Chalcogenide/Chalcogenolate Structural Isomers of Organo Group 13 Element Derivatives: Reactions of the Dimetallenes Ar'MMAr' $(Ar' = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)_2; M = Ga \text{ or } In)$ with N₂O or S₈ To Give $(Ar'M^{III}E)_2$ (E = O or S) and the Synthesis and Characterization of $[Ar'EM^I]_2$ (M = In or Tl; E = O, S)

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 Pr_{2}^{i}); M = Ga or In, E = O or S) were synthesized by the treatment of Ar'MMAr' with N₂O or elemental sulfur and characterized by NMR spectroscopy and X-ray crystallography. Their structures feature threecoordinate, +3 oxidation state metal centers with planar M₂E₂ cores. The cores were almost perfectly square for E = O, but for E = S, they were distorted parallelograms in 7–10. The M–E bond lengths were shorter than those in the higher aggregated species [RME]_n ($n \ge 4$) but comparable to those in M³⁺ aryloxides or thiolates featuring three-coordinate metals. Short M. Separations [2.553(1) Å in 7, 2.8882(4) Å in 8, 2.8276 Å (avg.) in 9, and 3.1577(8) Å in 10] are observed. Low oxidation heavier group 13/group 16 chalcogenolate isomers 16-19 of formula $[Ar'EM]_2$ (M = In or Tl, E = O or S) were also synthesized and characterized. In the +1 compounds [Ar'EIn]₂ (O, 16; S, 19) together, with the In +3 species [Ar'InE]₂ (O, 8; S, 10), represent the first structurally characterized isomeric pairs of organo group 13 metal/chalcogen derivatives. The E-M bonds in 16-19 were 2.3329 (avg.), 2.560 (avg.), 2.8189 (avg.), and 2.897 Å (avg.), respectively, which are 0.3–0.4 Å longer than the corresponding In-chalcogen distances in 8 and 10 as a result of the lower oxidation state, the large In^+ ionic size, and the reduced ionic contribution to the bond strength in 16 and 19. The compounds 16-19 also displayed M-arene interactions to the flanking aryl rings of the Ar' ligands. The Tl-arene contacts in the crystal structure of 17 are preserved in solution, as evidenced by ¹³C-Tl coupling. Attempts to thermally interconvert the isomeric pairs 8, 10 and 16, 18 led to decomposition of the complexes.

Introduction

Organometallic compounds of heavier group 13 metal chalcogenides of formula $[RME]_n$ (R = organic or related susbstituent; M = Al, Ga or In; E = O or S) have attracted considerable interest because of their potential application as semiconductor precursors for MOCVD.¹ A variety of these organometal oxides and sulfides have been synthesized, and a number of different structural types have been reported.^{2–7,9–13} They are mainly oligomers, whose association numbers generally range from 4 to 8. Tetrameric cubanes of formula [RME]₄

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 $(R = alkyl, silyl, and related group, M = Al, Ga, or In)^{3b,c,e,4a,b,d,5-7}$ in which the chalcogens μ_3 -bridge the metals are the most common structures, the stability of which is

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supported by theoretical calculations.⁸ Lower aggregation, in which some multiple bonded character is a possibility, is rare, and usually requires the use of sterically encumbering ligands. The dimeric oxo species $[RGaO]_2$ (R = HC{(CMe)(2,6- $Pr_{2}^{i}C_{6}H_{3}N)$ }2) (1)^{9a} and K₂[RGaO]₂ (R = {N(2,6-Pr_{2}^{i}C_{6}-Pr_{2}^{i}C $H_3N(C(H))_2$ (2),¹⁰ have been reported but both of these feature four-coordinate metals. A terminal sulfide complex TpBu'2GaS $(Tp = pyrazolylhydroborate) (3)^{11}$ featuring a very short Ga-S bond of 2.093(2) Å together with a structurally characterized dimeric gallium sulfide $[RGaS]_2$ (R = HC{(CMe)(2,6- $Pr_{2}^{i}C_{6}H_{3}N)$, 4), ^{9a} which feature four-coordinate metals, are the only organogallium sulfides with association number less than 4. The related aluminum sulfide dimer (Mes*AlS)₂ (Mes* = C_6H_2 -2,4,6-Bu^t₃) is also known.^{9b} In contrast, low aggregated indium chalcogenides of formula $[RInE]_n$ (n < 4) are unknown. Attempts to use Tp^{Bu₂}In to synthesize a gallium sulfide analogue of indium resulted in the sulfur-rich five-membered ring species $Tp^{Bu'_2}In(\eta^2-S_4)$ (5).¹² A similar structure of $Tm^{Bu'_2}In(\eta^2-S_4)$ (6)¹³ was obtained by reacting $Tm^{Bu'_2}In$ (Tm = 2-mercaptoimidazolylhydroborate) with elemental sulfur. We draw attention to the fact that it is possible to generate and study monomeric group 13 element two-coordinate species such as OAlX (X = F or Cl) in argon matrices at low temperature. However, none has been isolated at room temperature.¹⁴

The above complexes feature metals in the oxidation state +3. However, a different isomeric form, in which the metal has the oxidation state +1, is also possible. These are the monovalent metal species of formula REM, which are metal(I) alkoxides/aryloxides or metal(I) thiolates. Theoretical calculations on the model compounds M-O-H (I) and H-M=O (II) predicted that the M(I) hydroxide isomer was more stable than the metal(III) oxide by ca. 45 kcal mol^{-1} for Ga^{15} and ca. 59 kcal mol⁻¹ for In.¹⁶ Although well-defined Tl(I) species are wellknown,¹⁷ low oxidation state chalcogenolates of the other metals in the group are rare. No stable example of gallium(I) species of fomula $[REGa]_n$ has been reported, and the only stable structurally characterized In(I) chalcogenolate molecular species is the indium(I) phenoxide $[2,4,6-(CF_3)_3-C_6H_2OIn]_2$ (11).^{18a} In addition, there are two related indium(I) complexes, [CF₃SO₃In]₂ $(12)^{18b}$ and $\ln(\mu$ -OBu^t)₃Sn (13), ^{18c} which have also been structurally characterized. Several In(I) thiolates of formula InSR $(R = Et, Bu^n, C_6H_{11}, Ph, C_6H_4-2-Me, 2-naphthyl or C_6F_5)$ have been synthesized but their structures remain unknown.^{18d} Recent work in our group on group 13 metal 3+/1+ species featuring isomeric imido/amido derivatives has yielded quasi-isomeric gallium imide Ar'GaNAr[#] (Ar[#] = C_6H_3 -2,6-(C_6H_2 -2,6-Me₂-4-

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 Bu'_{2} (14)¹⁹ and the amide: GaN(SiMe₃)Ar'' (Ar'' = C₆H₃-2,6- $(C_6H_2-2,4,6-Me_3)_2)$ (15),¹⁹ which contain short M–N bonds with multiple character. The fact that the bulky terphenyl ligand can effectively stabilize two isomeric forms of the gallium compounds 14 and 15 prompted speculation as to whether the terphenyl ligand Ar' could also stabilize low oxidation heavier group 13/group 16 chalcogenolate isomers of formula [Ar'EM]₂ (M = Ga, In, or Tl; E = O or S). We now report the synthesis of a range of low aggregated heavier group 13 metal organochalcogenides $[Ar'ME]_2$ (M/E = Ga/O, 7; In/O, 8; Ga/S, 9; or In/S, 10) by the use of the sterically hindered terphenyl ligand Ar', all of which feature three-coordinate metal centers and twocoordinate chalcogenides. We also describe the synthesis and characterization of the isomeric M(I) chalcogenolates [Ar'EM]₂ (E/M = O/In, 16; O/Tl, 17; S/In, 18; or S/Tl, 19), which feature two-coordinate metals and three-coordinate chalcogen centers.

Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N₂ or in a vacuum atmospheres HE-43 drybox. Solvents were dried according to the method of Grubbs and degassed prior to use.²⁰ Tl(C₅H₅) (Aldrich) and InCl (Strem) were purchased and used as received. The dimetallenes Ar'MMAr' (M = Ga,²¹ In,²² and Tl²³), the chalcogenols Ar'EH (E = O²⁴ and S²⁵), and their lithium salts Ar'ELi (E = O²⁴ and S²⁵) were synthesized by literature methods. N₂O (99.99% purity) was purchased from Airgas Corporation and used without further purification. ¹H and ¹³C NMR spectra were recorded on Varian 300 spectrometers and referenced to known standards. Melting points were recorded using a Meltemp apparatus and were not corrected. Elemental analyses were not carried out on the complexes which crystallized with solvent.

[Ar'GaO]₂ (7). Ar'GaGaAr' (0.72 g, 0.77 mmol) was dissolved in 50 mL of toluene to afford a deep green solution. This was treated with N₂O, and the color was quickly discharged to afford a colorless solution within ca. 10 s. The toluene was then removed under reduced pressure to yield a colorless residue, which was dissolved in 75 mL of hexane. The hexane was concentrated to ca. 50 mL, and overnight storage at ca. −18 °C yielded colorless X-ray quality crystals of 7: yield 0.52 g (70%); mp >275 °C; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.06 (br, 24H, *o*-CH(CH₃)₂), 1.20 (br, 24H, *o*-CH(CH₃)₂), 2.70 (sept, 8H, CH(CH₃)₂), 7.11−7.25 (m, 18H, ArH); ¹³C {¹H}NMR (75.5 MHz, C₆D₆, 25 °C) δ 23.5 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 31.2 (CH(CH₃)₂), 123.7, 126.9, 129.8, 140.2, 145.6, 147.3 (ArC), one ArC resonance is likely obscured by the C₆H₆ signal, and *i*-C₆H₃ signal was not observed. Anal. Calcd for C₆₀H₇₄Ga₂O₂: C, 74.55; H, 7.72. Found: C, 74.01; H, 7.89.

[Ar'InO]₂ (8). Compound 8 was synthesized in an analogous manner to 7. However, the reaction was slower, and the discharge

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of the color was complete only after 2 min. Colorless X-ray quality crystals of **8** were grown from hexane upon slow cooling of saturated solutions at ca. -18 °C: yield 0.57 g (65%); mp >275 °C; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.01 (d, 48H, *o*-CH(*CH*₃)₂, ³J_{HH} = 6.6 Hz), 2.96 (sept, 8H, *CH*(CH₃)₂, ³J_{HH} = 6.6 Hz), 7.16–7.37 (m, 18H, Ar*H*); ¹³C {¹H}NMR (75.5 MHz, C₆D₆, 25 °C) δ 26.2 (CH(*CH*₃)₂), 26.6 (CH(*CH*₃)₂), 30.8 (*C*H(CH₃)₂), 123.4, 127.9, 129.4, 140.7, 142.1, 147.0, 147.8, 197.6 (Ar*C*).

[Ar'GaS]₂ (9). A suspension of crystalline sulfur (0.048 g, 1.50 mmol) in toluene (20 mL) was added dropwise over 20 min to a mixture of Ar'GaGaAr' (0.70 g, 0.75 mmol) and toluene (40 mL) at -78 °C. Upon slowly warming to room temperature, the deep green solution of Ar'GaGaAr' faded to colorless, and the mixture solution was stirred overnight. Toluene was then removed under reduced pressure to afford a colorless residue, which was dissolved in 70 mL of benzene. The benzene was concentrated to ca. 20 mL, and storage at ca. 7 °C for 1 week yielded colorless X-ray quality crystals of 9: yield 0.21 g (28%); mp 315 °C; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.05 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 7.2 Hz), 1.28 (d, 24H, *o*-CH(CH₃)₂, ${}^{3}J_{HH} = 7.2$ Hz), 2.82 (sept, 8H, CH(CH₃)₂, ${}^{3}J_{\rm HH} = 6.6$ Hz), 7.16 (d, 4H, *m*-C₆H₃, ${}^{3}J_{\rm HH} = 6.0$ Hz), 7.18 (d, 8H, *m*-Dipp, ${}^{3}J_{\text{HH}} = 7.8 \text{ Hz}$), 7.20 (t, 2H, *p*-C₆H₃, ${}^{3}J_{\text{HH}} = 6.6 \text{ Hz}$), 7.39 (t, 4H, *p*-Dipp, ${}^{3}J_{\text{HH}} = 7.8 \text{ Hz}$); ${}^{13}\text{C} \{{}^{1}\text{H}\}\text{NMR}$ (75.5 MHz, C₆D₆, 25 °C) δ 23.0 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 30.9 (CH(CH₃)₂), 123.6, 127.9, 129.2, 129.7, 139.9, 146.3, and 147.1 (ArC), *i*-C₆H₃ signal was not observed.

[**Ar'InS**]₂ (10). Compound 10 was synthesized in an analogous manner to 9 from Ar'InInAr' (0.60 g, 0.58 mmol) and sulfur (0.037 g, 1.16 mmol). Colorless X-ray quality crystals of 10 were grown from a mixture of hexane (20 mL) and toluene (2 mL) upon slow cooling of a saturated solution at ca. −50 °C for 5 days: yield 0.15 g (24%); mp >350 °C; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.05 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz), 1.32 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 7.2 Hz), 2.87 (sept, 8H, CH(CH₃)₂, ³J_{HH} = 7.2 Hz), 7.22 (m, 6H, *m*-C₆H₃ and *p*-C₆H₃), 7.24 (d, 8H, *m*-Dipp, ³J_{HH} = 7.2 Hz), 7.42 (t, 4H, *p*-Dipp, ³J_{HH} = 7.8 Hz); ¹³C {¹H}NMR (75.5 MHz, C₆D₆, 25 °C) δ 23.2 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 30.9 (CH(CH₃)₂), 124.0, 129.6, 141.9, 146.9, and 147.0 (ArC), two ArC resonances are likely obscured by the C₆H₆ signal, and *i*-C₆H₃ signal was not observed.

[Ar'OIn]₂ (16). Ar'OLi (0.70 g, 1.73 mmol) was dissolved in toluene (50 mL) and added dropwise over 30 min to a mixture of InCl (0.26 g, 1.73 mmol) and toluene (20 mL) at -78 °C. The solution was slowly warmed to room temperature and stirred overnight. Toluene was then removed under reduced pressure, and hexane (70 mL) was used to extract the colorless residue. Concentration to ca. 20 mL and overnight storage at ca. -18 °C afforded colorless X-ray quality crystals of 16: yield 0.45 g (52%); mp, decomposed to a black solid upon heating; ¹H NMR (300 MHz, C_6D_6 , 25 °C) δ 1.09 (d, 24H, *o*-CH(CH_3)₂, ³J_{HH} = 7.8 Hz), 1.20 (d, 24H, o-CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 7.2$ Hz), 2.99 (sept, 8H, CH(CH₃)₂, ${}^{3}J_{\text{HH}} = 6.6 \text{ Hz}$), 6.77 (t, 2H, *p*-C₆H₃, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}$), 7.04 (d, 4H, m-C₆H₃, ${}^{3}J_{HH} = 7.2$ Hz), 7.11 (d, 8H, m-Dipp, ${}^{3}J_{HH} = 7.8$ Hz), 7.18 (t, 4H, *p*-Dipp, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}$); ${}^{13}\text{C} \{{}^{1}\text{H}\}\text{NMR}$ (75.5 MHz, C_6D_6 , 25 °C) δ 24.5 (CH(CH_3)₂), 25.2 (CH(CH_3)₂), 30.8 (CH(CH₃)₂), 115.7, 124.6, 128.7, 129.2, 131.0, 141.1, 147.9, and 219.8 (ArC). Anal. Calcd for C₆₀H₇₄In₂O₂: C, 68.18; H, 7.06. Found: C, 67.70; H, 7.11.

[Ar'OTI]₂ (17). Ar'OH (0.55 g, 1.33 mmol) was dissolved in hexane (40 mL) and added dropwise over 20 min to a mixture of Tl(C₅H₅) (0.38 g, 1.40 mmol) and hexane (40 mL). The mixture was stirred overnight, filtered through a layer of Celite, and concentrated to ca. 30 mL. Overnight storage at ca. -30 °C for 3 days afforded colorless X-ray quality crystals of 17: yield 0.80 g (65%); mp >275 °C; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.13 (t, 48H, *o*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz), 3.09 (sept, 8H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 6.71 (t, 2H, *p*-C₆H₃, ³J_{HH} = 7.2 Hz), 7.02 (d, 4H,

m-C₆H₃,³*J*_{HH} = 7.2 Hz), 7.08 (br, 12H, *m*-Dipp, and *p*-Dipp); ¹³C {¹H}NMR (C₆D₆, 75.5 MHz, 25 °C) δ 25.1 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 31.1 (CH(CH₃)₂), 113.8 (*p*-C₆H₃), 125.1 (t, *m*-Dipp, *J*_{C-TI} = 52 Hz), 128.7, 129.8 (t, *p*-Dipp, *J*_{C-TI} = 23 Hz), 130.9, 143.3 (t, *i*-Dipp, *J*_{C-TI} = 70 Hz), 148.9 (t, *o*-Dipp, *J*_{C-TI} = 37 Hz), 165.1 (*i*-C₆H₃). Anal. Calcd for C₆₀H₇₄O₂Tl₂: C, 58.3; H, 6.04. Found: C, 58.01; H, 6.17.

[Ar'SIn]₂ (18). Compound 18 was synthesized in an analogous manner to 16 from Ar'SLi (0.40 g, 0.92 mmol) and InCl (0.14 g, 0.93 mmol). Pale green X-ray quality crystals were grown from a saturated toluene solution upon slow cooling and overnight storage at ca. -18 °C: yield 0.38 g (76%); mp, decomposed to a black solid upon heating; ¹H NMR (300 MHz, C₆D₆, 25 °C) δ 1.08 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz), 1.35 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz), 2.89 (sept, 8H, CH(CH₃)₂, ³J_{HH} = 6.6 Hz), 6.89 (t, 2H, *p*-C₆H₃, ³J_{HH} = 7.8 Hz), 6.94 (d, 4H, *m*-C₆H₃, ³J_{HH} = 7.2 Hz), 7.09 (t, 4H, *p*-Dipp, ³J_{HH} = 7.8 Hz), 7.21 (d, 8H, *m*-Dipp, ³J_{HH} = 7.8 Hz); ¹³C {¹H}NMR (75.5 MHz, C₆D₆, 25 °C) δ 25.0 (CH(CH₃)₂), 31.0 (CH(CH₃)₂), 122.1, 124.7, 129.2, 140.9, 142.9, 144.8, 147.3, and 219.8 (ArC).

[Ar'STI]₂ (19). Compound 19 was synthesized in an analogous manner to 17. However, upon removal of the hexane solvent, the colorless residue was extracted with hot (100 °C) toluene. Colorless X-ray quality crystals of 19 were grown from saturated toluene solutions upon slow cooling and overnight storage at ca. 0 °C: yield 0.52 g (50%); mp >275 °C; ¹H NMR (300 MHz, C₇D₈, 25 °C) δ 1.08 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.30 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.30 (d, 24H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 2.89 (sept, 8H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 6.82–7.00 (m, 6H, *p*-C₆H₃, *p*-C₆H₃), 7.04 (d, 4H, *m*-C₆H₃, ³J_{HH} = 7.5 Hz), 7.18 (d, 8H, *m*-Dipp, ³J_{HH} = 7.5 Hz); ¹³C{¹H}NMR (75.5 MHz, C₇D₈, 25 °C) δ 24.6 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 30.9 (CH(CH₃)₂), 121.3, 137.5, 143.1, 147.6, three ArC resonances are likely obscured by the C₆H₆ signal, and *i*-C₆H₃ signal was not observed.

X-ray Structure Determination. Crystals of 7-10 and 16-19 were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in a low temperature stream.²⁶ The data for 7-9, 17, and 19 were recorded near 90 K on a Bruker SMART 1000 instrument (Mo K α radiation ($\lambda = 0.71073$ Å) and a CCD area detector), while data for 16 were collected at 180 K, and data for 10 and 18 were collected at 90 K on a Bruker APEX instrument (Mo Ka radiation and a CCD area detector). For compounds 7, 8, 10, and 16-19, the SHELX version 6.1 program package was used for the structure solutions and refinements. Absorption corrections were applied using the SADABS program.²⁷ The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Crystals of 9 were formed to be twinned, and the relative contributions from the two twin components were determined by using Cellnow program.²⁸ Absorption corrections were applied using the TWINABS program, and the major component was used for structure determination.^{29,30} The BASF parameter refined to 0.436, indicating that a nearly equal percentage of the two domains

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Table 1. Selected Crystallographic Data for 7, 8.0.5C₆H₁₄, 9.4C₆H₆, 10.2C₇H₈, 16, 17, 18.3.5C₇H₈, and 19.2.4C₇H₈

cmpd	7	$8 \cdot 0.5 C_6 H_{14}$	$9 \cdot 4C_6H_6$	$10 \cdot 2C_7H_8$
formula	$C_{60}H_{74}Ga_2O_2$	$C_{66}H_{82}In_2O_2$	$C_{84}H_{98}Ga_2S_2$	$C_{74}H_{90}In_2S_2$
fw	966.63	1136.96	1311.18	1273.24
habit	block	block	block	block
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic
space group	Pccn	C2/m	Pnma	$P2_1/n$
a, Å	20.116(4)	15.8883(13)	12.998(2)	11.8879(17)
b, Å	15.881(3)	20.6514(15)	23.678(4)	21.738(3)
<i>c</i> , Å	16.472(3)	11.8851(9)	23.675(4)	12.6705(18)
α , deg	90	90	92.600(3)	90
β , deg	90	129.086(3)	96.329(3)	99.673(2)
γ , deg	90	90	96.269(3)	90
$V, Å^3$	5262.2(18)	3026.9(4)	7187(2)	3227.7(8)
Z	4	4	4	2
cryst dim, mm	$0.18 \times 0.17 \times 0.08$	$0.24 \times 0.21 \times 0.19$	$0.49 \times 0.48 \times 0.44$	$0.21 \times 0.11 \times 0.09$
$d_{\rm calcd}, {\rm g} \cdot {\rm cm}^{-3}$	1.220	1.247	1.212	1.143
μ , mm ⁻¹	1.064	0.802	0.851	0.810
no. of reflns	5162	13889	35493	7499
no. of obsd reflns	3508	4199	29557	4806
R1 obsd reflns	0.0574	0.0299	0.0437	0.0479
wR2, all	0.1624	0.0762	0.1240	0.1244
cmpd	16	17	18.3.5C7H	19 •2.4C ₇ H ₈
formula	$C_{60}H_{74}In_2O_2$	$C_{60}H_{70}O_2T_{12}$	C_{84} 5H102S2In2	C77He2S2Tl2
fw	1056.83	1235.94	1411.45	1486.33
habit	needle	block	plate	block
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	Pccn	$P2_1/n$	$P2_1/n$
a. Å	9.125(3)	13.0543(13)	16.5924(16)	16,5924(17)
b, Å	22.769(7)	19.3442(19)	16.5192(16)	16.5655(18)
<i>c</i> , Å	24.577(7)	20.716(2)	27.739(3)	28.365(3)
α , deg	90	90	90	90
β , deg	96.519(4)	90	105.0310(10)	109.397(6)
γ , deg	90	90	90	90
$V, Å^3$	5073(3)	5231.4(9)	7343.0(12)	7353.9(13)
Z	4	4	4	4
cryst dim, mm	$0.40 \times 0.17 \times 0.14$	$0.24 \times 0.21 \times 0.19$	$0.56 \times 0.52 \times 0.30$	$0.34 \times 0.21 \times 0.18$
$d_{\rm calcd}, {\rm g} \cdot {\rm cm}^{-3}$	1.381	1.564	1.277	1.342
μ , mm ⁻¹	0.951	6.193	0.728	4.471
no. of reflns	11628	6952	13264	11471
no. of obsd reflns	9324	5342	10814	9878
R1 obsd reflns	0.0292	0.0398	0.0643	0.0794
wR2, all	0.0693	0.0974	0.1406	0.1949

was present. Some details of the data collection and refinement are given in Table 1.

Results and Discussion

Synthesis of $[Ar'ME]_2$ (M/E = Ga/O, 7; In/O, 8; Ga/S, 9; or In/S, 10) and $(Ar'EM)_2$ (E/M = O/In, 16; O/Tl, 17; S/In, 18; or S/Tl, 19). Heavier organo group 13 metal chalcogenides $[RME]_n$ have been prepared preferentially by (1) protolysis of R₃M or RMMe₂ with H₂E followed by thermolysis,^{3a-d,4b,5c,h} (2) ligand exchange between organo metal halides and various chalcogen-transfer reagents, ^{5e,f,7a} (3) reaction of R₃M or R₂MH with elemental chalcogens,^{5a-d,11} or (4) oxidation of RM.^{3e,4c,d,6,7b,9-13} Recently, our group reported a facile synthetic route to the β -diketiminates [RGaE]₂ (R = $HC\{(CMe)(2,6-Pr_{2}^{i}C_{6}H_{3}N)\}_{2}, E = O \text{ or } S\}$ via oxidation of the monomeric:GaR (R = HC{(CMe)(2,6-Prⁱ₂C₆H₃N)}), which resulted in a low aggregated organogallium oxide or sulfide. We were thus encouraged to apply a similar strategy for the synthesis of aryl metal oxides and sulfides from the low oxidation dimetallenes Ar'GaGaAr' and Ar'InInAr'. The dimeric organo gallium and indium oxide, 7 and 8, were synthesized by the oxidation of Ar'GaGaAr' and Ar'InInAr' with excess N2O in toluene (Scheme 1). Colorless crystals of 7 and 8 were obtained upon storage in hexane at ca. -18 °C. Treatment of Ar'TITIAr' with N₂O, O₂, trimethylamine-N-oxide, or pyridine *N*-oxide did not result in characterizable Tl(III) products.



Scheme 1. Synthetic Routes to Compounds 7–10

M = Ga(7) or In(8)

Analysis of the reaction mixtures by ¹H NMR spectroscopy afforded resonances assignable only to starting materials and some decomposition products (Tl and Ar'H). It is also noteworthy that the isomeric [Ar'OTI]₂ was not formed in these experiments by insertion of O into the Tl–C bond, whereas the related Cu(I) aryl, CuAr[#] (Ar[#] = C₆H₂-2,6-Mesityl₂), was observed to react with O₂ and, upon acidic work up, afforded Ar[#]OH in modest yield.³¹ The dimeric organogallium and indium sulfides, **9** and **10**, were synthesized by the addition of stoichiometric amounts of sulfur to toluene solutions of Ar'GaGaAr' and Ar'InInAr' at -78 °C followed by overnight stirring at room temperature (Scheme 1). Upon storage of saturated benzene solution of **9** and toluene/hexane (1/20) mixture solution of **10**, colorless crystals of both **9** and **10** were

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Scheme 2. Synthetic Routes to Compounds 16–19



obtained. A similar reaction between Ar'TITIAr' and S_8 did not occur, and unreacted starting materials were recovered.

The dimeric indium phenoxide 16 and thiolate 18 were synthesized via transmetalation with Ar'OLi or Ar'SLi and InCl in toluene, respectively (Scheme 2). Upon storage of saturated hexane solution of 16 or a toluene solution of 18 at ca. -18°C, colorless crystals of 16 or pale green crystals of 18 were obtained. The dimeric thallium analogues 17 and 19 were synthesized by the reaction of Ar'OH and Ar'SH with $Tl(C_5H_5)$ in THF (Scheme 2). They were obtained in ca. 65% yield, as X-ray quality crystals, upon storage of saturated hexane solution of 17 and toluene solution of 19 at ca. -18 °C. A similar transmetalation reaction between Ar'OLi or Ar'SLi and "Gal"32 in toluene resulted only in decomposition to Ar'OH or Ar'SH and gallium metal. Attempts to reduce Ar'OGaCl₂ or Ar'SGaCl₂ with Na as well as the reaction between Ar'OH or Ar'SH and the dimetallene Ar'GaGaAr' were ineffective for the preparation of the target [Ar'OGa]₂ or [Ar'SGa]₂ compounds. The oxo and sulfide complexes 7-10 are characterized by high thermal stabilities and do not melt below 300 °C. They show signs of degradation after prolonged periods at this temperature. Attempts to thermally convert 8 and 10 to the aryloxide 16 or thiolate 18 were unsuccessful.

Structrual Characterization of the Dimeric Organo Group 13 Metal Oxide and Sulfide. $[Ar'GaE]_2$ (M/E = Ga/O, 7; In/O, 8; Ga/S, 9; or In/S, 10). The compounds 7–10 have centrosymmetric, dimeric structures and feature lowcoordinate metals [coordination number = 3] with a planar M₂E₂ core (Figures 1 and 2). The twinned crystals of compound 9 contained four independent molecules within one unit cell. Selected bond lengths and angles of 7–10 are provided in Table 2.

The M_2O_2 arrays in **7** and **8** are almost perfectly square (internal ring angles are within ca. 1° of 90°) with M–O



Figure 1. Thermal ellipsoid (50%) drawing of 7. Hydrogen atoms are not shown. Dihedral angles between Ga_2O_2 plane and C(1)-C(6) ring = 88.5°.



Figure 2. Thermal ellipsoid (50%) drawing of **10**. Hydrogen atoms are not shown. Dihedral angles between In_2S_2 plane and C(1)-C(6) ring = 85.93°.

distances of 1.828(3) Å in 7 and 2.026(1) Å in 8. Similar square planar Ga₂O₂ arrays were observed in β -diketiminato gallium oxide $[RGaO]_2$ (R = HC{(CMe)(2,6-Pr_2C_6H_3N)}_2, 1)⁹ and a related dianion $K_2[RGaO]_2$ (R = {N(2,6-Prⁱ₂C₆H₃N)C(H)}₂) (2).¹⁰ Ga-O distances are 1.8536(9) and 1.8485(9) Å in 1, and two different Ga-O distances of 1.814(3) and 1.905(3) Å, respectively, were found in 2. Thus the Ga-O distances in 1 and 2 are ca. 0.2 Å longer than those in 7, most probably as a result of the higher coordination number of the gallium. The Ga-O bond length is quite similar to the 1.821(3), 1.822(3), and 1.831(4) Å in the three-coordinate species $Bu_2^tGaO(C_6H_3-$ 2,6-Bu^t₂-4-Me) (23),^{33a} (2,2,6,6,- tetramethylpiperidino)₂GaOPh (24),^{33b} and Bu_2^t GaOCPh₃ (25)^{33c} in 7. The structurally characterized, higher aggregated organogallium oxides all involve four-coordinate metals and include one nonamer (MesGaO)₉ $(Mes = 2,4,6-Me_3C_6H_2, 20)^{4b}$ and two cubane tetramers $[Bu_{3}^{t}SiGaO]_{4}$ (21)^{4c} and $[GaCl(pz)_{3}GaO]_{4}$ (22, pz = tris-(pyrazolyl)borate).^{4a} In **20**, two six-membered (MesGaO)₃ rings are connected by three μ_2 -MesGaO units, thus generating two sets of Ga-O bonds [1.910 Å (avg.) in (MesGaO)₃ rings and 1.967 Å (avg.) in μ_2 -MesGaO units]. Compounds 21 and 22 both feature oxygens that symmetrically μ_3 -bridge the gallium atoms. The Ga-O distances are 1.91 (avg.) and 2.003(1) Å, respectively. Because of the higher metal coordination, 20-22 have considerably longer Ga-O bonds (all exceed 1.9 Å) than those in 1, 2, and 7. The In-O bonds in 8 have similar characteristics to its gallium analogue. The In-O bonds are shorter than the average In-O bonds of 2.14 Å in the tetrameric $[RInO]_4$ (R = (Me₃Si)₃C) (26)⁶ and are similar to 2.091(4) Å in three-coordinate indium species Cp*Fe(CO)₂In(OC₆H₄-4- $Bu^{t}Mes^{*}$ (Mes^{*} = C₆H₃-2,4,6-Bu^t₃) (**27**).³⁴

In contrast to the square planar M_2O_2 arrays in 7 and 8, 9 and 10 have planar M_2S_2 units with much greater angular disparities within the rings. There are acute M-S-M angles [9, 79.3° avg.; 10, 81.89(3)°] and angles almost 20° wider at the metals: S-M-S angles are 100.71° avg. [9] and 98.11(3)° [10]. The four independent molecules in crystals of 9 have

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Chalcogenide/Chalcogenolate Structural Isomers

 Table 2. Selected Structural Data for 7–10

Table 2. Selected Structural Data 101 7 10					
	7	$8 \cdot 0.5 C_6 H_{14}$	9 •4C ₆ H ₆	$10 \cdot 2C_7 H_8$	
M-E (Å)	1.830(3)	2.0258(13)	2.2181(10)	2.4123(13)	
	1.826(3)		2.2162(10)	2.4059(13)	
M •••• M (Å)	2.553(3)	2.8882(4)	2.8305(9)	3.1577(8)	
C(ipso)-M (Å)	1.944(4)	2.107(2)	1.940(3)	2.140(4)	
M-E-M (deg)	88.55(13)	90.94(8)	79.33(4)	81.89(3)	
E-M-E (deg)	91.45(13)	89.06(8)	100.67(4)	98.11(3)	
C(ipso)-M-E(deg)	135.05(14)	135.47(4)	128.27(10)	131.08(12)	
	133.39(15)		131.05(10)	130.81(12)	
C(ortho)-C(ipso)-M (deg)	113.4(3)	118.99(11)	116.5(2)	123.0(3)	
	126.5(3)		123.0(2)	115.8(3)	

similar Ga-S bond lengths, and the average bond distance is ca. 2.216 Å. These Ga-S bonds are shorter than those found in structurally characterized, four-coordinate organogallium sulfides, which have Ga-S distances in the range of ca. 2.25–2.27 Å; for example, in the dimer $[RGaS]_2$ (R = $HC\{(CMe)(2,6-Pr_{2}^{i}C_{6}H_{3}N)\}_{2}, 4\},^{9}$ ca. 2.23–2.25 Å in the trimers $[RGa(S)py]_3(R = Bu^t, 28)^{5c}$ Me, 29,^{5d} Et, 30^{5d}), ca. 2.35–2.40 Å in the cubane tetramers $[RGaS]_4$ (R = Bu^t, 31^{5a,b} Et₂MeC. **32**;^{5e} Et₃C, **33**;^{5e} (Me₃Si)₃C, **34**;^{5h} 2,2,6,6-tetramethylpiperidino, **35**^{5g} or Cp(CO)Fe, **36**^{5f}), ca. 2.32 to 2.40 Å in the hexamer $[Bu'GaS]_6$ (37),^{5c} and ca. 2.30 to 2.37 Å in heptamer $[Bu'GaS]_7$ (38).^{5c} The terminal sulfide complex Tp^{Bu'}₂GaS (3)¹¹ also has four-coordinate gallium centers; however, a significantly shorter Ga-S distance of 2.093(2) Å was observed due to terminal coordination of the sulfide and/or Ga-S multiple bond character. The Ga-S distances in 9 are within the range 2.20–2.27 Å found in other low coordinate Ga-S species, for example, $\{ [(SiMe_3)_2CH]_2Ga\}_2S, (39),^{35a} (2,4,6-'Bu_3-C_6H_2S)_3Ga (40),^{35b} (2,4,6-Bu'_3-C_6H_2S)_2GaSMe (41),^{35b} and Bu''Ga(SC_6H_2-2,4,6-Bu'_3-C_6H_2S)_2GaSMe (41),^{35b} and Bu''_3-C_6H_2S)_2GaSMe (41),^{35b} and Bu''_3-C_6H_2S)_2S (41),^{35b} and Bu''_3-C_6H_2S (41$ Bu^t₃)₂ (**42**).^{35c} The In-S bonds of 2.4123(13) and 2.4059(13) Å in 10 display similar effects. They are substantially shorter than the In-S bond length range of 2.54-2.58 Å in the tetrameric [RInS]₄ (R = $(SiMe_3)_3C$, 43;^{7b} MoCp(CO)₃, 44;^{7a} or $FeCp(CO)_2$, **45**^{7a}), in which the indiums are four-coordinate, but they are similar to the 2.39-2.40 Å in the three-coordinate indium thiolate species $(2,4,6-^{t}Bu_{3}-C_{6}H_{2}S)_{3}In$ (46).³⁶

The M-E-M angles of 79.33(4) and 81.89(3)° in 9 and 10 are ca. 8 and 7° narrower than 88.55(13) and $90.94(8)^\circ$ in 7 and 8. Greater bending at sulfur is expected and is consistent with generally narrower angles in divalent sulfur compounds [92° in SH₂ vs 104.5° in H₂O].³⁷ The M····M separations of 2.553(1), 2.8882(4), 2.8276 (avg.), and 3.1577(8) Å in 7-10 are the shortest observed for [RME]_n species^{2,4-7,9,10} and only slightly exceed the sum of their covalent radii.³⁸ However, the short M ... M separations do not imply significant M ... M bonding since the metals have considerable cationic character affording effective ionic radii which are considerably smaller than covalent radii. The faces of the M₂E₂ arrays are shielded by the flanking C_6H_3 -2,6- Pr_2^i groups of the Ar' ligand, which are orientated above and below the M_2E_2 plane. This is further quantified by the dihedral angle between the M_2E_2 rings and central Ph ring which are 88.5 (7), 85.93 (8), 76.1-86.8 (9), and 85.93° (10). The protection by the steric encumbering ligands thus stabilizes the dimeric forms of 7-10.

Structrual Characterization of the Dimeric Organo Group 13 Metal Aryloxides and Thiolates. $[Ar'EM]_2$ (E/ M = O/In (16), O/TI (17), S/In (18), or S/TI (19)). Although various attempts to synthesize $[Ar'EGa]_2$ did not result in isolation of the target compounds (see above), the indium congeners 16 and 18 were obtained in good yield via transmetalation by the reaction of Ar'ELi and InCl. Compounds 16 and 18, together with 8 and 10, represent the first structurally characterized isomeric pairs of organo group 13 metal/chalcogen derivatives (Figures 3 and 4). Selected bond lengths and angles of 16 and 18 as well as 17 and 19 are provided in Table 3.

Unlike the quasi-isomeric pair of the gallium amide and imide 14 and 15, which are monomers, compounds 16 and 18 both associate to form dimers with bridging indium atoms in the +1oxidation state. The In ... In separations of 3.598 and 4.673 Å in 16 and 18 preclude any significant metal-metal interaction and are a consequence of aryloxide and thiolate bridging. The In...In separations may be compared to those in currently known associated organoindium(I) compounds, which usually have very weak In-In interactions and long In... In distances. The In ••• In separation is 3.94-3.96 Å in hexameric [Cp*In]₆ (47), where it is believed that the metal-metal distances are dictated by the interactions of the six Cp* groups, which impose a longer metal-metal separation, 4.07-4.17 Å, in its more crowded gallium congener [Cp*Ga]6. 39b In · · · In separations of ca. 2.99-3.15 Å are observed in tetrameric [InC(SiMe₂Et)₃]₄ (48),^{39g} [InC(SiMe₂Prⁱ)₃]₄ (49),^{39g} and [InC(SiMe₃)₃]₄ (50),^{39d-f} and ca. 2.98–3.63 Å in dimeric Ar'InInAr' (51),²² [In{ η^{5} - $C_5(CH_2Ph)_5$]₂ (**52**),^{39c} and {In[(NMesCMe)_2CH]}₂ (**53**).^{39h} The



Figure 3. Thermal ellipsoid (50%) drawing of 16. Hydrogen atoms are not shown. Dihedral angles between In_2O_2 plane and C(1)-C(6) ring = 57.0°, C_6H_3 -2,6- Pr_2^i (centroid)-In range = 3.099-3.134 Å.

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 Table 3. Selected Structural Data for 16–19

	16	17	18 · 3.5C7H8	19 · 2.4C ₇ H ₈
M(1)-E(1) (Å)	2.3216(15)	2.579(3)	2.8434(14)	2.913(13)
M(1)-E(2) (Å)	2.3533(16)	$2.540(3)^{a}$	2.7987(14)	2.884(3)
M(2)-E(1) (Å)	2.3420(16)		2.8069(14)	2.884(3)
M(2)-E(2) (Å)	2.3147(15)		2.8261(15)	2.908(3)
C(1) - E(1) (Å)	1.357(2)	1.322(5)	1.772(5)	1.760(12)
C(1)-E(2) (Å)	1.356(3)		1.765(5)	1.763(11)
M(1)-E(1)-M(2) (deg)	100.99(6)	96.75(11)	111.33(4)	111.98(11)
M(1)-E(2)-M(2) (deg)	100.86(6)		112.10(5)	112.14(10)
E(1)-M(1)-E(2) (deg)	78.89(5)	81.84(11)	68.01(4)	67.83(9)
E(1)-M(2)-E(2) (deg)	79.26(5)		68.14(4)	67.91(9)
C(1)-E(1)-M(1) (deg)	133.49(13)	129.6(3)	121.90(17)	122.9(4)
C(1)-E(1)-M(2) (deg)	116.56(13)	$122.3(5)^{a}$	120.19(17)	121.2(4)
C(2)-C(1)-E(1) (deg)	120.41(19)	121.7(4)	120.4(4)	120.9(9)
C(32)-C(31)-E(1) (deg)	121.0(2)		120.5(4)	121.0(9)

^a Crytals of 13 have an inversion center, thus it generates E(1A) as E(2) and M(1A) as M(2).

In–O bond lengths in **16** [2.3216(15), 2.3533(16), 2.3420(16), and 2.3147(15) Å] are similar to the 2.320 Å (avg.) in the molecular compound [2,4,6-(CF₃)₃-C₆H₂OIn]₂ (**11**)^{18a} but are considerably shorter than the 2.58–2.65 Å in the In(I) triflate complex [CF₃SO₃In]₂ (**12**).^{18b} Compound **16** has In–O bonds ca. 0.3 Å longer than the 2.026(1) Å observed in **8**, which is, most probably, a consequence of the lower metal oxidation state in **16**. Compound **18** is the first structurally authenticated organoindium(I) thiolate and has In–S bonds in the range of 2.80–2.84 Å. These are ca. 0.4 Å longer than the 2.4123(13) and 2.4059(13) Å in **7**, as a consequence of the lower oxidation state and reduced ionic contribution to the bond strength.

Although the O₂In₂ array of **16** is planar with acute O–In–O angles of 78.89(5) and 79.26(5)° and In–O–In angles of 100.99(6) and 100.86(6)°, the S₂In₂ array of **18** is slightly folded [the dihedral angle between In(1)–S(1)–In(2) and In(1)– S(2)–In(2) = 171.4°] with highly acute S–In–S angles of 68.01(4) and 68.14(4)° and obtuse In–S–In angles of 111.33(5) and 112.10(5)°. The In(I) centers in **16** and **18** both feature close contacts with the flanking aryl ring of each Ar' ligand with In–C₆H₃-2,6-Prⁱ₂(centroid) distances ranging from 3.099 to 3.134 Å, while in **18**, In(I) metals symmetrically η^6 -coordinate to both flanking aryl rings on each Ar' ligand with In–C₆H₃-2,6-Prⁱ₂(centroid) distances that range from 3.144 to 3.177 Å. These In–arene distances are longer than ca. 2.83–2.89 Å



Figure 4. Thermal ellipsoid (50%) drawing of **18**. Hydrogen atoms are not shown. Fold angle of In_2S_2 [defined as dihedral angle between In(1)-S(1)-In(2) and $In(1)-S(2)-In(2)] = 171.4^\circ$, C₆H₃-2,6-Prⁱ₂(centroid)-In range = 3.144-3.177 Å.

spanned by $[(1,3,5-Me_3-C_6H_2)_2In][InBr_4]$ (54)^{40a} and shorter than 3.490(4) and 3.325(4) Å in $[(\eta^6-C_7H_8)In(\mu-\eta^5-C_5Me_5)In(\eta^6-C_7H_8)][(C_6F_5)_3BO(H)B(C_6F_5)_3]$ (55),^{40b} indicating that both 16 and 18 have a moderate In–arene interaction. The coordination geometry of the sulfurs in 18 is nearly planar [$\Sigma^{\circ}S(1) = 353.42$; $\Sigma^{\circ}S(2) = 357.55$]. This might be a result of the large Ar' substituent which enforces a nearly planar environment at sulfur upon dimerization. Greater bending at sulfur with the E–In–E and In–E–C angles of 68.1 (avg.) and 120.5° (avg.) in 18 is also observed, which are both ca. 11° smaller than those in 16. The related dimeric terphenyl thiolate alkali metal salts (Ar*SM)₂ (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-Prⁱ_3)_2; M = K-Cs) with similar S₂M₂ cores also feature flanking ring–metal ion interactions, which are determined by ionic sizes. The coordination geometry of the thiolato sulfurs varies from pyramidal to nearly planar on descending the group.⁴¹

Compounds **17** and **19** are a part of a growing class of structurally characterized Tl(I) derivatives of RE⁻ (R = alkyl, aryl, or related species; E = O and S; Figures 5 and 6). Tl(I) compounds with the formula of (ROTI)_n or (RSTI)_n have been shown to mainly aggregate as coordination polymers^{17i,k,42} or oligomers.^{17f,42a,43,44} The Tl–E bond lengths of 2.540(3) and 2.579(3) Å in **17** and 2.913(3), 2.884(3), 2.884(3), and 2.908(3) Å in **19** are within the range of 2.460–2.748 Å spanned by the previous reported alkoxide dimers (ROTI)₂ (R = N=C(CN)-COPh, **56**;^{43e} (3-Buⁱ-pyrazolyl)₃SO₂, **57**;^{43g} C₆H₂-2,4,6-(CF₃)₃, **58**;^{43b} and C₆H₅-2-(C₆H₅-2-OH), **59**^{43f}) and ca. 2.880–2.903 Å in the thiolate dimer [(BuⁱO)₃STI]₂ (**60**).⁴⁴ The Tl₂E₂ arrays of **17** and **19** are slightly folded (**17**, 160.6°; **19**, 175.2°) with acute

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Figure 5. Thermal ellipsoid (50%) drawing of **17**. Hydrogen atoms are not shown. Fold angle of Tl_2O_2 [defined as dihedral angle between Tl(1)-O(1)-Tl(1A) and Tl(1)-O(1A)-Tl(1A)] = 160.8°, C_6H_3 -2,6- Pr_2^i (centroid)-Tl range = 3.075-3.154 Å.

E–TI–E angles of 81.84(11)° in **17** and 67.87(9)° (avg.) in **19** as well as obtuse TI–E–TI angles of 96.75(11)° in **17** and 112.06(11)° (avg.) in **19**. The TI(I) centers in **17** and **19** also feature close contacts with the flanking rings of Ar' (TI– (centroid) distances range from 3.075 to 3.154 Å in **17** to 3.108–3.180 Å in **19**. These TI–arene distances are similar to ca. 2.94–3.03 and 2.94–3.35 Å spanned by $[Mes_2TIOTeF_5]_2$ (**63**),^{45a} { $[Mes_2TI][AlCl_4]_2$ (**62**),^{45b} and $[(Mes)_6TI_4(GaBr_4)_4]$ (**61**).^{45c} Furthermore, the TI–arene contacts in **17** are preserved in solution as shown by ¹³C NMR spectroscopy which had ¹³C–TI coupling to the ortho (52 Hz), meta (70 Hz), and paracarbons (37 Hz) of the dipp ring. The poor solubility of **19** in C₆D₆ and C₇D₈ prevented collection of usable ¹³C NMR data, and the TI–C coupling constants could not be extracted. A nearly planar coordination geometry of the sulfurs in **19** is also



Figure 6. Thermal ellipsoid (30%) drawing of **19**. Hydrogen atoms are not shown. Fold angle of Tl_2S_2 [defined as dihedral angle between Tl(1)-S(1)-Tl(2) and $Tl(1)-S(2)-Tl(2)] = 175.2^\circ$, C_6H_3 -2,6- Pr_2^i (centroid)-Tl range = 3.108-3.180 Å.

observed [$\Sigma^{\circ}S(1) = 357.2$; $\Sigma^{\circ}S(2) = 354.4$] with a greater bending angle [the E–Tl–E and Tl–E–C angles in **19** are ca. 14 and 10° smaller than those in **17**].

Conclusion

In summary, dimeric arylgallium/indium chalcogenides 7-10 of formula [Ar'ME]₂ (M = Ga or In; E = O or S) were synthesized and fully characterized. They feature three-coordinate, +3 oxidation state metal centers with planar M₂E₂ cores. Low oxidation heavier group 13/group 16 chalcogenolate isomers 16–19 of formula [Ar'EM]₂ (M = In or Tl; E = O or S) were also synthesized and fully characterized. The In +1 compounds [Ar'EIn]₂ (O, 17; S, 19) together, with the In +3 species [Ar'InE]₂ (O, 8; S, 10), represent the first structurally characterized isomeric pairs of organo group 13 metal/chalcogen derivatives. The difficulties encountered in synthesizing the Ga(I) chalcogenolates and Tl(III) chalcogenides reflect the increasing stabilization of the s-valence electrons descending the group.

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Supporting Information Available: X-ray data (CIFs) for 7–10 and 16–19 plus thermal ellipsoidal plots of 8 and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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