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A Structural Investigation of Dimethylthallium(III) Thiolate and Selenolate Rings and Polymers

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The effects of increased steric bulk in dimethylthallium(III) chalcogenolates on oligomerization was examined. The facile reaction of Me_3Tl with a series of benzenethiols and -selenols in toluene or thf resulted in the formation of $[Me_2TlS(2,6\text{-}Me_2C_6H_3)]_\infty$ (**2**), $[Me_2TlS(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**3**), $[Me_2TlSe(C_6H_5)]_2$ (**4**), $[Me_2TlSe(2,4,6\text{-}Me_3C_6H_2)]_\infty$ (**5**), and $[Me_2TlSe(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**6**). The solid-state structure of **4** is dimeric with short intermolecular Tl···Se interactions, which yields an asymmetric Tl_2Se_2 core and a distorted tetrahedral C_2Se_2 bonding environment for the thallium. The increase in the steric bulk of the chalcogenolate ligand in compounds **2** and **5** results in the formation of polymeric structures with μ-E[2,(4),6-$Me_3C_6H_2$] (E = S, Se) groups and distorted tetrahedral C_2E_2 bonding environments for the thallium. A further increase in the steric bulk of the phenylchalcogenolate resulted in the formation of chains of weakly coordinated monomers by means of the intermolecular Tl···E interactions in **3** (E = S) and **6** (E = Se). This work represents the first systematic study of diorganothallium thiolates and selenolates and compounds **4**–**6** represent the first structurally characterized examples of R_2TlSeR' species. A comparison of the structures of $[Me_2TlS(C_6H_5)]_2$ (**1**) and **2**–**6** with other group 13 analogue structures suggests that the degree of oligomerization differs for $[Me_2MSR']_n$ (M = Tl) versus the analogous (M = Al, Ga, and In) species. These findings are important in understanding the factors that govern oligomerization (i.e. ring size) and polymerization of diorganotriel chalcogenolates.

Introduction

Inorganic rings and polymers of the *p*-block elements continue to be extensively studied due to their interesting structural and bonding properties, as well as their applications as precursors for useful materials.[1,2] In particular, the diorganochalcogenolate compounds of the group 13 elements $[R_2MER']_n$ (where M = Al, Ga, In and E = S, Se, Te; M = Tl and E = O) have been studied for a number of years as potential precursors for the fabrication of group 13 to 16 semiconducting thin films by means of various chemical vapor deposition techniques.[3–6] Structural studies have shown that the vast majority of these compounds are dimeric in the solid-state (Figure 1, $n = 2$).[7] However, examples of oligomeric ($n = 3$, 4) and polymeric ($n = \infty$) structures have been observed for the dimethyltriel thiolate $[Me_2MSR']_n$ compounds, such as $[Me_2InStBu]_3$, $[Me_2MS(2,6\text{-}Me_2C_6H_3)]_4$ (M = Al, Ga, In), and $[Me_2AlSPh]_\infty$.[8–10] Our studies of $[Me_2InER']_n$ (E = O, S, Se) and $[Me_2TlOR']_n$ species that incorporated chalcogenolate ligands with varying steric bulk [R′ = C_6H_5, 2,(4),6-$Me_3C_6H_2$, 2,4,6-$tBu_3C_6H_2$] expanded this series to include monomeric ($n = 1$) and weakly associated polymeric ($n = 1, \infty$) structures.[11,12]

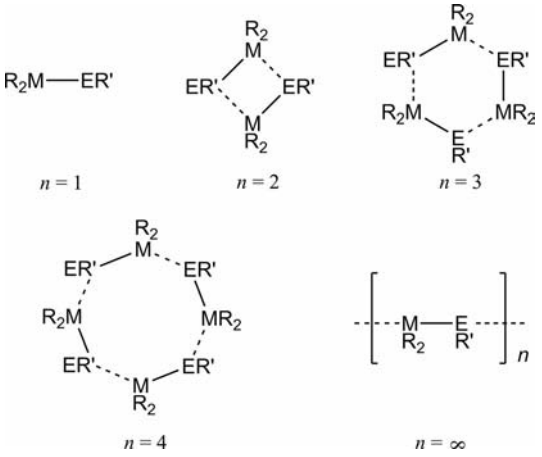

Figure 1. The schematic drawings of the possible oligomers of $[R_2MER']_n$.

Despite the extensive number of studies that have been devoted to this class of compounds, the diorganothallium selenolate analogues $[R_2TlSeR']_n$ are virtually unknown. Furthermore, structural studies of the simple diorganothallium thiolate analogues $[R_2TlSR']_n$ (i.e. where R′ does not

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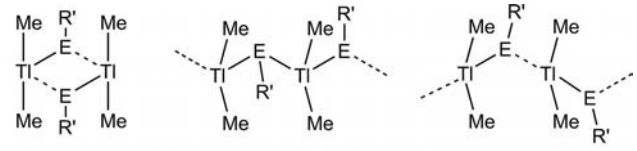
possess donor atoms) are limited to $[Me_2TlSPh]_2$ (**1**), which exhibits a dimeric (n = 2) structure in the solid-state and an asymmetric Tl_2S_2 core.[13] The Me_2TlEMe (E = S, Se) compounds were also reported some time ago but were characterized by elemental analysis and molecular weight determination only, the latter of which suggested that they are both dimeric in the solid-state.[14,15] To further expand our previous studies of the $[Me_2TlOR']_n$ species, and in order to compare their structures with those of the Al, Ga, and In analogous, we have synthesized and structurally characterized $[Me_2TlS(2,6\text{-}Me_2C_6H_3)]_\infty$ (**2**), $[Me_2TlS(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**3**), $[Me_2TlSe(C_6H_5)]_2$ (**4**), $[Me_2TlSe(2,4,6\text{-}Me_3C_6H_2)]_\infty$ (**5**), and $[Me_2TlSe(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**6**).



Results and Discussion

Syntheses and Spectroscopic Characterization

Compounds **1**–**6** were prepared by means of a hydrocarbon elimination reaction between trimethylthallium and the corresponding thiol or selenol compound. All of the reactions occurred rapidly at room temperature with the evolution of methane gas. The reaction mixtures were stirred for one hour and then filtered in order to remove any of the precipitated product. The crystalline materials were isolated by means of slow evaporation of the reaction mixtures or by means of solvent layering. Although all of the reactions were quantitative, as determined by the ^1H NMR spectra of the reaction mixtures, the reported yields (28–80%) are for the crystalline material that was obtained from the reaction filtrate. $[Me_2TlSPh]_2$ (**1**) has been previously synthesized by the stoichiometric reaction of $(Me_2Tl)(CO_3)$ or Me_2TlOH with PhSH.[16,17] However, these syntheses require the preparation of the hydroxide or carbonate from Me_3Tl and are therefore less direct routes to **1**. The attempts to prepare $[Me_2TlTePh]_n$ by means of the reaction of Me_3Tl and C_6H_5TeH or Me_2TlBr and C_6H_5TeLi in thf at –90 °C resulted in the precipitation of elemental tellurium when the reaction mixtures were warmed to room temperature.

The FT-Raman spectra of compounds **1**–**6** show a strong resonance in the 457 to 474 cm^{-1} region. This corresponds to the ν_{sym}(Me–Tl–Me) stretching mode and is a characteristic feature in the spectra of the Me_2TlX compounds.[15–17] Furthermore, the ^1H and $^{13}C\{^1H\}$ NMR spectra show readily discernible doublet patterns for the Me_2TlER' resonances as a result of the $^2J(^1H,^{203/205}Tl)$ and $^1J(^{13}C,^{203/205}Tl)$ couplings, respectively. The observed ν_{asym}(Me–Tl–Me) vibrational frequencies, the chemical shift values (^1H NMR, δ = 0.39–1.13 ppm; $^{13}C\{^1H\}$ NMR δ = 18.0–40.6 ppm), and the coupling constants ($^2J_{H,Tl}$ = 346–372 Hz; $^1J_{C,Tl}$ = 2225–3434 Hz) do not correspond to the changes in the C_{Me}–Tl–C_{Me} bond angle or the Tl–E bond lengths observed in the solid-state structures (vide infra).

X-ray Crystal Structures

Crystals that were suitable for X-ray crystallographic analysis were isolated for compounds **2**–**6** by the slow evaporation of the reaction mixtures at 23 °C. The selected bond lengths and angles for **1** and **3** to **6** are given in Table 1.

Table 1. The selected bond lengths [Å] and angles [°] for **1** and **3**–**6**.[a]

	1[13]	**3**	**4**	**5**	**6**
Tl1–C1	2.10(3)	2.158(4)	2.156(9)	2.173(8)	2.156(5)
Tl1–C2	2.11(3)	2.163(5)	2.146(10)	2.167(7)	2.156(5)
Tl1–E1	2.748(8)	2.7185(9)	3.1741(9)	2.859(1)	2.8057(5)
Tl1–E1*	2.991(8)	2.9969(9)	2.848(1)	2.8865(9)	3.0149(5)
C1–Tl1–C2	163.5(9)	158.4(2)	164.3(3)	154.9(4)	158.0(2)
E1–Tl1–E1*		120.13(1)	92.64(2)	107.16(2)	115.19(1)
Tl1–E1–Tl1*		140.64(4)	87.36(2)	119.66(3)	145.16(2)

[a] E = S (**1**, **3**), Se (**4**–**6**).

Despite several attempts in various solvents, crystals of $[Me_2TlS(2,6\text{-}Me_2C_6H_3)]_\infty$ (**2**) that were of sufficient quality for the adequate refinement of the X-ray crystallographic data could not be obtained.[18] However, the preliminary data was sufficient in order to confirm that the compound exists as a polymer in the solid-state with bridging μ-S(2,6-$Me_2C_6H_3$) groups, which give a four-coordinate C_2S_2 bonding environment and a distorted tetrahedral geometry at the thallium.

The structure of $[Me_2TlS(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**3**) (Figure 2) shows a polymer with μ-S(2,4,6-$tBu_3C_6H_2$) bridging

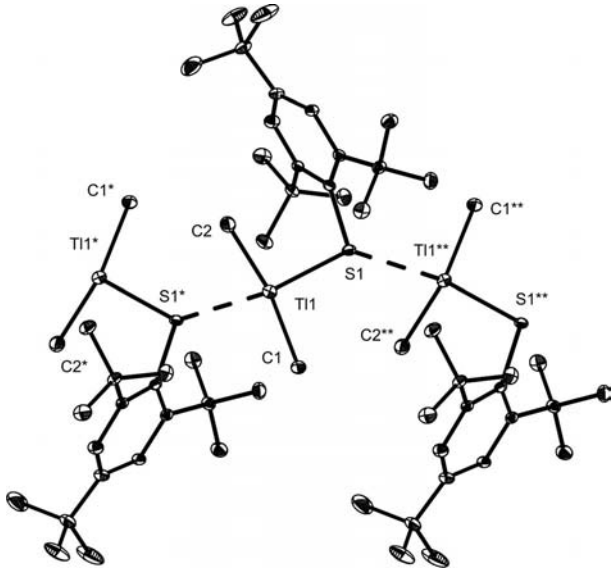


Figure 2. The X-ray crystal structure of **3** (30% probability ellipsoids). The hydrogen atoms are not shown for the sake of clarity. The symmetry transformations that were used to generate the equivalent atoms are (*) $-x$, $-0.5 + y$, $0.5 - z$ and (**) $-x$, $0.5 + y$, $0.5 - z$.

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groups. The Tl–S bond lengths are significantly different [Tl1–S1 2.7185(9) Å, Tl1–S1* 2.9969(9) Å] with the Tl1–S1* bond approximately 0.18 Å longer than the Tl1–S1 bond. Furthermore, the sum of the C1–Tl1–C2 [158.4(2)°], C1–Tl1–S1 [97.6(1)°], and C2–Tl1–S1 [100.9(1)°] bond angles is approximately 357°. This suggests that a distorted T-shaped C_2S bonding environment exists at Tl with a weak intermolecular Tl···S interaction. The polymeric structure may therefore be viewed as being composed of weakly associated monomers.

The structure of $[Me_2TlSe(C_6H_5)]_2$ (**4**) (Figure 3) is similar to that of **1** and shows that the compound is a dimer in the solid-state and is linked by means of intermolecular Tl···Se interactions. It exhibits a four-membered [–Tl–Se–Tl–Se–] ring core and a distorted tetrahedral C_2Se_2 bonding environment for the thallium. Like **1**, and unlike the phenolate analogue $[Me_2TlOPh]_2$,[12] the Tl–E bond lengths [Tl1–Se1 3.1741(9) Å, Tl1–Se2 2.848(1) Å] are significantly different and the structure may be considered a weakly associated dimer. The sum of the bond angles at Se in **4** is approximately 297° and the phenyl groups are in a *trans* orientation.

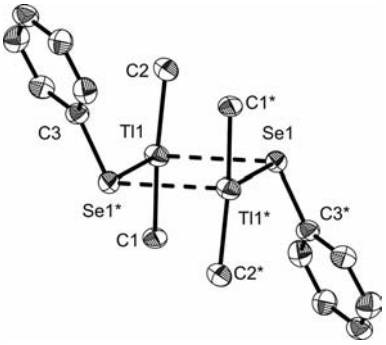

Figure 3. The X-ray crystal structure of **4** (30% probability ellipsoids). The hydrogen atoms are not shown for the sake of clarity. The symmetry transformations that were used to generate the equivalent atoms are (*) 1 – *x*, –*y*, 1 – *z*.

The X-ray crystal structure of $[Me_2TlSe(2,4,6\text{-}Me_3C_6H_2)]_\infty$ (**5**) (Figure 4) shows that the compound is a polymer in the solid-state and is linked by means of bridging μ-Se(2,4,6-$Me_3C_6H_2$) groups, which gives a four-coordinate C_2Se_2 bonding environment and a distorted tetrahedral geometry at the thallium. The Tl–C [Tl1–C1 2.173(8) Å, Tl1–C2 2.167(7) Å] and Tl–Se [Tl1–Se1 2.859(1) Å, Tl1–Se1* 2.8865(9) Å] bond lengths are similar to those obtained for **4**. However, both the Se1–Tl1–Se1* [107.16(2)°] and Tl1–Se1–Tl1* [119.66(3)°] bond angles of **5** are significantly larger than those observed in **4**, which is a result of the polymeric structure of **5** versus the dimeric structure of **4**. The Tl1–E1 and Tl1–E1* bond lengths in **5** [Tl1–Se1 2.859(1) Å, Tl1–Se1* 2.8865(9) Å] are similar and each of the selenolate groups is equally associated with the two neighbouring Tl atoms. The (2,4,6-$Me_3C_6H_2$) groups alternate along the [–Tl–Se–]$_\infty$ chain in a syndiotactic-type of arrangement.

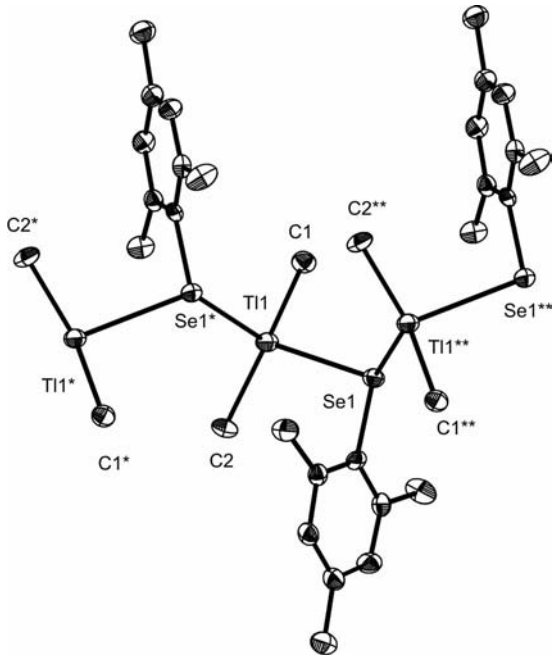

Figure 4. The X-ray crystal structure of **5** (30% probability ellipsoids). The hydrogen atoms are not shown for the sake of clarity. The symmetry transformations that were used to generate the equivalent atoms are (*) 1 – *x*, –*y*, –0.5 + *z* and (**) 1 – *x*, –*y*, 0.5 + *z*.

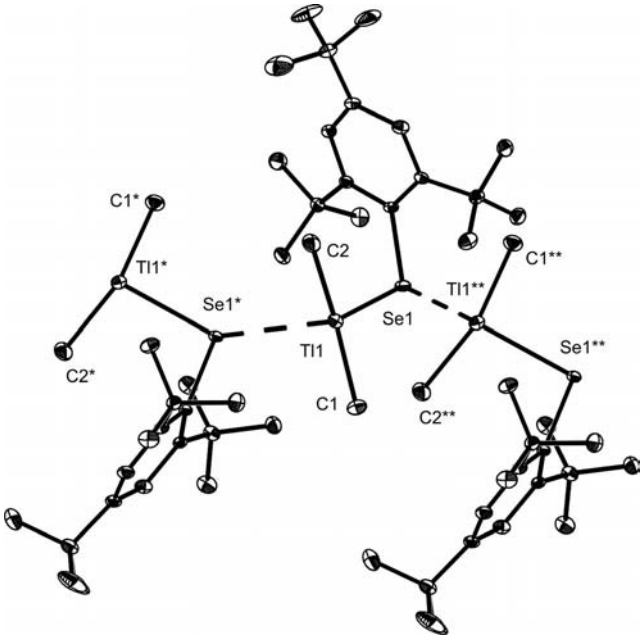

Figure 5. The X-ray crystal structure of **6** (30% probability ellipsoids). The hydrogen atoms are not shown for the sake of clarity. The symmetry transformations that were used to generate the equivalent atoms are (*) –*x*, –0.5 + *y*, 0.5 – *z* and (**) –*x*, 0.5 + *y*, 0.5 – *z*.

$[Me_2TlSe(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (**6**) (Figure 5) is isostructural with **3** and shows a weakly associated polymeric structure that is linked by means of the μ-Se(2,4,6-$tBu_2C_6H_3$) bridging groups. As in **3**, the Tl–E bond lengths

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are significantly different [Tl1–Se1 2.8057(5) Å, Tl1–Se1* 3.0149(5) Å]. In this case, however, the percentage difference in the Tl–E bond length (7%) is not great as that found for the corresponding bond length in **3** (10%), which suggests that a stronger secondary interaction exists and that **6** is a more tightly bonded polymer. This is presumably a result of the larger atomic radius of Se versus S. As in **3**, the sum of the C1–Tl1–C2 [158.0(2)°], C1–Tl1–E1 [97.17(14)°], and C2–Tl1–E1 [101.40(15)°] bond angles is approximately 357°, which gives a distorted T-shaped C_2Se bonding environment at Tl with a weak intermolecular Tl···Se interaction.

Comparison to Previously Reported $[RMER']_n$ Structures

The Tl–C bond lengths of **3**–**6** are within the range of those reported for the $[Me_2TlER']_n$ (E = O, S) compounds [2.05(4)–2.20(7) Å].[13,19,20] The C_{Me}–Tl–C_{Me} bond angles in **1** [163.5(9)°][13] and **4** [164.3(3)°] are similar to those observed in the dimeric $[Me_2TlOR']_2$ complexes [156.9(2)–171.9(2)°].[12] This results in a distorted see-saw type of geometry at Tl, despite the absence of a valence lone pair of electrons. Furthermore, the C_{Me}–Tl–C_{Me} bond angles in **3**–**6** are approximately 14 to 26° greater than the C_{Me}–In–C_{Me} bond angles in the corresponding indium analogues.[11]

The majority of the previously reported $[R_2MER']_n$ (M = Al, Ga, In; E = O, S, Se, Te) compounds exhibit dimeric (n = 2) structures in the solid-state.[7] Other oligomers typically contain methyl groups on the group 13 metal (R = Me), and have sulfur or selenium as the chalcogen (E = S, Se) (Table 2).[9,10] Our structural and computational studies of the indium complexes $[R_2InER']_n$ (E = O, S, Se) have shown that the nature of the chalcogen, as well as the steric properties of the R and R′ groups, are important in determining the degree of oligomerization in these compounds.[11] The compounds that have E = O are dimeric with strong intermolecular In···O bonds, unless R′ is sufficiently bulky (i.e. R′ = 2,4,6-tBu$_3$C$_6$H$_2$) to preclude dimerization in which case a monomeric structure is observed. Alternatively, $[Me_2InER']_n$ (E = S, Se) compounds exhibit dimeric, trimeric, tetrameric, polymeric, and weakly associated polymeric structures, which depends on the nature of the R′ group.

A comparison between the $[Me_2InER']_n$ and $[Me_2TlER']_n$ compounds (Table 2) shows that they have similar structures and degrees of oligomerization for most of the combinations of E and R′, with the exception of E = S, R′ = C_6H_5 and E = S, R′ = 2,(4),6-$Me_3C_6H_2$. If these –SR′ analogues are specifically considered, we see that $[Me_2MSC_6H_5]_n$ (M = Al, In) both exhibit similar polymeric structures, while M = Tl has a dimeric structure. In addition, $\{Me_2MS[2,(4),6\text{-}Me_3C_6H_2]\}_n$ (M = Al, Ga, In) all show tetrameric structures, while M = Tl is polymeric. This demonstrates that the degree of oligomerization in the $[Me_2MER']_n$ species is affected not only by the choice of chalcogen (i.e. S/Se vs. O) but also by the triel metal atom (i.e. Tl vs. Al/Ga/In).

Conclusions

Despite the large number of structural studies of diorgano group 13 chalcogenolates, this work represents the first systematic study of diorganothallium thiolate and selenolate analogues, and the first structurally characterized examples of the diorganothallium selenolates. The observed solid-state structures of **1**–**6** suggest that the degree of oligomerization of $[Me_2TlER']_n$ (E = S, Se) may be varied upon altering the steric bulk of the R′ ligand. However, similar structures are observed when E = S or Se for a given R′ group. A comparison of these structures to previously reported $[Me_2TlOR']_n$ solid-state structures further demonstrated that the degree of oligomerization in the $[Me_2MER']_n$ species may be affected by the choice of chalcogen (i.e. S/Se vs. O). A comparison between compounds **1**–**6** and the corresponding $[Me_2MSR']_n$ (M = Al, Ga, In) analogues demonstrated that the observed structures are also affected by the triel metal atom (i.e. Tl vs. Al/Ga/In). These findings are important in understanding the factors that govern oligomerization (i.e. ring size) and polymerization in diorganotriel chalcogenolates.

Experimental Section

General Remarks: The solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 23 °C with either a JEOL GMX 270 MHz + spectrometer (270 and 67.9 MHz, respectively) or a Varian Mercury 200 MHz + spectrometer (200 and 50 MHz, respectively), and the chemical shifts are calibrated to the residual solvent signal. The FTIR spectra were recorded as Nujol mulls with NaCl plates with a Mattson Genesis II FTIR spectrometer in the range of 4000 to 400 cm^{-1}. The FT-Raman spectra were recorded with a Thermo Nicolet NXR 9600 Series FT-Raman spectrometer in the range of 3900 to 70 cm^{-1}. The melting points were recorded with an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. The elemental analyses were performed by Chemisar Laboratories Inc., Guelph, Ontario. 2,6-Dimethylbenzenethiol (95%), benzeneselenol (97%), mesitylmagnesium bromide (1.0 M in diethyl ether), 1-bromo-2,4,6-tri-*tert*-butylbenzene (99%), selenium powder (–100 mesh, 99.5+%), butyllithium (1.6 M in hexanes), lithium aluminum hydride powder (95%), methyllithium (1.6 M in diether ether), thallium(I) iodide (99.999%), iodomethane (99.5%), and

Table 2. The degree of oligomerization of the $[Me_2MER']_n$ (M = Al, Ga, In, Tl; E = O, S, Se) species [E (n)].

R′	Al	Ga	In	Tl
C_6H_5	S (∞)[a]	–	O (2),[b] S (∞),[b] Se (2)[b]	O (2),[c] S (2),[d] Se (2)[d]
2,(4),6-$Me_3C_6H_2$	S (4)[e]	S (4)[e]	O (2),[b] S (4),[f] Se (∞)[b]	O (2),[c] S (∞),[d] Se (∞)[d]
2,4,6-tBu$_3$C$_6$H$_2$	–	–	O (1),[b] S (1/∞),[b] Se (1/∞)[b]	O (1),[c] S (1/∞),[d] Se (1/∞)[d]

[a] Ref.[10] [b] Ref.[11] [c] Ref.[12] [d] This work. [e] Ref.[9b] [f] Ref.[9a] (1/∞) represents a weakly associated polymer.

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sulfur powder (99.98%) were purchased from the Aldrich Chemical Co. Toluene and tetrahydrofuran were dried by means of an MBraun SPS column solvent purification system. All of the reactions were performed under an atmosphere of inert dinitrogen by using the standard Schlenk technique. 2,4,6-Trimethylbenzeneselenol, 2,4,6-tri-*tert*-butylbenzenethiol, and 2,4,6-tri-*tert*-butylbenzeneselenol were prepared by the literature methods.[11,21] Me_3Tl was prepared by a modified literature procedure as indicated below.[22,23]

Caution: Thallium is a cumulative poison that may be absorbed through the skin. All compounds must be handled with extreme care.

Me_3Tl: TlI (9.1 g, 27 mmol) was added to a solution of MeI (4.6 g, 32 mmol) in diethyl ether (30 mL) and the stirred suspension was cooled to –100 °C. Methyllithium (1.6 M in diethyl ether, 38 mL, 61 mmol) was added dropwise over a 15 min period. The cold bath was then removed and the reaction mixture was warmed to 23 °C. After stirring for 18 h, the solvent was removed in vacuo. The crude product was gradually heated to 88 °C (≈ 1 °C/min) under dynamic vacuum and the colorless crystals of Me_3Tl were collected by fractional sublimation with an inline trap held at –30 °C (4.1 g, 16 mmol, 61%). ^{1}H NMR ([D$_8$]thf): δ = 0.26 [d, $^2J_{Tl\text{-}H}$ = 266 Hz, 9 H, *Me*$_3$Tl] ppm.

Caution: Me_3Tl detonates above approximately 90 °C,[22] therefore the sublimation temperature must be monitored closely.

[$Me_2TlS(C_6H_5)]_2$ (1): C_6H_5SH (0.110 g, 1.00 mmol) was added to a solution of $TlMe_3$ (0.250 g, 1.00 mmol) in toluene (8 mL). The solution was stirred at room temperature for 1 h and filtered to yield **1** (0.165 g, 0.479 mmol, 48%). $C_{16}H_{22}S_2Tl_2$ (687.21): calcd. C 27.96, H 3.23, N 0.00; found C 28.13, H 3.18, N < 0.10; m.p. 194–196 °C. FTIR: $\tilde{\nu}$ = 698 (s), 738 (vs), 791 (vs), 908 (w), 980 (w), 1024 (m), 1066 (m), 1082 (m), 1153 (w), 1261 (w), 1300 (w), 1400 (w), 1435 (s), 1568 (m), 1581 (m), 1643 (vw), 1714 (vw), 1745 (vw), 1807 (vw), 1871 (w), 1946 (w), 2308 (w), 3008 (m), 3055 (m) cm^{-1}. FT-Raman: 117 (m), 166 (m), 323 (w), 310 (vw), 419 (vw), 474 [vs, ν_{sym}(Me–Tl–Me)], 530 (w), 616 (vw), 697 (w), 791 (vw), 1002 (m), 1023 (m), 1082 (m), 1117 (vw), 1155 (w), 1171 (m), 1436 (vw), 1581 (w), 2917 (m), 3010 (w), 3058 (m), 3134 (vw) cm^{-1}. ^{1}H NMR ([D$_6$]dmso): δ = 1.01 [d, $^2J_{Tl\text{-}H}$ = 372 Hz, 6 H, *Me*$_2$TlS(C$_6$H$_5$)], 7.14 [m, 1 H, Me$_2$TlS(C$_6$*H*$_5$)], 7.32 [m, 2 H, Me$_2$TlS(C$_6$*H*$_5$)], 7.51–7.56 [m, 2 H, Me$_2$TlS(C$_6$*H*$_5$)] ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 20.2 [d, $^1J_{Tl\text{-}13C}$ = 2913 Hz, *Me*$_2$TlS(C$_6$H$_5$)], 122.4 [s, Me$_2$TlS(*C*$_6$H$_5$)], 127.9 [s, Me$_2$TlS(*C*$_6$H$_5$)], 134.2 [s, Me$_2$TlS(*C*$_6$H$_5$)], 146.2 [s, Me$_2$TlS(*C*$_6$H$_5$)] ppm.

[$Me_2TlS(2,6\text{-}Me_2C_6H_3)]_\infty$ (2): 2,6-$Me_2C_6H_3SH$ (0.111 g, 0.802 mmol) was added to a solution of $TlMe_3$ (0.200 g, 0.802 mmol) in toluene (8 mL). The solution was stirred at room temperature for 1 h, filtered, and concentrated to 3 mL. The resulting colorless product was then dissolved in thf (4 mL). The solution was allowed to sit at 4 °C for 1 d and filtered to yield **2** as colorless crystals (0.127 g, 0.341 mmol, 43%). $C_{10}H_{15}STl$ (371.66): calcd. C 32.32, H 4.07, N 0.00; found C 32.46, H 4.25, N < 0.10; m.p. 205 °C. FTIR: $\tilde{\nu}$ = 588 (w), 656 (vw), 721 (w), 760 (m), 903 (w), 982 (vw), 1014 (vw), 1051 (w), 1080 (vw), 1163 (vw), 1246 (w), 1259 (w), 1321 (vw), 1539 (w), 1579 (w) cm^{-1}. FT-Raman: 116 (s), 236 (w), 422 (vw), 461 [vs, ν_{sym}(Me–Tl–Me)], 518 (w), 589 (w), 767 (m), 1056 (m), 1116 (vw), 1166 (m), 1248 (m), 1376 (vw), 1401 (vw), 1429 (vw), 1458 (vw), 1583 (m), 2840 (vw), 2915 (m), 3008 (w), 3052 (w) cm^{-1}. ^{1}H NMR ([D$_8$]thf): δ = 0.69 [d, $^2J_{Tl\text{-}H}$ = 372 Hz, 6 H, *Me*$_2$TlS(2,6-Me$_2$C$_6$H$_3$)], 2.43 [s, 6 H, Me$_2$TlS(2,6-*Me*$_2$C$_6$H$_3$)], 6.67 [t, $^3J_{H\text{-}H}$ = 7.0 Hz, 1 H, Me$_2$TlS(2,6-Me$_2$C$_6$*H*$_3$)], 6.93 [$^3J_{H\text{-}H}$ = 7.0 Hz, 2 H, Me$_2$TlS(2,6-Me$_2$C$_6$*H*$_3$)] ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 18.0 [d, $^1J_{Tl\text{-}13C}$ = 2648 Hz, *Me*$_2$TlS(2,6-Me$_2$C$_6$H$_3$)], 23.5 [s, Me$_2$TlS(2,6-*Me*$_2$C$_6$H$_3$)], 122.4 [s, Me$_2$TlS(2,6-Me$_2$*C*$_6$H$_3$)], 126.1 [s, Me$_2$TlS(2,6-Me$_2$*C*$_6$H$_3$)], 140.9 [s, Me$_2$TlS(2,6-Me$_2$*C*$_6$H$_3$)], 142.4 [s, Me$_2$TlS(2,6-Me$_2$*C*$_6$H$_3$)] ppm.

[$Me_2TlS(2,4,6\text{-}tBu_3C_6H_2)]_\infty$ (3): 2,4,6-$tBu_3C_6H_2SH$ (0.223 g, 0.802 mmol) was added to a solution of $TlMe_3$ (0.200 g, 0.802 mmol) in toluene (8 mL). The solution was stirred at room temperature for 1 h, filtered and concentrated to 6 mL. The solution was allowed to sit at 4 °C for 1 d and filtered to yield **3** as colorless crystals (0.328 g, 0.641 mmol, 80%). $C_{20}H_{35}STl$ (511.93): calcd. C 46.92, H 6.89, N 0.00; found C 47.25, H 7.08, N < 0.10; m.p. 329 °C. FTIR: $\tilde{\nu}$ = 646 (w), 723 (w), 754 (m), 779 (s), 876 (m), 920 (vw), 1022 (w), 1038 (m), 1095 (w), 1163 (w), 1213 (m), 1238 (m), 1259 (w), 1281 (vw), 1358 (m), 1406 (m), 1591 (m), 2305 (vw), 2370 (vw) cm^{-1}. FT-Raman: 143 (s), 171 (s), 256 (w), 333 (vw), 460 [vs, ν_{sym}(Me–Tl–Me)], 518 (vw), 566 (w), 611 (w), 779 (vw), 823 (w), 927 (vw), 1039 (m), 1129 (w), 1164 (m), 1185 (vw), 1282 (vw), 1381 (vw), 1448 (w), 1591 (m), 2701 (vw), 2913 (s), 2963 (s), 2996 (w), 3026 (w), 3105 (vw) cm^{-1}. ^{1}H NMR ([D$_8$]thf): δ = 0.89 [d, $^2J_{Tl\text{-}H}$ = 356 Hz, 6 H, *Me*$_2$TlS(2,4,6-*t*Bu$_3$C$_6$H$_2$)], 1.63 [s, 9 H, Me$_2$TlS(2,4,6-*tBu*$_3$C$_6$H$_2$)], 1.96 [s, 18 H, Me$_2$TlS(2,4,6-*tBu*$_3$C$_6$H$_2$)], 7.62 [s, 2 H, Me$_2$TlS(2,4,6-*t*Bu$_3$C$_6$*H*$_2$)] ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 19.3 [d, $^1J_{Tl\text{-}13C}$ = 2225 Hz, *Me*$_2$TlS(2,4,6-*t*Bu$_3$C$_6$H$_2$)], 31.4 [s, Me$_2$TlS(2,4,6-*tBu*$_3$C$_6$H$_2$)], 31.7 [s, Me$_2$TlS(2,4,6-*tBu*$_3$C$_6$H$_2$)], 34.3 [s, Me$_2$TlS(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 37.4 [s, Me$_2$TlS-(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 37.9 [s, Me$_2$TlS(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 120.2 [s, Me$_2$TlS(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 114.1 [s, Me$_2$TlS(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 152.2 [s, Me$_2$TlS(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)] ppm.

[$Me_2TlSe(C_6H_5)]_2$ (4): C_6H_5SeH (0.126 g, 0.802 mmol) was added to a solution of $TlMe_3$ (0.200 g, 0.802 mmol) in thf (8 mL). The solution was stirred at room temperature for 1 h and filtered to remove the precipitated product. The solution was then concentrated to 4 mL and was allowed to sit at 4 °C for 1 d. The colorless crystals of **4** were then collected by filtration (0.114 g, 0.292 mmol, 36%). $C_{16}H_{22}Se_2Tl_2$ (781.01): calcd. C 24.61, H 2.84, N 0.00; found C 24.26, H 3.16, N < 0.10; m.p. 207 °C. FTIR: $\tilde{\nu}$ = 696 (s), 733 (vs), 785 (vs), 1020 (m), 1065 (m), 1151 (m), 1261 (w), 1296 (w), 1396 (w), 1433 (vs), 1572 (m), 1745 (vw), 1871 (vw), 1948 (w), 2301 (vw), 3006 (m), 3055 (w) cm^{-1}. FT-Raman: 144 (s), 199 (m), 253 (w), 307 (vw), 469 [vs, ν_{sym}(Me–Tl–Me)], 526 (w), 615 (w), 668 (w), 788 (w), 1002 (s), 1020 (w), 1070 (m), 1153 (w), 1167 (w), 1575 (w), 2913 (m), 3007 (w), 3057 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.13 [d, $^2J_{Tl\text{-}H}$ = 346 Hz, 6 H, *Me*$_2$TlSe(C$_6$H$_5$)], 7.11 [m, 3 H, Me$_2$TlSe(C$_6$*H*$_5$)], 7.35 [m, 2 H, Me$_2$TlSe(C$_6$*H*$_5$)] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 40.6 [d, $^1J_{Tl\text{-}13C}$ = 3434 Hz, *Me*$_2$TlSe(C$_6$H$_5$)], 125.4 [s, Me$_2$TlS(*C*$_6$H$_5$)], 128.6 [s, Me$_2$TlS(*C*$_6$H$_5$)], 135.6 [s, Me$_2$TlS(*C*$_6$H$_5$)] ppm.

[$Me_2TlSe(2,4,6\text{-}Me_3C_6H_2)]_\infty$ (5): 2,4,6-$Me_3C_6H_2SeH$ (0.159 g, 0.802 mmol) was added to a solution of $TlMe_3$ (0.200 g, 0.802 mmol) in thf (8 mL). The solution was stirred at room temperature for 1 h, filtered, and concentrated to 4 mL. The solution was allowed to sit at 4 °C for 1 d and filtered to yield **5** as colorless needle crystals (0.096 g, 0.222 mmol, 28%). $C_{11}H_{17}SeTl$ (432.59): calcd. C 30.55, H 3.96, N 0.00; found C 30.77, H 3.98, N < 0.10; m.p. 197 °C. FTIR: $\tilde{\nu}$ = 706 (w), 723 (m), 789 (s), 850 (s), 879 (w), 951 (w), 1020 (s), 1093 (w), 1159 (m), 1261 (m), 1296 (m), 1599 (w), 1726 (vw), 1759 (vw), 2305 (w), 2357 (vw), 2725 (w) cm^{-1}. FT-Raman: 115 (vs), 143 (s), 330 (w), 464 [vs, ν_{sym}(Me–Tl–Me)], 518 (w), 540 (w), 779 (vw), 1021 (w), 1094 (vw), 1165 (m), 1294 (m), 1378 (w), 1599 (m), 2911 (s), 3002 (m) cm^{-1}. ^{1}H NMR ([D$_8$]thf): δ = 0.78 [d, $^2J_{Tl\text{-}H}$ = 368 Hz, 6 H, *Me*$_2$TlSe(2,4,6-Me$_3$C$_6$H$_2$)], 2.25 [s, 3 H, Me$_2$TlSe(2,4,6-*Me*$_3$C$_6$H$_2$)], 2.46 [s, 6 H, Me$_2$TlSe(2,4,6-

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Table 3. Crystallographic data for **3**–**6**.

	3	**4**	**5**	**6**
Empirical formula	$C_{20}H_{35}STl$	$C_{16}H_{22}Se_2Tl_2$	$C_{11}H_{17}SeTl$	$C_{20}H_{35}SeTl$
Fw	511.91	781.00	432.58	558.81
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	*P*2(1)/*c*	*Pbca*	*Pca*2(1)	*P*2(1)/*c*
a [Å]	13.1663(13)	11.9139(17)	22.887(6)	13.2032(17)
b [Å]	9.1552(9)	7.5855(11)	7.0094(17)	9.2144(12)
c [Å]	17.2455(16)	21.023(3)	7.6804(19)	17.350(2)
α [°]	90	90	90	90
β [°]	92.5450(10)	90	90	92.924(2)
γ [°]	90	90	90	90
V [Å^3]	2076.7(3)	1899.9(5)	1232.1(5)	2108.0(5)
Z	4	4	4	4
F(000)	1008	1392	792	1080
ρ_{calcd} (g cm^{-3})	1.637	2.730	2.332	1.761
μ [mm^{-1}]	7.875	20.763	16.020	9.386
T [K]	173(1)	198(1)	173(1)	173(1)
Reflections collected	13580	10950	7935	13891
Independent reflections (R_{int})	4642 (0.0538)	2139 (0.1049)	2644 (0.0763)	4685 (0.0649)
R_1[a]	0.0303	0.0619	0.0347	0.0306
wR_2[b]	0.0850	0.1735	0.0761	0.0827
Largest diff. peak [e Å^{-3}]	1.863	3.750	3.704	0.895
Largest diff. hole [e Å^{-3}]	–1.456	–3.292	–1.197	–2.771

[a] $R_1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ for $[F_o^2 > 2\sigma(F_o^2)]$. [b] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^4)]\}1/2$.

Me$_3$C$_6$H$_2$)], 6.84 [s, 2 H, Me$_2$TlSe(2,4,6-*Me*$_3$C$_6$H$_2$)] ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 18.0 [d, $^1J_{Tl\text{-}13C}$ = 2628 Hz, *Me*$_2$TlSe(2,4,6-Me$_3$C$_6$H$_2$)], 20.2 [s, Me$_2$TlSe(2,4,6-*Me*$_3$C$_6$H$_2$)], 37.4 [s, *Me*$_2$TlSe(2,4,6-Me$_3$C$_6$H$_2$)], 99.9 [s, Me$_2$TlSe(2,4,6-Me$_3$*C*$_6$H$_2$)], 126.9 [s, Me$_2$TlSe(2,4,6-Me$_3$*C*$_6$H$_2$)], 133.0 [s, Me$_2$TlSe(2,4,6-Me$_3$*C*$_6$H$_2$)], 142.1 [s, Me$_2$TlSe(2,4,6-Me$_3$*C*$_6$H$_2$)] ppm.

[Me$_2$TlSe(2,4,6-*t*Bu$_3$C$_6$H$_2$)]$_\infty$ (6): 2,4,6-*t*Bu$_3$C$_6$H$_2$SeH (0.260 g, 0.802 mmol) was added to a solution of TlMe$_3$ (0.200 g, 0.802 mmol) in toluene (8 mL). The solution was stirred at room temperature for 1 h, filtered, and concentrated to 6 mL. The solution was allowed to sit at 4 °C for 1 d and filtered to yield **6** as colorless crystals (0.341 g, 0.610 mmol, 76%). $C_{20}H_{35}SeTl$ (558.83): calcd. C 42.99, H 6.31, N 0.00; found C 43.27, H 6.65, N < 0.2; m.p. 215 °C. FTIR: $\tilde{\nu}$ = 644 (w), 727 (w), 744 (m), 777 (s), 876 (m), 899 (w), 922 (w), 1016 (m), 1093 (vw), 1126 (vw), 1161 (w), 1184 (m), 1213 (m), 1236 (m), 1254 (w), 1279 (w), 1358 (s), 1587 (m), 1755 (vw), 2303 (w), 2729 (vw), 3103 (vw) cm^{-1}. FT-Raman: 136 (s), 167 (s), 256 (w), 457 [vs, ν_{sym}(Me–Tl–Me)], 514 (w), 566 (m), 780 (w), 822 (m), 927 (w), 1016 (m), 1128 (w),1163 (m), 1199 (vw), 1279 (vw), 1355 (vw), 1446 (m), 1588 (m), 2701 (vw), 2912 (s), 2962 (s), 3025 (w) cm^{-1}. ^{1}H NMR ([D$_8$]thf): δ = 0.39 [d, $^2J_{Tl\text{-}H}$ = 354 Hz, 6 H, *Me*$_2$TlSe(2,4,6-*t*Bu$_3$C$_6$H$_2$)], 1.13 [s, 9 H, Me$_2$TlSe(2,4,6-*tBu*$_3$C$_6$H$_2$)], 1.45 [s, 18 H, Me$_2$TlSe(2,4,6-*tBu*$_3$C$_6$H$_2$)], 7.11 [m, 2 H, Me$_2$TlSe(2,4,6-*t*Bu$_3$C$_6$*H*$_2$)] ppm. ^{13}C{^{1}H} NMR ([D$_8$]thf): δ = 18.2 [d, $^1J_{Tl\text{-}13C}$ = 2294 Hz, *Me*$_2$TlSe(2,4,6-*t*Bu$_3$C$_6$H$_2$)], 31.4 [s, Me$_2$TlSe(2,4,6-*tBu*$_3$C$_6$H$_2$)], 34.0 [s, Me$_2$TlSe(2,4,6-*tBu*$_3$C$_6$H$_2$)], 37.6 [s, Me$_2$TlSe(2,4,6-*tBu*$_3$C$_6$H$_2$)], 119.9 [s, Me$_2$TlSe(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 139.9 [s, Me$_2$TlSe(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 143.8 [s, Me$_2$TlSe(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)], 152.0 [s, Me$_2$TlSe(2,4,6-*t*Bu$_3$*C*$_6$H$_2$)] ppm.

X-ray Structural Analysis: Crystals of compounds **2**–**6** were isolated from the reaction mixtures as indicated above. The single-crystals were coated with Paratone-N oil, mounted by using a 20 micron cryo-loop, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected with a Bruker AXS P4/SMART 1000 diffractometer by using the ω and θ scans with a scan width of 0.3° and 10 s (**2**, **6**), 20 s (**3**), or 30 s (**4**, **5**) exposure times. The detector distance was 5 cm. The data were reduced (SAINT)[24] and corrected for absorption (SADABS).[25] The structures were solved by direct methods and were refined by full-matrix least-squares on F^2 (SHELXTL).[26] All of the non-hydrogen atoms were refined by using anisotropic displacement parameters. The hydrogen atoms were included in the calculated positions and were refined by using a riding model.

The X-ray crystallographic data for **3**–**6** is presented in Table 3. CCDC-832989 (for **3**), -832993 (for **4**), -832994 (for **5**) and -832995 (for **6**) contain the supplementary crystalloraphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] T. Chivers, I. Manners, *Inorganic Rings and Polymers of the p-Block Elements – from Fundamentals to Applications*, RSC Publishing, Cambridge, UK, **2009**.

[2] a) M. Afzaal, D. Crouch, P. O'Brien, *Mater. Sci. Eng. B* **2005**, *116*, 391; b) P. Lobinger, H. S. Park, H. Hohmeister, H. W. Roesky, *Chem. Vap. Deposition* **2001**, *7*, 105; c) H. W. Kim, N. H. Kim, J. H. Myung, *J. Mater. Sci.* **2005**, *40*, 4991; d) P. O'Brien, D. J. Otway, J. R. Walsh, *Chem. Vap. Deposition* **1997**, *3*, 227.

[3] a) A. N. MacInnes, M. B. Power, A. R. Barron, *Chem. Mater.* **1992**, *4*, 11; b) A. N. MacInnes, M. B. Power, A. R. Barron, *Chem. Mater.* **1993**, *5*, 1344; c) S. L. Stoll, E. G. Gillan, A. R. Barron, *Chem. Vap. Deposition* **1996**, *2*, 182; d) E. G. Gillan, A. R. Barron, *Mater. Res. Soc. Symp. Proc.* **1996**, *415*, 87; e) A. N. MacInnes, M. B. Power, A. F. Hepp, A. R. Barron, *J. Organomet. Chem.* **1993**, *449*, 95.

[4] a) A. R. Barron, *Adv. Mater. Opt. Electron.* **1995**, *5*, 245, and references cited therein; b) P. O'Brien, S. Haggata, *Adv. Mater.*

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Opt. Electron. **1995**, *5*, 117, and references cited therein; c) H. J. Gysling, A. A. Warnberg, *Chem. Mater.* **1992**, *4*, 900; d) J. Y. Cho, H.-C. Jeong, K.-S. Kim, D. H. Kang, H.-K. Kim, I.-W. Shim, *Bull. Korean Chem. Soc.* **2003**, *24*, 645.

[5] a) R. J. Phillips, M. J. Shane, J. A. Switzer, *J. Mater. Res.* **1989**, *4*, 923; b) D. S. Richeson, L. M. Tonge, J. Zhao, H. O. Marcy, T. J. Marks, B. J. W. Wessels, C. R. Kannewurf, *Appl. Phys. Lett.* **1989**, *54*, 2154; c) A. D. Berry, R. T. Holm, R. L. Mowery, N. H. Turner, M. Fatemi, *Chem. Mater.* **1991**, *3*, 72; d) G. Malandrino, A. M. Borzi, F. Castelli, I. L. Fragalà, W. Dastrù, R. Gobetto, P. Rossi, P. Dapporto, *Dalton Trans.* **2003**, 269; e) R. Amano, Y. Shiokawa, *Inorg. Chim. Acta* **1993**, *203*, 9.

[6] J. P. Oliver, *J. Organomet. Chem.* **1995**, *500*, 269, and references cited therein.

[7] See for example: a) A. V. Firth, J. C. Stewart, A. J. Hoskin, D. W. Stephan, *J. Organomet. Chem.* **1999**, *591*, 185; b) S. Szumacher, I. Madura, J. Zachara, A. R. Kunicki, *J. Organomet. Chem.* **2005**, *690*, 1125; c) C. Schnitter, A. Klemp, H. W. Roesky, H.-G. Schmidt, C. Ropken, R. Herbst-Irmer, M. Noltemeyer, *Eur. J. Inorg. Chem.* **1998**, 2033; d) M. Webster, D. J. Browning, J. M. Corker, *Acta Crystallogr., Sect. C* **1996**, *52*, 2439; e) M. R. Kopp, B. Neumuller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 796; f) H. Rahbarnoohi, R. L. Wells, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, *Organometallics* **1997**, *16*, 3959; g) H. Rahbarnoohi, R. Kumar, M. J. Heeg, J. P. Oliver, *Organometallics* **1995**, *14*, 502.

[8] M. Taghiof, M. J. Heeg, M. Bailey, D. G. Dick, R. Kumar, D. G. Hendershot, H. Rahbarnoohi, J. P. Oliver, *Organometallics* **1995**, *14*, 2903.

[9] a) B. Yearwood, S. U. Ghazi, M. J. Heeg, N. Richardson, J. P. Oliver, *Organometallics* **2000**, *19*, 865; b) H. Rahbarnoohi, M. Taghiof, M. J. Heeg, D. G. Dick, J. P. Oliver, *Inorg. Chem.* **1994**, *33*, 6307.

[10] P. M. Dickson, J. P. Oliver, *J. Organomet. Chem.* **2000**, *597*, 105.

[11] G. G. Briand, A. Decken, N. S. Hamilton, *Dalton Trans.* **2010**, *39*, 3833.

[12] G. G. Briand, A. Decken, J. I. McKelvey, Y. Zhou, *Eur. J. Inorg. Chem.* **2011**, 2298.

[13] P. J. Burke, L. A. Gray, P. J. C. Hayward, R. W. Matthews, M. McPartlin, D. G. Gillies, *J. Organomet. Chem.* **1977**, *136*, C7.

[14] G. E. Coates, R. A. Whitcombe, *J. Chem. Soc.* **1956**, 3351.

[15] G. D. Shier, R. S. Drago, *J. Organomet. Chem.* **1966**, *5*, 330.

[16] H. Kurosawa, K. Yasuda, R. Okawara, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 861.

[17] M. V. Castano, A. Sanchez, J. S. Casas, J. Sordo, J. L. Briansó, J. F. Piniella, X. Solans, G. Germain, T. Debaerdemaeker, J. Glaser, *Organometallics* **1988**, *7*, 1897.

[18] Crystal data for **2**: $C_{20}H_{30}S_2Tl_2$, fw 743.30, monoclinic, space group $P2_1/c$, a = 19.834(7) Å, b = 8.438(3) Å, c = 14.485(4) Å, α = 90°, β = 110.663(5)°, γ = 90°, V = 2268.3(13) Å^3, Z = 4, ρ_{calcd} = 2.177 g cm^{-3}.

[19] Y. M. Chow, D. Britton, *Acta Crystallogr., Sect. B* **1975**, *31*, 1929.

[20] J. S. Casas, M. S. García-Esende, J. Sordo, *Coord. Chem. Rev.* **1999**, *193–195*, 283, and references cited therein.

[21] M. Bochmann, K. J. Webb, *Inorg. Synth.* **1997**, *31*, 158.

[22] H. Gilman, R. G. Jones, *J. Am. Chem. Soc.* **1946**, *68*, 517.

[23] R. Boese, A. J. Downs, T. M. Greene, A. W. Hall, C. A. Morrison, S. Parsons, *Organometallics* **2003**, *22*, 2450.

[24] *SAINT*, v. 7.23A, Bruker AXS Inc., Madison, Wisconsin, **2006**.

[25] G. M. Sheldrick, *SADABS 2008*, Bruker AXS Inc., Madison, Wisconsin, **2008**.

[26] *SHELXTL*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

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