and vacuum-distilled prior to use; tetrahydrothiophene (THT) was distilled and stored over 4A molecular sieves.

Zn(SAr″)$_2$(NC$_5$H$_3$Me$_2$-2,6) (2a). To a stirred suspension of **1a** (0.15 g, 0.24 mmol) in 10 mL of petroleum ether at room temperature was added 2,6-lutidine (0.026 g, 0.24 mmol). The solid dissolved to give a clear colorless solution from which a white solid precipitated during the course of 30 min. The precipitate was filtered off and recrystallized from toluene to give colorless crystals (0.15 g, 0.205 mmol, 85%); mp >300 °C. ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 18 H, *p*-*t*-Bu), 1.40 (s, 36 H, *o*-*t*-Bu), 2.20 (s, 6 H, Me of lutidine), 6.96 (d, 2 H, *m*-H of lutidine, J = 8 Hz), 7.18 (s, 4 H, Ar″), 7.50 (t, 1 H, *p*-H of lutidine, J = 8 Hz). Anal. Calcd for $C_{43}H_{67}NS_2Zn$: C, 71.03; H, 9.22; N, 1.93; S, 8.83. Found: C, 70.92; H, 9.50; N, 1.79; S, 9.03.

Zn(SeAr″)$_2$(NC$_5$H$_3$Me$_2$-2,6) (2b) was made as described for **2a**: colorless crystals (90%); mp 192–194 °C. Cryoscopic molecular weight determinations in benzene revealed partial dissociation of the lutidine ligand (found 540, calcd 821.3). ^{1}H NMR (CDCl$_3$): δ 1.43 (s, 18 H, *p*-*t*-Bu), 1.63 (s, 36 H, *o*-*t*-Bu), 2.15 (s, 6 H, Me of lutidine), 6.90 (d, 2 H, *m*-H of lutidine, J = 8 Hz), 7.19 (s, 4 H, Ar″), 7.57 (t, 1 H, *p*-H of lutidine, J = 8 Hz). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.55 (*p*-C*Me*$_3$, 32.29 (*o*-C*Me*$_3$), 34.71 (*p*-*C*Me$_3$), 38.87 (*o*-*C*Me$_3$), 121.59 (*m*-C), 146.37 (*p*-C), 153.71 (*o*-C); lutidine δ 23.43 (Me), 139.95, 157.05. Anal. Calcd for $C_{43}H_{67}NSe_2Zn$: C, 62.88; H, 8.22; N, 1.70. Found: C, 62.65; H, 8.32; N, 1.48.

Zn(SAr″)$_2$(NC$_5$H$_5$)$_2$ (3a). **1a** (0.10 g, 0.16 mmol) was dissolved in 10 mL of pyridine, and the solution was stirred for 2 h. The solvent was removed in vacuo and the white residue recrystallized from toluene with the addition of a small amount of pyridine (0.10 g, 0.13 mmol, 81%); mp 268–270 °C. ^{1}H NMR (CDCl$_3$): δ 1.31 (s, 18 H, *p*-*t*-Bu), 1.54 (s, 36 H, *o*-*t*-Bu), 7.25 (s, 4 H, Ar″), 7.16, 7.97, 8.02 (m, 10 H, py). Anal. Calcd for $C_{46}H_{68}N_2S_2Zn$: C, 71.00; H, 8.75; N, 3.60; S, 8.75. Found: C, 71.09; H, 8.59; N, 3.36; S, 8.47.

Zn(SAr″)$_2$(imid)$_2$ (4a). A suspension of **1a** (0.50 g, 0.81 mmol) was treated with *N*-methylimidazole (imid) (0.67 g, 8.2 mmol) as described for **2a**. The starting material dissolved, followed by the precipitation of the product, which was recrystallized from toluene (0.60 g, 0.76 mmol, 94%); mp 286–288 °C. Cryoscopic molecular weight determinations (benzene): found 660, calcd 784.6. ^{1}H NMR (CDCl$_3$): Ar″ δ 1.15 (s, 18 H, *p*-*t*-Bu), 1.41 (s, 36 H, *o*-*t*-Bu), 7.13 (s, 4 H, Ar″); imid δ 3.35 (s, 6 H, Me), 5.99 (s, 2 H), 6.45–6.47 (m, 4 H). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.74 (*p*- and *o*-C*Me*$_3$), 34.62 (*p*-*C*Me$_3$), 38.26 (o-*C*Me$_3$), 121.26 (*m*-C), 128.26 (*ipso*-C), 144.17 (*p*-C), 153.27 (*o*-C); imid δ 33.84 (Me), 119.59, 138.59, 138.86. Anal. Calcd for $C_{44}H_{70}N_4S_2Zn$: C, 67.37; H, 8.93; N, 7.15; S, 8.18. Found: C, 67.39; H, 9.33; N, 7.17; S, 8.74.

Zn(SeAr″)$_2$(imid)$_2$ (4b). As for **4a**, white crystals formed (93%); mp 198–200 °C. ^{1}H NMR (CDCl$_3$): Ar″ δ 1.28 (s, 18 H, *p*-*t*-Bu), 1.59 (s, 36 H, *o*-*t*-Bu), 7.28 (s, 4 H, Ar″); imid δ 3.48 (s, 6 H, Me), 6.16 (s, 2 H), 6.60–6.64 (m, 4 H). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.71 (*p*-C*Me*$_3$), 32.22 (*o*-C*Me*$_3$), 34.75 (*p*-*C*Me$_3$), 38.80 (*o*-*C*Me$_3$), 121.34 (*m*-C), 128.17 (*ipso*-C), 145.26 (*p*-C), 154.32 (*o*-C); imid δ 33.92 (Me), 119.65, 137.90, 138.65. Anal. Calcd for $C_{44}H_{70}N_4Se_2Zn$: C, 60.18; H, 7.98; N, 6.38. Found: C, 59.98; H, 7.94; N, 6.17.

Zn(SAr″)$_2$(imid) (5a). A suspension of **1a** (0.50 g, 0.81 mmol) was treated with *N*-methylimidazole (0.065 g, 0.79 mmol) as described for **2a**. The starting material dissolved, followed by the precipitation of the product, which was recrystallized from toluene (0.49 g, 0.70 mmol, 89%); mp >300 °C. ^{1}H NMR (CDCl$_3$): Ar″ δ 1.13 (s, 18 H, *p*-*t*-Bu), 1.44 (s, 36 H, *o*-*t*-Bu), 7.16 (s, 4 H, Ar″); imid δ 3.16 (s, 6 H, Me), 4.58, 5.20, 6.20 (3 H). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.64 (*p*- and *o*-C*Me*$_3$), 34.00 (*p*-*C*Me$_3$), 38.26 (*o*-*C*Me$_3$), 121.78 (*m*-C), 128.18 (*ipso*-C), 145.68 (*p*-C), 153.48 (*o*-C); imid δ 34.75 (Me), 119.68, 136.13, 138.86. Anal. Calcd for $C_{40}H_{64}N_2S_2Zn$: C, 68.39; H, 9.39; N, 3.99; S, 9.13. Found: C, 68.52; H, 9.18; N, 3.97; S, 9.29.

Zn(SeAr″)$_2$(imid) (5b). This was prepared from **1b** as described for **5a** and recrystallized from hot toluene (84%); mp 248–250 °C. Cryoscopic molecular weight determinations (benzene): found 803, calcd 796.3. ^{1}H NMR (CDCl$_3$): Ar″ δ 1.09 (s, 18 H, *p*-*t*-Bu), 1.43 (s, 36 H, *o*-*t*-Bu), 7.14 (s, 4 H, Ar″); imid δ 3.12 (s, 6 H, Me), 4.61, 5.29, 6.16 (3 H). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.62 (*p*-C*Me*$_3$), 32.04 (*o*-C*Me*$_3$), 34.08 (*p*-*C*Me$_3$), 39.07 (*o*-*C*Me$_3$), 121.92 (*m*-C), 128.23 (*ipso*-C), 146.67 (*p*-C), 154.38 (*o*-C); imid δ 34.83 (Me), 119.75, 136.31, 138.89. Anal. Calcd for $C_{40}H_{64}N_2Se_2Zn$: C, 60.34; H, 8.10; N, 3.52. Found: C, 60.34; H, 8.14; N, 3.34.

Zn(SAr″)$_2$(NC$_5$H$_4$CHO) (6a). To a stirred suspension of **1a** (0.23 g, 0.37 mmol) in 10 mL of petroleum ether was added pyridinecarboxaldehyde (0.04 g, 0.37 mmol). Stirring was continued, and the pale-pink precipitate was filtered off, washed with petroleum ether (3 × 10 mL), and dried in vacuo; yield 0.15 g (0.21 mmol, 57%); mp 164–166 °C. The microcrystalline compound is insoluble in toluene and slightly soluble in dichloromethane and chloroform. The ligand is exchanged with pyridine. ^{1}H NMR (CD$_2$Cl$_2$): Ar″ δ 1.36 (s, 18 H, *p*-*t*-Bu), 1.76 (s, 36 H, *o*-*t*-Bu), 7.36 (s, 4 H, Ar″); C$_5$H$_4$NCHO δ 7.20–7.89 (m, 5 H), 10.25 (s, 1 H, CHO). ^{13}C NMR (CDCl$_3$): Ar″ δ 31.62 (*p*-CMe$_3$), 31.76 (*o*-C*Me*$_3$), 34.65 (*p*-*C*Me$_3$), 38.24 (*o*-*C*Me$_3$), 121.69 (*m*-C), 128.21 (*ipso*-C), 147.92 (*p*-C), 150.57 (*o*-C); C$_5$H$_4$NCHO δ 122.57, 125.51, 150.23. Anal. Calcd for $C_{42}H_{63}NOS_2Zn$: C, 69.35; H, 8.73; N, 1.93; S, 8.81. Found: C, 69.08; H, 8.86; N, 1.96; S, 8.87.

Zn(SAr″)$_2$(PMe$_3$) (7a). To a suspension of **1a** (0.10 g, 0.16 mmol) in 10 mL of petroleum ether was added PMe$_3$ (0.10 g, 1.31 mmol) via syringe. The starting material dissolved within a few seconds, followed by the precipitation of the flocculant white product, which was dissolved by adding more petroleum ether and warming on a water bath. Cooling to 0 °C gave colorless needles (0.035 g, 0.05 mmol, 31.4%). The compound sublimes at 120 °C/10^{-2} Torr. ^{1}H NMR (CDCl$_3$): δ 0.54 (d, 9 H, J_{P-H} = 8.6 Hz, PMe$_3$), 1.17 (s, 18 H, *p*-*t*-Bu), 1.57 (s, 36 H, *o*-*t*-Bu), 7.20 (s, 4 H, Ar″). ^{13}C NMR (CDCl$_3$): δ 12.5 (d, J_{P-C} = 11.6 Hz, PMe$_3$), 30.8 (*p*-C*Me*$_3$), 31.1 (*o*-C*Me*$_3$), 35.0 (*p*-*C*Me$_3$), 38.7 (*o*-*C*Me$_3$), 121.8 (*m*-C), 136.1 (*ipso*-C), 145.4 (*p*-C), 152.1 (*o*-C). ^{31}P NMR (CDCl$_3$): δ –47.17. Anal. Calcd for $C_{39}H_{67}PS_2Zn$: C, 67.26; H, 9.70; S, 9.21. Found: C, 67.20; H, 9.58; S, 10.10.

Zn(SeAr″)$_2$(PMe$_3$) (7b). This was prepared from **1b** as described for **7a** as colorless needles (35.6%). The compound sublimes at 143 °C/10^{-2} Torr. ^{1}H NMR (CDCl$_3$): δ 0.54 (d, 9 H, J_{P-H} = 8.6 Hz, PMe$_3$), 1.17 (s, 18 H, *p*-*t*-Bu), 1.55 (s, 36 H, *o*-*t*-Bu), 7.20 (s, 4 H, Ar″). ^{13}C NMR (CDCl$_3$): δ 13.5 (d, J_{P-C} = 11.6 Hz, PMe$_3$), 31.5 (*p*-C*Me*$_3$), 32.4 (*o*-C*Me*$_3$), 34.7 (*p*-*C*Me$_3$), 39.0 (*o*-*C*Me$_3$), 121.7 (*m*-C), 127.9 (*ipso*-C), 145.9 (*p*-C), 153.7 (*o*-C). ^{31}P NMR (CDCl$_3$): δ –52.02. Anal. Calcd for $C_{39}H_{67}PSe_2Zn$: C, 59.28; H, 8.55. Found: C, 59.07; H, 8.35.

Zn(SAr″)$_2$(PMePh$_2$) (8a). To a suspension of **1a** (0.25 g, 0.40 mmol) in 10 mL of petroleum ether was added PMePh$_2$ (0.08 g, 0.40 mmol) via syringe. The starting material dissolved within, followed by the precipitation of the product, which was dissolved by adding more petroleum ether and warming on a water bath. After standing, **8a** crystallized at room temperature (0.20 g, 0.24 mmol, 60%); mp 216–218 °C. ^{1}H NMR (CDCl$_3$): δ 0.82 (d, 3 H, J_{P-H} = 6.7 Hz, PMe), 1.02 (s, 18 H, *p*-*t*-Bu), 1.27 (s, 36 H, *o*-*t*-Bu), 7.02 (s, 4 H, Ar″), 7.14–7.16 (m, 10 H, Ph). ^{31}P NMR (CDCl$_3$): δ –24.0. Anal. Calcd for $C_{49}H_{71}PS_2Zn$: C, 71.72; H, 8.72; S, 7.81. Found: C, 71.82; H, 8.87; S, 8.02.

Zn(SAr″)$_2$(PMePh$_2$)$_2$ (9a). To a suspension of **1a** (0.12 g, 0.19 mmol) in 10 mL of petroleum ether was added PMePh$_2$ (0.40 g, 2.0 mmol) via syringe. The resulting clear solution was left to stand at room temperature overnight to give colorless crystals (0.05 g, 0.049 mmol, 25%); mp 192–194 °C. ^{1}H NMR (CDCl$_3$): δ 1.30 (d, 6 H, J_{P-H} = 3.6 Hz, PMe), 1.29 (s, 18 H, *p*-*t*-Bu), 1.55 (s, 36 H, *o*-*t*-Bu), 7.31 (s, 4 H, Ar″), 7.36–7.45 (m, 20 H, Ph). ^{31}P NMR (CDCl$_3$): δ –25.6. Anal. Calcd for $C_{62}H_{84}P_2S_2Zn$: C, 72.98; H, 8.24; S, 6.29. Found: C, 72.57; H, 8.42; S, 6.21.

Zn(SeAr″)$_2$(PMePh$_2$)$_2$ (9b). To a suspension of **1a** (0.25 g, 0.35 mmol) in 10 mL of petroleum ether was added PMePh$_2$ (0.70 g, 3.5 mmol) to give **9b** as colorless crystals (0.17 g, 0.15 mmol, 43%); mp 104–105 °C. ^{1}H NMR (CDCl$_3$): δ 1.04 (s, 18 H, *p*-*t*-Bu), 1.08 (d, 6 H, J_{P-H} = 3.6 Hz, PMe), 1.31 (s, 36 H, *o*-*t*-Bu), 7.08 (s, 4 H, Ar″), 7.04–7.15 (m, 20 H, Ph). ^{31}P NMR (CDCl$_3$): δ –25.2. Anal. Calcd for $C_{62}H_{84}P_2Se_2Zn$: C, 66.81; H, 7.60. Found: C, 67.02; H, 7.45.

Zn(SAr″)$_2$(dmpe) (10a). The procedure for **8a** was followed to give **10a** as colorless crystals from petroleum ether (0.12 g, 0.16 mmol, 47%); mp 210–212 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, 12 H, PMe$_2$, J_{P-H} = 2.8

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Hz), 1.29 (s, 18 H, *p-t*-Bu), 1.57 (t, 4 H, CH_2P, J_{P-H} = 4.6 Hz), 1.69 (s, 36 H, *o-t*-Bu), 7.26 (s, 4 H, Ar″). ^{13}C NMR ($CDCl_3$): δ 10.39 (PMe_2), 24.60 (CH_2P), 31.56 (*p*-CMe_3), 32.26 (*o*-CMe_3), 34.58 (*p*-CMe_3), 38.35 (*o*-CMe_3), 121.37 (*m*-C), 128.21 (*ipso*-C), 144.28 (*p*-C), 152.94 (*o*-C). ^{31}P NMR ($CDCl_3$): δ −41.51. Anal. Calcd for $C_{42}H_{74}P_2S_2Zn$: C, 65.47; H, 9.68; S, 8.32. Found: C, 66.18; H, 9.64; S, 8.74.

Zn(SAr″)₂(THT) (11a). To a suspension of **1a** (0.10 g, 0.16 mmol) in 10 mL of petroleum ether was added tetrahydrothiophene (0.097 g, 1.1 mmol). The starting material dissolved within a few seconds, followed by the precipitation of the white solid. The mixture was stirred for 1 h, and the precipitate was filtered off (0.10 g, 0.14 mmol, 80%) and recrystallized from hot toluene with a few drops of THT added, to give colorless needles which sublime slowly at 150 °C/10^{-2} Torr. ^1H NMR ($CDCl_3$): δ 1.19 (s, 22 H, *p-t*-Bu overlapping with THT), 1.55 (s, 40 H, *o-t*-Bu overlapping with THT), 7.22 (s, 4 H, Ar″). Anal. Calcd for $C_{40}H_{66}S_3Zn$: C, 67.81; H, 9.39; S, 13.57. Found: C, 67.45; H, 9.68; S, 14.10.

Zn(SeAr″)₂(THT) (11b). The procedure for **11a** was followed to give **11b** from **1b** (0.099 g, 0.16 mmol) and THT (0.10 g, 1.13 mmol) as colorless crystals (0.032 g, 0.054 mmol, 34%); mp 210 °C dec. ^1H NMR ($CDCl_3$): δ 1.19 (s, 22 H, *p-t*-Bu overlapping with THT), 1.60 (s, 40 H, *o-t*-Bu overlapping with THT), 7.30 (s, 4 H, Ar″). Anal. Calcd for $C_{40}H_{66}SSe_2Zn$: C, 59.88; H, 8.29. Found: C, 60.13; H, 8.48.

X-ray Crystallography. X-ray measurements on **2a**, **8a**, and **12b** were carried out using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo Kα radiation [λ(Mo Kα) = 0.710 69 Å]. The structures were solved by the Patterson method using SHELX-S[11] and refined by least-squares techniques using SHELX-80.[12] The F_o data were adjusted using the DIFABS[13] procedure at the isotropic refinement stage. Calculations for **2a** were made on a T800 transputer hosted by a 286 AT PC and for **8a** and **12b** on a 486DX266 PC. For **2a**, H(21) was located on the 2-fold axis and refined; all other hydrogen atoms were allowed to ride on their parents (r_{CH} = 0.96 Å) in calculated positions, a common U_{iso} being refined for all. The $PMePh_2$ ligand in **8a** showed rotational disorder about the P–Ph bonds and was modeled with occupancies of 0.52 and 0.48 with idealized geometry for the four C_6H_5 images. Two of the *t*-Bu groups were also rotationally disordered. In compound **12b** the OSC_4H_8 ligand was also disordered about the Zn–O bond and was modeled as two orientations, related by the 2-fold axis such that the α-carbons of the two images [C(19) and C(19a)] coincided to give full occupancies at these sites.

Data for **4a** were collected on a SiemensR3m/V diffractometer. Calculations were done on a VAX3100 computer. All hydrogen atoms were allowed to ride on their parents in calculated positions except for those in one of the imidazole rings in which there is site disorder between N(4) and C(42) and consequently two positions for C(45) (65:35% occupancy). The structure was solved by Patterson methods using the SHELXTL PLUS software. Semiempirical absorption corrections were applied. Crystal data and details of data collection and refinement are collected in Table 1.

Results and Discussion

Reactions of Zn(EAr″)₂ (E = S, Se) with Nitrogen Ligands. Solid $[Zn(SAr'')_2]_2$ (**1a**) suspended in petroleum ether rapidly dissolves when 1 equiv of 2,6-lutidine (2,6-dimethylpyridine) is added. During the course of ca. 30 min a white precipitate is formed which, on recrystallization from toluene, gives colorless crystals of $Zn(SAr'')_2(NC_5H_3Me_2\text{-}2,6)$ (**2a**). The monomeric nature and the presence of three-coordinate zinc suggested by NMR and molecular weight determinations are confirmed by X-ray crystallography (see below). The analogous reaction with $[Zn(SeAr'')_2]_2$ (**1b**) gives $Zn(SeAr'')_2(NC_5H_3Me_2\text{-}2,6)$ (**2b**).

In spite of the presence of bulky chalcogenolato ligands, slightly smaller nitrogen ligands give stable 1:2 adducts; e.g., pyridine reacts with **1a** to give $Zn(SAr'')_2(py)_2$ (**3a**). The 1:2 complexes are nevertheless sufficiently crowded to facilitate the dissociation of one donor ligand to give isolable three-coordinate species. Thus, an excess of *N*-methylimidazole reacts with **1a** or **1b** to give the bis(imidazole) complexes $Zn(EAr'')_2(imid)_2$, **4a** (E = S) and **4b** (E = Se), respectively. Recrystallization of these compounds from toluene leads to the isolation of the corresponding 1:1 adducts $Zn(EAr'')_2(imid)$ (**5a,b**) as feathery crystalline needles. Molecular weight determinations in benzene confirm the monomeric nature of these complexes.

Table 1. Summary of Crystallographic Parameters for **2a**, **4a**, **8a**, and **12b**

	2a	**4a**	**8a**	**12b**
formula	$C_{43}H_{67}$-NS_2Zn	$C_{44}H_{70}$-N_4S_2Zn	$C_{49}H_{71}$-PS_2Zn	$C_{40}H_{66}O$-SSe_2Zn
fw	727.53	784.57	820.60	818.34
T, K	298	298	298	298
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
a, Å	18.475(2)	17.438(5)	16.971(2)	17.706(6)
b, Å	20.352(9)	15.894(5)	15.887(1)	9.141(2)
c, Å	11.835(1)	17.964(5)	19.509(5)	27.338(8)
β, deg	95.03(2)	109.58(2)	117.87(1)	104.63(3)
V, Å³	4432.86	4691(2)	4649.88	4281.21
Z	4	4	4	4
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$C2/c$
D(calcd), g cm^{-3}	1.090	1.108	1.158	1.204
μ, cm^{-1}	6.83	6.52	6.892	20.60
θ range, deg	$2.2 \leq \theta \leq 29.3$	$1.0 \leq \theta \leq 24.0$	$2.3 \leq \theta \leq 29.9$	$2.5 \leq \theta \leq 25.0$
F(000)	1576	1644	1768	1712
tot. data measd	8779	8010	21 412	5573
R_{int}	0.033	0.109	0.074	0.065
no. of obsd reflcns	2572	2768	5131	1647
significance test	$F_o > 3\sigma(F_o)$	$F_o > 6\sigma(F_o)$	$F_o > 2\sigma(F_o)$	$F_o > 2\sigma(F_o)$
no. of params	216	348	633	246
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.0458	0.0665	0.055	0.068
$R_w = (\sum w\|F\|^2/\sum wF_o^2)^{1/2}$	0.0492	0.0933	0.059	0.073

We have earlier reported the synthesis of zinc chalcogenolato complexes of aldehydes and ketones which can be regarded as models for the active zinc center in liver alcohol dehydrogenase.[14] In the enzyme, zinc is bound to two cysteine sulfurs and one histidine ligand, while the fourth coordination site is occupied by the alcohol or aldehyde substrate.[15] A complex with a similar S_2NO ligand environment is obtained when pyridine carboxaldehyde is added to **1a**; $Zn(SAr'')_2(NC_5H_4CHO)$ (**6a**) is obtained as pale-pink crystals. The pyridinecarboxaldehyde acts as a chelate; the IR spectrum shows the ν_{CO} frequency at 1666 cm^{-1}, 54 cm^{-1} lower than in the free ligand. The reactions are summarized in Scheme 1.

Phosphine Complexes. The reaction of **1a** and **1b** with an excess of trimethylphosphine gives $Zn(EAr'')_2(PMe_3)$, **7a** and **7b**, respectively. These adducts are more volatile than **1a** and **1b** and are therefore of interest as precursors for the gas-phase deposition of zinc chalcogenides; at 0.01 mmHg **7a** sublimes at 120 °C and **7b** at 143 °C.

Treatment of **1a** and **1b** with the more bulky $PMePh_2$ leads to the expected 1:1 adducts $Zn(EAr'')_2(PMePh_2)$ **8a** and **8b**. Crystals of **8a** were found suitable for X-ray diffraction (see below). Surprisingly, the addition of an ca. 10-fold excess of $PMePh_2$ to **1a** allows the isolation of the 1:2 complex $Zn(SAr'')_2(PMePh_2)_2$ (**9a**) in high yield. A bis(phosphine) complex is also obtained from **1a** and $Me_2PCH_2CH_2PMe_2$ (dmpe) to give $Zn(SAr'')_2(dmpe)$ (**10a**) as colorless blocks.

Well-defined zinc phosphine complexes are quite rare, and to the best of our knowledge only phosphine adducts of zinc halides have so far been structurally characterized, examples being

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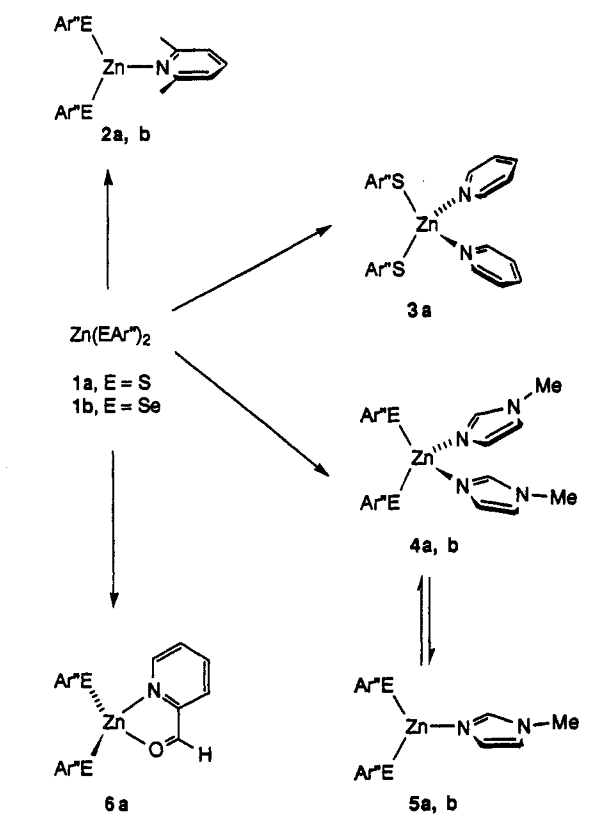
Scheme 1



$[ZnBr_3(PPh_3)]^-$,[16] the trimetallic complex $V(THF)_2[ZnCl_3(PPh_3)]_2$,[17] and, more recently, $[ZnI_2(PEt_3)]_2$.[18] In all cases the coordination geometry of the metal center is tetrahedral; **7** and **8** are apparently the first examples of trigonal-planar phosphine complexes.

Sulfur Complexes. Similar to the reactions described above, the addition of tetrahydrothiophene (THT) to a suspension of **1a** in petroleum ether gives a clear solution within seconds from which $Zn(SAr'')_2(THT)$ (**11a**) is obtained as a white flocculant precipitate. The selenium analogue **11b** is similarly obtained as colorless needles. 1:2 adducts as in the case of phosphines were not found. Both **11a** and **11b** sublime slowly at 150 and 170 °C, respectively and decompose above 210 °C. Crystals were obtained from hot toluene to which a small quantity of free THT was added, with **11b** apparently giving crystals of better quality. However, the specimen found suitable for X-ray diffraction was identified as a complex of tetrahydrothiophene *S*-oxide, $Zn(SeAr'')_2(OSC_4H_8)$ (**12b**). The oxide was identified as an impurity in THT and was shown to accumulate in the zinc complex, an illustration of the preference of zinc for O rather then the softer S donor ligands.

Structural Studies. The crystal structures of complexes **2a**, **4a**, **8a**, and **12b** were determined. Selected bond lengths and angles are collected in Table 2. In all cases the dimensions of the chalcogenolato ligands are unremarkable, and there are no close intermolecular contacts. The complexes show however a considerable variation of bond angles and ligand conformations.

$Zn(SAr'')_2(NC_5H_3Me_2)$ (2a). The molecular structure of **2a** is shown in Figure 1. The complex has C_2 symmetry and adopts an almost T-shaped geometry, with a wide S–Zn–S angle of 156.26(4)°. The dihedral angles formed by the aryl and lutidine rings with the ZnS_2 plane are 76.6(2) and 74.4(2)°, respectively. The Zn–S bonds are relatively short, 2.207(3) Å, only marginally longer than the terminal Zn–S distances in **1a** (average 2.194 Å)[5] and in $Zn(SAr'')_2(Et_2O)$ (2.196 Å).[8] The lutidine ligand is located on the C_2 axis and coordinated to Zn with a relatively long Zn–N bond of 2.144(7) Å. The structure provides an interesting comparison with that of the mercury analogue $Hg(SAr'')_2(pyridine)$,[19] which exhibits a similar "tuning fork" geometry with a coplanar conformation of the thiolato ligands but an S–M–S skeleton which deviates much less from linearity [angle S–Hg–S = 172.1(1)°], in line with a very weakly coordinated pyridine ligand [Hg–N = 2.677(7) Å].

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2a**, **4a**, **8a**, and **12b**

	$Zn(SAr'')_2(NC_5H_3Me_2\text{-}2,6)$ (**2a**)		
Zn–S	2.207(3)	Zn–N	2.144(7)
C(1)–S	1.803(6)	C(19)–N	1.331(7)
C(1)–C(2)	1.419(6)	C(2)–C(3)	1.398(6)
C(2)–C(7)	1.555(7)	C(19)–C(20)	1.403(8)
C(20)–C(21)	1.358(9)	C(19)–C(22)	1.553(10)
S–Zn–S(a)[a]	156.26(4)	N–Zn–S	101.87(4)
Zn–S–C(1)	110.4(2)	C(2)–C(1)–S	118.7(4)
C(6)–C(1)–S	121.6(4)	C(6)–C(1)–C(2)	119.7(4)
Zn–N–C(19)	119.7(4)	Zn–N–C(19a)[a]	119.8(5)
C(19)–N–C(19a)[a]	120.5(5)	C(22)–C(19)–N	118.9(5)
	$Zn(SAr'')_2(C_3H_3N_2Me)_2$ (**4a**)		
Zn–S(1)	2.317(3)	Zn–S(2)	2.313(3)
Zn–N(1)	2.041(8)	Zn–N(3)	2.054(12)
S(1)–C(1)	1.801(9)	S(2)–C(19)	1.801(10)
N(1)–C(37)	1.302(13)	N(1)–C(39)	1.381(16)
C(37)–N(2)	1.348(15)	C(38)–N(2)	1.366(15)
C(40)–N(2)	1.495(13)	C(38)–C(39)	1.335(15)
S(1)–Zn–S(2)	115.5(1)	N(1)–Zn–S(1)	108.3(2)
N(1)–Zn–S(2)	108.0(3)	N(3)–Zn–S(1)	114.5(3)
S(2)–Zn–N(3)	107.8(3)	N(1)–Zn–N(3)	101.7(4)
Zn–S(1)–C(1)	110.8(3)	Zn–S(2)–C(19)	111.9(4)
C(2)–C(1)–S(1)	121.2(8)	C(20)–C(19)–S(2)	119.4(8)
Zn–N(1)–C(37)	125.0(8)	Zn–N(1)–C(39)	129.3(7)
N(1)–C(37)–N(2)	111.1(10)	N(1)–C(39)–C(38)	109.9(10)
	$Zn(SAr'')_2(PMePh_2)$ (**8a**)		
Zn–S(1)	2.225(3)	Zn–S(2)	2.211(3)
Zn–P(1)	2.413(4)	C(6)–S(1)	1.797(5)
C(24)–S(2)	1.805(5)	P(1)–C(42)	1.704(8)
P(1)–C(48)	1.698(6)	P(1)–C(49)	1.813(7)
S(1)–Zn–S(2)	138.2(1)	P(1)–Zn–S(1)	100.4(2)
P(1)–Zn–S(2)	121.4(2)	C(6)–S(1)–Zn	115.8(2)
C(24)–S(2)–Zn	103.9(2)	C(42)–P(1)–Zn	113.8(3)
C(48)–P(1)–Zn	121.1(3)	C(49)–P(1)–Zn	119.4(3)
C(49)–P(1)–C(42)	105.6(4)	C(49)–P(1)–C(48)	101.5(3)
C(48)–P(1)–C(42)	91.1(3)		
	$Zn(SeAr'')_2(OSC_4H_8)$ (**12b**)		
Zn–Se(1)	2.313(3)	O(1)–Zn	1.925(11)
C(6)–Se(1)	1.911(12)	C(7)–C(1)	1.565(17)
S(1)–O(1)	1.508(11)	C(19)–S(1)	1.914(19)
C(19a)[b]–S(1)	1.858(19)		
Se(1)–Zn–Se(1a)[b]	129.0(2)	O(1)–Zn–Se(1)	115.5(1)
C(6)–Se(1)–Zn	100.2(4)	S(1)–O(1)–Zn	142.4(3)
C(19)–S(1)–O(1)	97.6(8)	C(19)–S(1)–C(19a)[b]	82.9(9)

[a] Key to symmetry operations relating the designated atoms to the reference atom at (*x*, *y*, *z*): −*x*, *y*, 0.5 − *z*. [b] Key to symmetry operations relating designated atoms to the reference atoms at (*x*, *y*, *z*): 1.0 − *x*, *y*, 1.5 − *z*.

$Zn(SAr'')_2(imid)_2$ (4a). The structure of **4a** (Figure 2) is that of a distorted tetrahedron, with a wide S–Zn–S angle of 115.5(1)° and a narrow N–Zn–N angle of only 101.7(4)°. The values presumably reflect the different steric requirements of the two sets of ligands. The Zn–S bonds (average value 2.315 Å) are

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Table 3. Geometric Parameters of Zinc Thiolato Complexes with Nitrogen Bases

compound	r_{Zn-N}, Å	r_{Zn-S}, Å	N-Zn-N, deg	S-Zn-S, deg	ref
2a	2.144(7)	2.207(3)		156.26(4)	*a*
4a	2.041(8), 2.054(12)	2.313(3), 2.317(3)	101.7(4)	115.5(1)	*a*
$Zn(SC_6HMe_4)_2(imid)_2$	2.037(6), 2.057(6)	2.301(2), 2.298(2)	101.9(2)	109.46(8)	20b
$Zn(SC_6H_4Me)_2(phen)$	2.104(5), 2.120(5)	2.265(2), 2.256(2)	78.7(2)	126.16(7)	20a
$Zn(SC_6H_2\text{-}i\text{-}Pr_3)_2(bipy)$	2.088(6), 2.109(6)	2.251(2), 2.259(2)	77.9(2)	119.32(8)	20b
$Zn(SPh)_2(Me_2phen)^b$	2.086(4)	2.255(2)	80.2(2)	134.5(1)	20d

[a] This work. [b] Data for orthorhombic low-temperature modification.

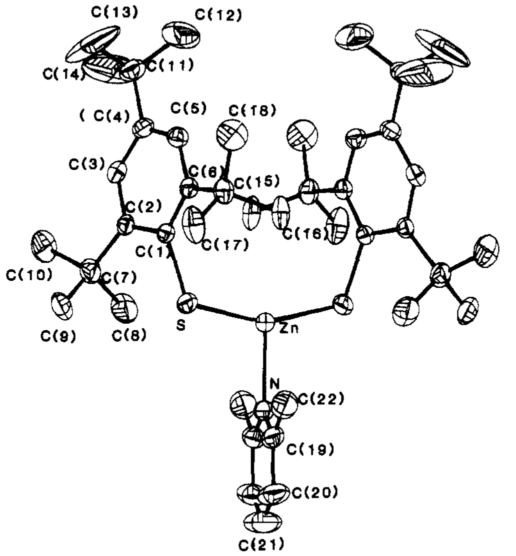

Figure 1. Molecular structure of **2a**, showing the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability.

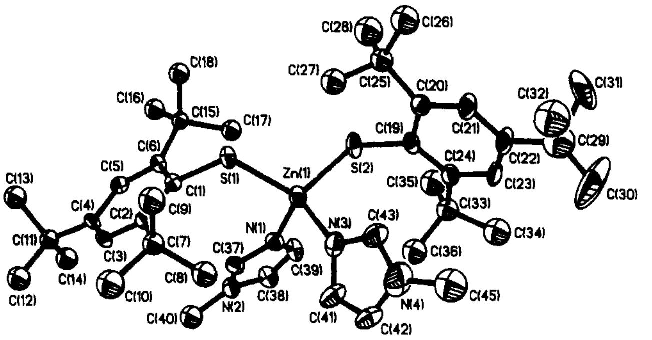

Figure 2. Molecular structure of **4a**. Thermal ellipsoids are drawn at 30% probability.

significantly longer than those in the three-coordinate analogue **2a**, while the Zn-N bonds are shorter (average 2.048 Å), ruling out steric crowding as the reason for the bond length distribution. A number of four-coordinate zinc thiolato complexes with mono- or bidentate nitrogen ligands are known[20] and in general show very similar bond angles and distances, with chelating ligands such as 2,2′-bipyridyl or 1,10-phenanthroline possessing a narrower N-Zn-N angle and longer Zn-N bond lengths. The geometric parameters of representative examples are compared in Table 3.

$Zn(SAr'')_2(PMePh_2)$ (8a). Complex **8a** is, to our knowledge, the first structurally characterized halide-free phosphine complex of zinc (Figure 3). The $PMePh_2$ ligand is disordered with respect to rotation about the P-Zn vector and was modeled for two positions; only one of these positions is shown in the figure. The Zn-S distances (average 2.218 Å) and the S-Zn-S bond angle (138.2(1)°) lie between those found for **2a** and **4a**. The conformation of the thiolato ligands differs significantly from the geometries observed before: one Ar″ substituent is turned away from the phosphine ligand, so as to minimize steric interactions between Ar″ and the phosphorus phenyl groups, while the other is twisted toward it. Apparently, narrowing the S-Zn-S angle from 156.26° in **2a** to 138.2° in **8a** would force the two Ar″ groups so close together that a coplanar conformation of the two thiolato ligands as in **2a** is no longer possible. The Zn-P bond length of 2.414(4) Å is comparable to the Zn-P distance in the anion $[ZnBr_3(PPh_3)]^-$ [2.425(9) Å][16] but slightly longer than that in the trialkylphosphine complex $[ZnI_2(PEt_3)]_2$ [2.361(5) Å].[18]

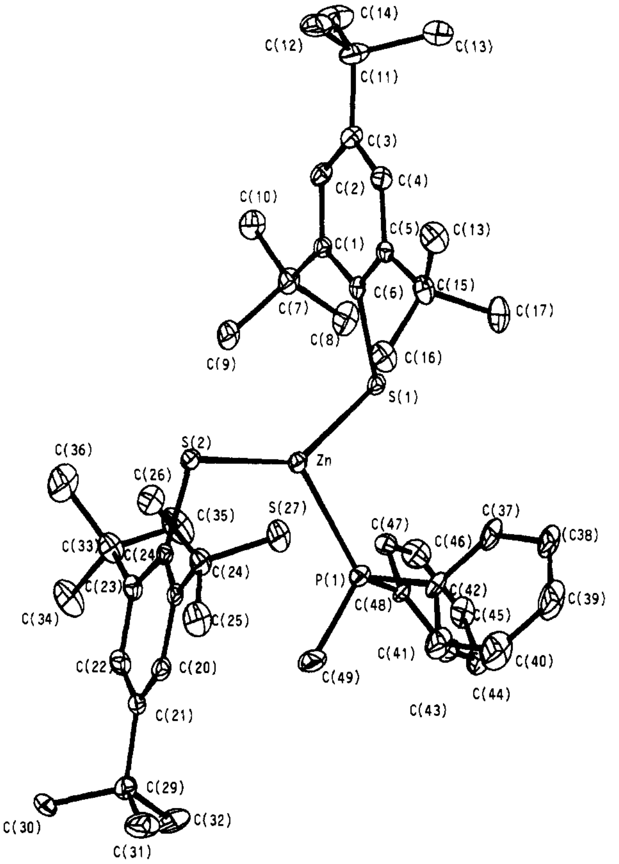

Figure 3. Molecular structure of **8a**. Only the major components of the disordered *t*-Bu groups and of the PMe_2Ph phenyl rings are shown. Thermal ellipsoids are drawn at 30% probability.

$Zn(SeAr'')_2(O{=}SC_4H_8)$ (12b). Crystals of **12b** were of sufficient quality for the main structural features to be determined while the donor ligand was significantly disordered (see Experimental Section) (Figure 4; only one of four orientations is shown). The Se-Zn-Se angle of 129.0(2)° is narrower than the corresponding angles in the structures of **2a** and **8a**, and both Ar″ substituents are rotated away from each other and toward the donor ligand. As expected, the Zn-Se bond length of 2.313(3)

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Table 4. Bond Angles and Opposite Bond Lengths in Trigonally Coordinated Zinc Complexes

compound	ligand atom L	Zn–L bond length,[a] Å	bond angle opposite to L, deg	E	Zn–E^1 bond length, Å	bond angle opposite to E^1, deg	Zn–E^2 bond length, Å	bond angle opposite to E^2, deg	ref
2a	N	2.145 (2.415)	156.3	S	2.207(3)	101.9			*b*
8a	P	2.414 (2.344)	138.2	S	2.226	121.4	2.210	100.4	*b*
12b	O	1.925 (2.215)	129.0	Se	2.313 (2.163)	115.5			*b*
$[ZnR(SCPh_3)]_2$ (**13**)[c]	C	1.976 (2.226)	96.8	S	2.381	127.1	2.416	135.1	9
$[ZnR(S\text{-}C_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)]_3$ (**14**)[c]	C	1.957 (2.207)	103.1	S	2.317	132.7	2.289	123.1	9
14	C	1.957 (2.207)	101.6	S	2.327	136.7	2.298	121.3	9
14	C	1.956 (2.206)	104.1	S	2.324	134.6	2.294	121.4	9
$[ZnR(SC_6H_2\text{-}t\text{-}Bu_3\text{-}2,4,6)]_3$ (**15**)[c]	C	1.950 (2.200)	105.0	S	2.316	119.3	2.356	135.0	9
15	C	1.966 (2.216)	95.4	S	2.311	139.6	2.325	125.0	9
$Zn(SC_6H_2\text{-}t\text{-}Bu_3\text{-}2,4,6)_2(Et_2O)$ (**16**)	O	2.133 (2.423)	159.6	S	2.194	100.8	2.197	99.6	8
$[Zn(SC_6HMe_4\text{-}2,3,5,6)_3]^-$ (**17**)	S	2.243	134.1	S	2.217	110.1	2.230	115.8	10a

[a] Bond lengths normalized to S in parentheses. [b] This work. [c] R = CH_2SiMe_3.

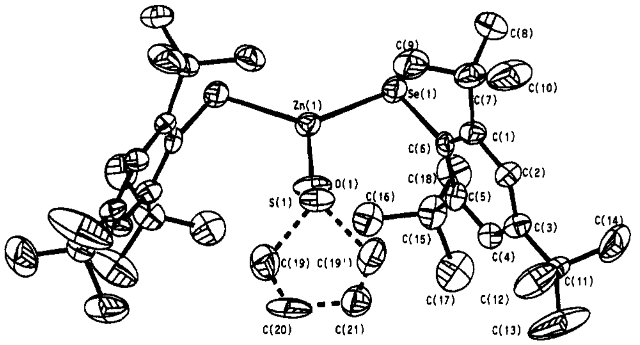


Figure 4. Molecular structure of **12b**. Only one orientation of the disordered C_4H_8SO ligand is shown. Thermal ellipsoids are drawn at 30% probability.

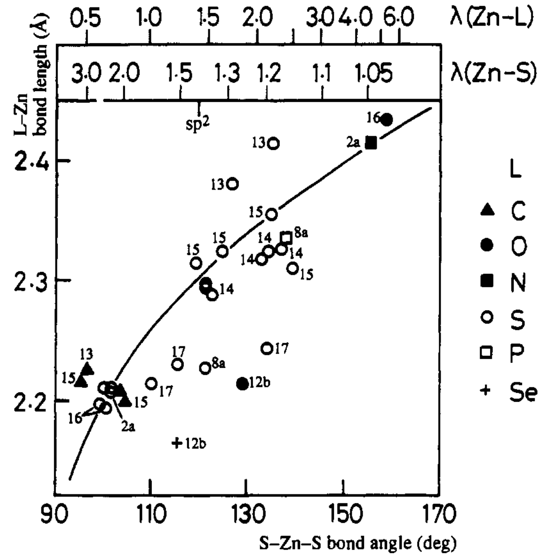
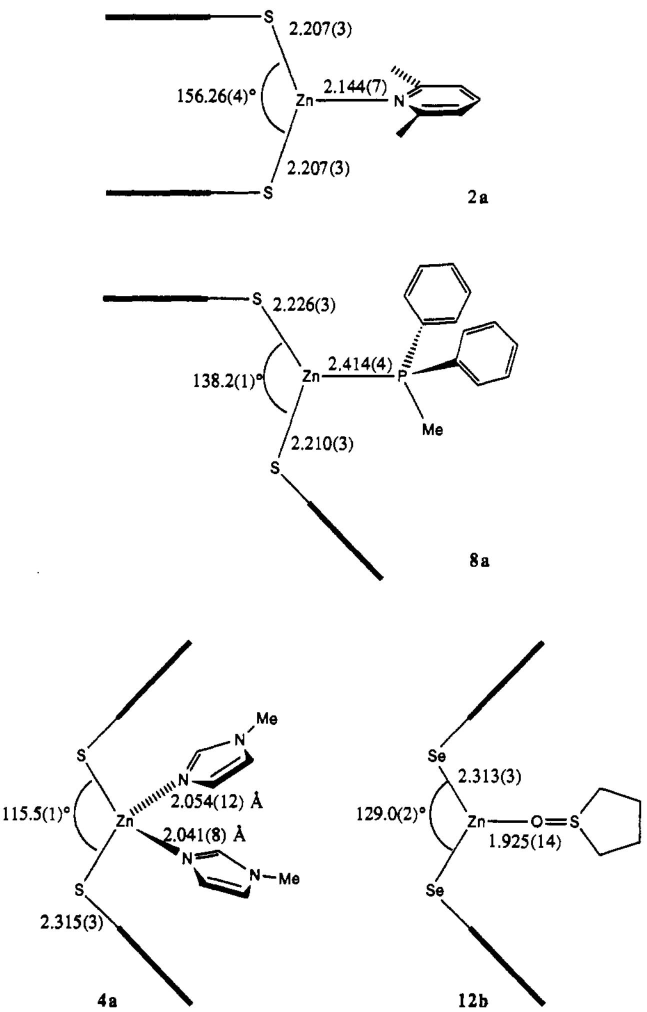


Figure 5. Relationship between the Zn–L bond length and the bond angle opposite to L for a number of trigonal-planar zinc chalcogenolato complexes (L = C, O, N, P, S, Se) (cf. Table 4). Two scales of λ values have been included, relating to the Zn–L and Zn–S bonds, respectively (cf. eq 1). A value of λ = 1.414 corresponds to sp² hybridization of Zn (λ(Zn–L) = λ(Zn–S)) (cf. footnote 23).

Å is shorter than the terminal Zn–Se distances in the four-coordinate complexes $[Zn(SeAr'')_2(OCHC_6H_4OMe\text{-}4)]_2$ [2.345(3) Å][14] and $[Zn(SePh)_4]^{2-}$ (average 2.469 Å)[21]. The Zn–O bond is short, 1.925(11) Å, and the Zn–O–S angle comparatively large [142.4(3)°], while the sulfur atom is pyramidal [angle O(1)–S(1)–C(19) = 97.6(8)°]. The overall structure of the compound complements those of the other three-coordinate complexes **2a** and **8a** by demonstrating the existence of yet another conformation of the chalcogenolato ligands in the solid state and a distribution of angles around the metal center which most closely resemble those expected for sp²-hybridized zinc, as opposed to the nearly T-shaped geometry of **2a**.

Chart 1



Bonding Considerations. Important features of the structurally characterized complexes **2a**, **4a**, **8a**, and **12b** are summarized in Chart 1. The changes in the conformation of the Ar″E ligands with respect to rotation about the Zn–E bond have already been explained above on the basis of steric repulsion. The marked relationship between the length of a Zn–L bond and the S–Zn–S angle found here has also been detected for similar complexes whose geometries have been reported in the literature.[8,9,10a] Table 4 summarizes these data which, after normalization (see below), are also plotted in Figure 5. The high density of points in the

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(21) Ueyama, N.; Sugawara, T.; Sasaki, K.; Nakamura, A.; Yamashita, S.; Wakatsuki, Y.; Yamazaki, H.; Yasuoka, N. *Inorg. Chem.* **1988**, *27*, 741.

lower left of Figure 5 has made it necessary to omit two points for carbon in this region. A discussion by Coulson[22] of the effect of hybridization on the lengths of bond sto carbon provides an interpretation of the relationship.

Coulson's method is to relate bond length to the position of the centroid of the charge cloud of the larger lobe of the hybrid orbital between the central atom, zinc in our case, and the bonded ligand atom. For a planar, trigonally hybridized species, we define an s/p hybrid orbital Ψ by[22,23]

$$\Psi = (\mathrm{s} + \lambda \mathrm{p})/(1 + \lambda^2) \qquad (1)$$

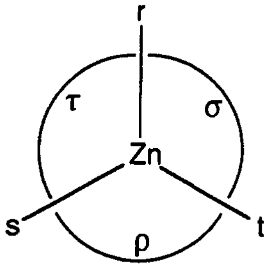
If the zinc 4s and 4p atomic orbitals are represented by Slater orbitals of the forms

$$\Psi_{4\mathrm{s}} = \left(\frac{\alpha^9}{315\pi}\right)^{1/2} r^3 \mathrm{e}^{-\alpha r} \qquad \Psi_{4\mathrm{p}} = \left(\frac{\alpha^9}{105\pi}\right)^{1/2} r^3 (\cos\theta) \mathrm{e}^{-\alpha r}$$

(with α = Slater exponent), then the centroid of charge, $\bar{a}$, in the larger lobe of a hybrid orbital defined as in eq 1 may be written, in atomic units (Bohr radius = 0.529 Å), as follows:

$$\bar{a} = \frac{9}{4\alpha}\left(\frac{1 + 4\lambda/\sqrt{3} + 3\lambda^2/2}{1 + \sqrt{3}\lambda + \lambda^2}\right) \equiv \frac{9}{4\alpha} f(\lambda)$$

The bond angles and ligands are schematically represented as



To relate the hybrid character of a particular zinc–ligand bond, as expressed by λ, to the bond angles we use the formula[22]

$$\lambda^r = \left(\frac{\sec\sigma \sec\tau}{-\sec\rho}\right)^{1/2}$$

which, in the case of two equal ligands ($t = s$, $\tau = \sigma$), reduces to

$$\lambda^r = \sec(\rho/2)(-\sec\rho)^{-1/2}$$

With these formulas we can derive a relationship between the hybrid character of a bond, and hence the bond length, and the opposite bond angle.

Figure 5 shows the relationship between the Zn–L bond lengths and the S–Zn–S angles for a number of complexes $Zn(SR)_2L$. Since we have a number of bonds to atoms other than sulfur in our data, we first correct the observed bond lengths for such atoms using the difference between the covalent radius of sulfur and that of the atom in question. Since the Zn–L the bond length will be greater than the distance from the zinc nucleus to the calculated center of charge, there will be a constant term, d, to be added to the calculated value of $\bar{a}$. Thus, in Å, the normalized Zn–L bond length, l, will be given by eq 2.

$$l = d + (9 \times 0.529/4\alpha) f(\lambda) \quad [\text{Å}] \qquad (2a)$$

$$\equiv d + m f(\lambda) \qquad (2b)$$

The relationship between the Zn–L bond lengths and the S–Zn–S bond angle is expressed by the calculated curve shown in Figure 5. The curve has been fitted to the normalized data by eye, using eq 2 with d = 0.908 Å and m = 1.047. This value of m gives α = 1.137, which appears reasonable compared to the figure calculated by Slater's rules ($Z^*/n^* = 4.35/3.7 = 1.176$)[24] although a somewhat higher figure of 1.491 has been deduced from SCF calculations of atomic structure.[25]

The value of d is just 0.11 Å less than the covalent radius of sulfur (1.02 Å).[24] Since the Zn–L bond length in this model is the sum of d and $\bar{a}$ (eq 2), this would appear to imply that the distance between the nucleus and the centroid of charge in the large hybrid orbital lobe of the zinc atom is marginally larger than the covalent radius of zinc, measured in the direction of the ligand atom to which the hybrid lobe predominantly bonds.

It is interesting to note that those species in which the zinc center is coordinated solely to group 16 atoms, i.e. **12b** and **17** (particularly the former), show bond lengths which are unexpectedly short in terms of this correlation.

Conclusion

The reaction of $[Zn(EAr'')_2]_2$ (E = S, Se) in noncoordinating solvents with a variety of O, N, S, and P ligands gives access to a series of novel three- and four-coordinate complexes $Zn(EAr'')_2L_n$ (n = 1, 2), including rare examples of halide-free zinc phosphine complexes. The three-coordinate complexes show significant variability in metal–ligand bond lengths and angles; the chalcogenolato ligands adopt a number of distinct conformations as a result. In the absence of excess ligand four-coordinate compounds dissociate readily in solution to give three-coordinate adducts. The geometric features are explained in terms of changes in the degrees of hybridization of the zinc–ligand bonding orbitals involved: Zn–E bond distances increase with decreasing E–Zn–E angles, i.e. with decreasing s character of the Zn–E bonds, while at the same time the bond lengths to the donor ligands L shorten as the s character of this bond increases. The comparison of three- and four-coordinate complexes shows that even in complexes of such sterically demanding ligands as EAr'' the bond length distribution is governed by electronic rather than steric factors.

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Supplementary Material Available: Tables giving summaries of data collection and refinement, atomic coordinates, anisotropic displacement coefficients of the non-hydrogen atoms, hydrogen atom parameters, and full bond distances and angles (27 pages). Ordering information is given on any current masthead page.

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(22) Coulson, C. A. *Victor Henri Memorial Volume*; Deoer: Liege, 1948; p 15.

(23) Note that eq 1 relates to the hybridization of the bonding *orbital* Ψ, *not* the central atom. In a three-coordinate complex $Zn(SR)_2(L)$ the λ values relating to the Zn–S and the Zn–L bonds are identical only if the complex possesses strict trigonal-planar geometry with angles of 120° between the ligands (λ = 1.414). In this case the zinc atom can be said to be sp^2-hybridized (this point has been marked on the λ scale in Figure 5). For a T-shaped complex with a S–Zn–S angle of 180°, λ(Zn–S) = 1.0, while λ(Zn–L) = ∞ since in this case the orbital involved in bonding the ligand L does not possess any s character (here, Zn can be thought of as sp-hybridized with respect to S but not to L). Intermediate values of λ(Zn–S) and λ(Zn–L) relating to a range of geometries in three-coordinate zinc complexes are shown in Figure 5.

(24) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983.

(25) Clementi, E.; Raimondi, D. L. *J. Chem. Phys.* **1963**, *38*, 2686.