

Comparison of the reactivity of germanium and tin terminal chalcogenido complexes: the syntheses of chalcogenolate and dichalcogenidostannacyclopentane derivatives

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The reactions of $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ ($\text{E} = \text{S, Se, Te}$) and $(\eta^4\text{-Me}_8\text{taa})\text{SnE}$ ($\text{E} = \text{S, Se}$) towards methyl iodide and ethylene sulfide highlight interesting similarities and differences in the reactivity of germanium and tin terminal chalcogenido functionalities.

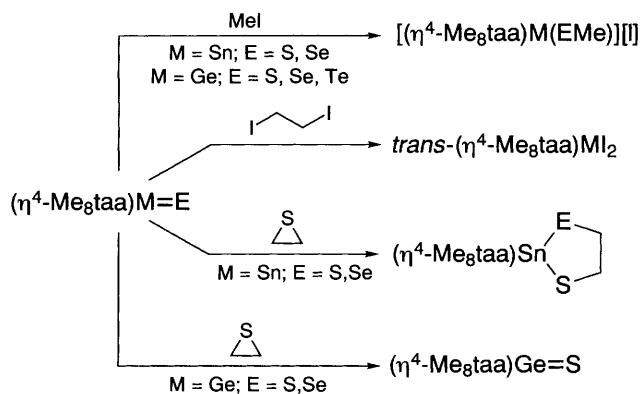
Complexes that exhibit terminal multiple bonds to the heavier chalcogens are currently subjects of considerable attention. Much of the work in this area, however, has focused on transition-metal complexes,¹ with comparatively fewer studies on terminal chalcogenido complexes of the p-block elements. Nevertheless, some significant advances have been achieved in recent years, as illustrated by the successful isolation and structural characterization of several terminal chalcogenido complexes of the heavier group 14 elements. Notable examples of such complexes include $\text{Ph}(\eta^2\text{-C}_{10}\text{H}_6\text{NMe}_2)\text{SiE}$ ($\text{E} = \text{S, Se}$),² $(\text{Tbt})(\text{Tip})\text{SiS}$,^{3†} $\{\eta^3\text{-}[(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2]\}\text{GeS}$,⁴ $(\text{Tbt})(\text{Tip})\text{GeE}$ ($\text{E} = \text{S, Se}$),⁵ $(\text{por})\text{SnE}$ ($\text{E} = \text{S, Se}$),⁶ $[(\text{Tbt})(\text{Tip})\text{SnE}]$ ($\text{E} = \text{S, Se}$)^{7‡} and $\{\eta^2\text{-}[(\text{C}_9\text{H}_6\text{N})(\text{Me}_3\text{Si-CH})_2]\}_2\text{SnE}$ ($\text{E} = \text{Se, Te}$).⁸ Furthermore, we have also described the use of the octamethyldibenzotetraaza[14]annulene dianion $[\eta^4\text{-Me}_8\text{taa}]^{2-}$ to support terminal chalcogenido complexes of germanium and tin, namely $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ ($\text{E} = \text{S, Se, Te}$)⁹ and $(\eta^4\text{-Me}_8\text{taa})\text{SnE}$ ($\text{E} = \text{S, Se}$).¹⁰ In this paper, we highlight some similarities and differences in the reactivity of the germanium- and tin-chalcogenido functionalities in $(\eta^4\text{-Me}_8\text{taa})\text{ME}$.

In terms of analogous reactivity, each of the terminal chalcogenido complexes $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ ($\text{E} = \text{S, Se, Te}$) and $(\eta^4\text{-Me}_8\text{taa})\text{SnE}$ ($\text{E} = \text{S, Se}$) reacts with MeI to give the corresponding methylchalcogenolate derivatives, $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{EMe})]\text{I}$ ($\text{E} = \text{S, Se, Te}$) and $[(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\text{EMe})]\text{I}$ ($\text{E} = \text{S, Se}$), as illustrated in Scheme 1. Although a precedent for alkylation of terminal chalcogenido ligands is provided by Veith's observation that $\{\eta^3\text{-}[(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2]\}\text{Ge}(\text{SMe})\text{I}$ is obtained upon reaction of $\{\eta^3\text{-}[(\mu\text{-Bu}^t\text{N})_2\text{-}$

$(\text{SiMeNBu}^t)_2]\}\text{GeS}$ with MeI,^{4b,11} it should be noted that Corriu has reported that the silicon derivative $\text{Ph}(\eta^2\text{-C}_{10}\text{H}_6\text{NMe}_2)\text{SiS}$ is unreactive towards methyl iodide.² The germanium and tin chalcogenido complexes $(\eta^4\text{-Me}_8\text{taa})\text{ME}$ also react with 1,2-diiodoethane; however, in each case the diiodide complex $(\eta^4\text{-Me}_8\text{taa})\text{MI}_2$ ($\text{M} = \text{Ge, Sn}$) was obtained, rather than a chalcogenolate derivative.

The molecular structures of $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{SMe})]\text{I}$, $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{SeMe})]\text{I}$ and $[(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\text{SeMe})]\text{I}$ have been determined by X-ray diffraction, as illustrated in Fig. 1 for the latter complex.[†] As would be expected, alkylation of the terminal chalcogenido ligand is accompanied by an increase in M–E bond length. For example, the Ge–S bond length of 2.110(2) Å in $(\eta^4\text{-Me}_8\text{taa})\text{GeS}$ increases to 2.193(2) Å in the cation $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{SMe})]^+$. Other structural details of the GeSMe moiety in $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{SMe})]^+$ are similar to those in related complexes. Thus, the Ge–S bond length [2.193(2) Å] and Ge–S–C bond angle [102.8(4)°] in $[(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{SMe})]^+$ are similar to those in $\{\eta^3\text{-}[(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2]\}\text{Ge}(\text{SMe})\text{I}$ [2.261(3), 2.255(4) Å; 105.4(6), 106.0(6)°]^{4b} and Ph_3GeSMe [2.224(1) Å, 101.4(3)°].¹² Furthermore, although we are not aware of any structurally characterized methylselenolate complexes of either germanium or tin, the respective metal–chalcogen bond lengths and M–E–C angles are within the range observed for related derivatives.

Whereas the reactions with methyl iodide are common to both germanium and tin chalcogenido complexes, the reactions with ethylene sulfide proceed differently for the two systems (Scheme 1). For the case of tin, both the sulfido and selenido complexes react with ethylene sulfide to give five-membered 1,3-dichalcogenido-2-stannacyclopentane derivatives $(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{E})$. The structure of the disulfido derivative $(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{S})$ has been determined by X-ray diffraction. Notably, even though dictated by ligand constraints, $(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{S})$ is the only structurally characterized example of a tetraazamacrocyclic tin(IV) complex with a *cis* disposition of coligands of which we are aware.¹⁴ As with the chalcogenolate derivatives described



Scheme 1

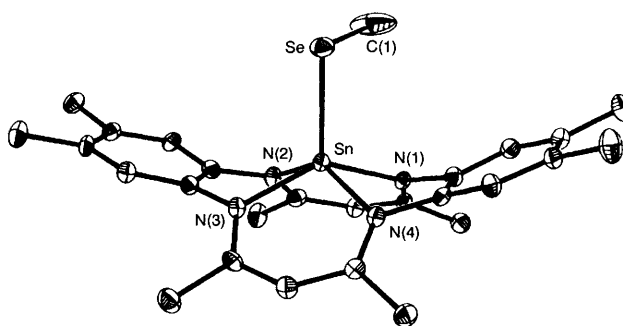


Fig. 1 Molecular structure of $[(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\text{SeMe})]\text{I}$ (only the cation is shown)

above, the Sn–S bond length in $(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{S})$ [2.482(2) Å] is considerably longer than that in its multiply bonded parent $(\eta^4\text{-Me}_8\text{taa})\text{SnS}$ [2.274(3) Å],¹⁰ but is within the range of values observed for other complexes bearing a $\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{S})$ moiety [2.39–2.49 Å].¹⁵

In contrast to the tin system, the germanium chalcogenido complexes $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ (E = Se, Te) do not react with ethylene sulfide to yield stable five-membered 1,3-dichalcogenido-2-germanacyclopentane derivatives $(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\eta^2\text{-ECH}_2\text{CH}_2\text{S})$. In preference, chalcogen exchange to give the terminal sulfido complex $(\eta^4\text{-Me}_8\text{taa})\text{GeS}$ is observed.¹⁶ Nevertheless, by analogy with the tin system, a potential mechanism for the formation of the sulfido complex involves the formation of a mixed 1,3-dichalcogenido-2-germanacyclopentane $(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\eta^2\text{-ECH}_2\text{CH}_2\text{S})$ (E = Se, Te) intermediate followed by cycloreversion. Since the stability of the germanium and tin complexes $(\eta^4\text{-Me}_8\text{taa})\text{M}(\eta^2\text{-ECH}_2\text{CH}_2\text{S})$ with respect to cycloreversion and formation of $(\eta^4\text{-Me}_8\text{taa})\text{MS}$ is determined in part by the difference in respective M–S single and M=S multiple bond strengths, one factor that is undoubtedly responsible for the striking differences of the germanium and tin systems is the ability of germanium to form stronger multiple bonds to the chalcogens than does tin.¹⁰

In summary, each of the terminal chalcogenido ligands of $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ (E = S, Se, Te) and $(\eta^4\text{-Me}_8\text{taa})\text{SnE}$ (E = S, Se) are subject to facile alkylation by methyl iodide to give cationic chalcogenolate derivatives $[(\eta^4\text{-Me}_8\text{taa})\text{M}(\text{EMe})]^+$. However, in contrast to the similar reactivity observed with MeI, only the tin derivatives $(\eta^4\text{-Me}_8\text{taa})\text{SnE}$ (E = S, Se) react readily with ethylene sulfide to give $(\eta^4\text{-Me}_8\text{taa})\text{Sn}(\eta^2\text{-SCH}_2\text{CH}_2\text{E})$. In preference, the germanium complexes $(\eta^4\text{-Me}_8\text{taa})\text{GeE}$ (E = Se, Te) react with ethylene sulfide to yield the terminal sulfido complex $(\eta^4\text{-Me}_8\text{taa})\text{GeS}$, rather than a five-membered $(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\eta^2\text{-ECH}_2\text{CH}_2\text{S})$ derivative. Assuming that $(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\eta^2\text{-ECH}_2\text{CH}_2\text{S})$ is the intermediate responsible for the chalcogenido ligand exchange reaction, the contrast between the germanium and tin systems is presumably a consequence of the greater difference in the strengths of the multiply bonded M=S and singly bonded M–S interactions for germanium vs. tin.

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Footnotes

† Tbt = 2,4,6-[(Me₃Si)₂CH]₃C₆H₂, Tip = 2,4,6-Pr₃C₆H₂.

‡ The monomeric species [(Tbt)(Tip)SnE] have only been generated in solution, and actually exist as chalcogenido-bridged dimers [(Tbt)(Tip)Sn(μ-E)]₂ in the solid state. See ref. 7.

§ The tellurolate derivative $(\eta^4\text{-Me}_8\text{taa})\text{Ge}(\text{TeMe})\text{I}$, however, is relatively unstable and has not been isolated in pure form. Its characterization is based on NMR spectroscopic identification.

¶ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/113.

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