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Terminal chalcogenido complexes of Group 13 and 14 elements

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Contents

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Abstract

The syntheses, structures and reactivity of multiply bonded terminal chalcogenido complexes of the Group 13 and 14 elements is reviewed. In particular, specific attention is given to complexes that can be generated under ambient conditions and retain the terminal chalcogenido moiety in the solid state.

Keywords: Gallium; Indium; Germanium; Tin; Chalcogen

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1. Introduction and scope

The existence of multiple bonds between pairs of elements has long attracted the interests of organic, inorganic, physical, and theoretical chemists alike, from both a structural and synthetic perspective.[1,2] For example, prompted by the so-called 'classical double bond rule' (*vide infra*), synthetic chemists have been presented with the challenge of isolating multiply bonded complexes of the heavier members of the *p*-block elements. Consequently, this area has experienced significant advances in recent years [6–28],[3] as aptly illustrated by the syntheses of many complexes which contain multiple bonds to the chalcogens (E = O, S, Se, Te).[4] The intention of this review is to provide an account of the synthesis, structures, and reactivity of multiply bonded terminal chalcogenido complexes of the Group 13 and 14 elements. In particular, specific attention will be given to complexes that can be generated and studied under ambient conditions and, for the most part, retain the terminal chalcogenido moiety in the solid state.

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[1] For some leading articles on multiple bonding of the transition elements, see references [1–5].

[2] For some leading articles on multiple bonding of the transition elements, see references [6–28].

[3] While many of the studies concerned with multiple bonding of the heavier members of the *p*-block elements have concentrated on complexes with double bonds, some interesting examples of complexes with triple bonds have been isolated. For example, $Cp(CO)_2Mo{\equiv}Ge[C_6H_3Mes_2]$ is a particularly interesting example of a germanium complex with a valence triple bond [29,30]. Homonuclear triply bonded RMMR complexes of Si, Ge, Sn and Pb have not, however, been isolated, although they have been subject to theoretical calculations [31–33].

[4] For a brief discussion on the origin of the term 'chalcogen' and its use in reference to the Group 16 elements, see references [4] and [34].

1.1. Multiple bonding to the heavy p-block elements and the classical double bond rule

One of the most interesting characteristics of multiple bonding is the observation that there exists a distinct difference between the light and heavier *p*-block elements with respect to the formation of stable multiple bonds.[5] Thus, compounds with multiple bonds to the second period[6] *p*-block elements, i.e. carbon, nitrogen and oxygen, are common; indeed, olefins, alkynes, aromatics, carbonyls and nitriles comprise some of the most important and fundamental classes of compounds in chemistry as a whole. By comparison, however, the heavier *p*-block elements exhibit a much reduced tendency to engage in multiple bonding [7,8,35]. In fact, historically such compounds were so elusive to the synthetic chemist that they were believed to be 'non-existent' [36],[7] a belief which led to the formulation of 'the classical double bond rule'.

The classical double bond rule (or, more simply, 'the double bond rule') has been frequently cited in the literature concerned with the problem of multiple bonding to the heavy main group elements. For example, a landmark 1975 review by Jutzi on 'New element–carbon $(p\text{-}p)\pi$ bonds' describes the classical double bond rule as: 'elements having a principal quantum number greater than 2 should not be able to form $(p\text{-}p)\pi$ bonds to themselves or with other elements' [6]. Similarly, Cowley [11] has noted how "...the consensus developed that compounds featuring $(p\text{-}p)\pi$-bonds between the heavier main-group elements would not be stable. Such a view is often referred to as 'the double bond rule' ". More recently, in the preface to *Advances in Organometallic Chemistry*: *Multiply Bonded Main Group Metal and Metalloids*, the editors state "the textbook *double bond rule*: 'Elements outside the first row of the periodic table do not form stable multiple bonds' " [37]. As a further example, the authors of a chapter in the aforementioned text make reference to "the so-called double bond-rule, which forbade the formation of $(p_\pi\text{-}p_\pi)$ multiple bonds between silicon and other elements...." [38]. Interestingly, a striking feature of these articles which cite 'the double bond rule' in this form is that no specific reference is given to the original introduction of the term. Furthermore, in several other instances where a reference to the 'double bond rule' is cited [7,9,17,39,40] the reader is simply referred to other papers where the rule is stated without any reference. To the best of our ability, the original source of 'the classical double bond rule' in the above form could not be located, and it seems likely that the term may never have been knowingly published as an original contribution. Interestingly, in a 1986 Correspondence to *Angewandte Chemie*, Goubeau noted "that there is not only one 'double bond rule'... there are several double bond rules" [41]. Goubeau's rules for the formation of π-bonds may be

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[5] We use the word 'stable' in the same sense as used by Norman [9] to indicate that the compounds can be isolated under ambient conditions.

[6] It should be noted that some authors mistakenly refer to the second period (or row) elements (Li, Be, B, C, N, O, F) as the first row elements.

[7] It should be noted that the author (Dasent) did not mean to imply that such compounds would never exist, but rather intended to emphasize their inherent instability.

summarized as: (i) electron deficiency on both bonding partners; (ii) the sum of the Pauling electronegativities of the partners must be at least 5; and (iii) the difference between the Pauling electronegativities of the bonding partners must be small [42,43]. Although it is clear how rule (ii) indicates that the tendency to form a multiple bond would diminish upon descending the periodic table, it is not apparent at which point Goubeau's rules, published in 1957, developed into *the* 'double bond rule' used today.[8] Nevertheless, regardless of its precise origin, the 'double bond rule' has certainly evolved as a term used by chemists to describe the observation that multiple bonds are rare amongst the heavy *p*-block elements.

1.1.1. Sigma vs. pi bond energies for p-block elements

While the 'double bond rule' conveys the message that multiple bonds to the heavy main group elements are rare, it does not provide any insight into why such a situation exists. In this regard, it is often assumed that the trend embodied in the 'double bond rule' is merely a consequence of reduced $p_\pi - p_\pi$ overlap for the heavier congeners, a notion that was originally suggested by Pitzer [44]. This rationalization is, however, a common misconception. Specifically, calculations by Mulliken [45,46] demonstrated that π-overlap does *not* vary in the manner suggested by Pitzer. For example, the π-overlap populations for N_2 and P_2 are similar (Table 1) [8]; furthermore, Schmidt and Gordon have noted that the π-overlap (0.65) in the $-P{=}P-$ moiety is actually greater than the π-overlap (0.62) in the $-N{=}N-$ fragment [47]. Nevertheless, despite the fact that the overlaps are comparable, Kutzelnigg [8] has pointed out that the strength of an interaction also depends on the ionization potentials of the atoms involved, in such a manner that results in the bond dissociation energy of N_2 being greater than that of P_2. Schleyer has likewise described such an effect in a comparison of multiply bonded carbon and silicon compounds [48].

As first recognized by Mulliken [45,46], the key to understanding the different abilities of the second and higher period elements to partake in multiple bonding resides with the *relative* strengths of their σ and π-bonds [8,12]. In order to illustrate this argument, the variation in σ and π-bond energies of some homonu-

Table 1
Sigma- and π-overlap populations for N_2 and P_2[a]

	N_2	P_2
Total overlap population	0.71	0.73
σ-Overlap population	0.17	0.23
π-Overlap population	0.27 (×2)	0.25 (×2)

[a] Data taken from Kutzelnigg [8].

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[8] In this regard, although the earliest mention of the double bond rule of which we are aware is provided in Jutzi's 1975 paper [6], Professor Jutzi has communicated to us that he does not consider himself as the originator of the term.

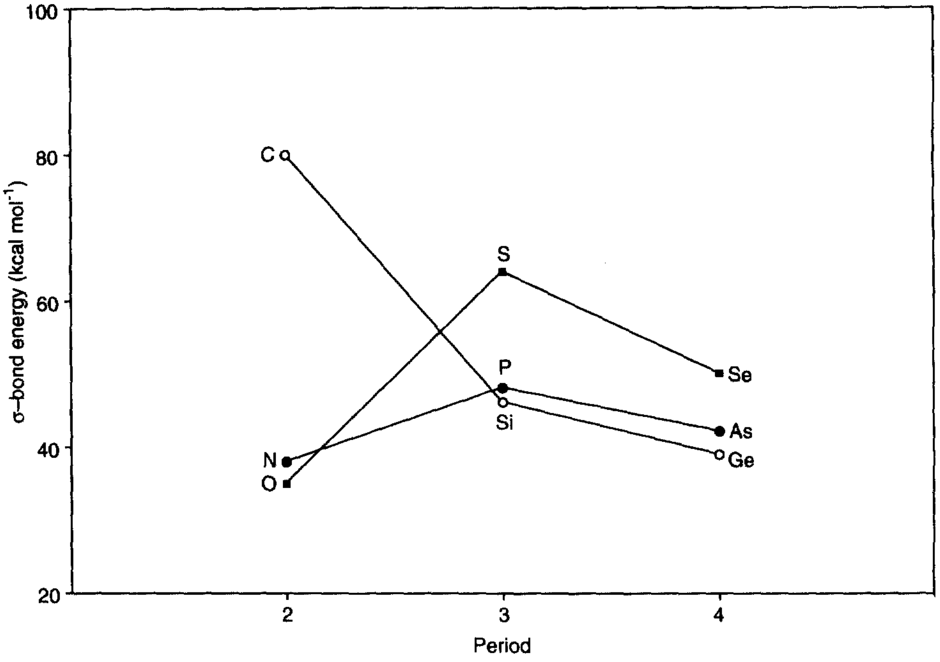

Fig. 1. Variation in σ-bond energies for some homonuclear interactions (data taken from Kutzelnigg [8]).

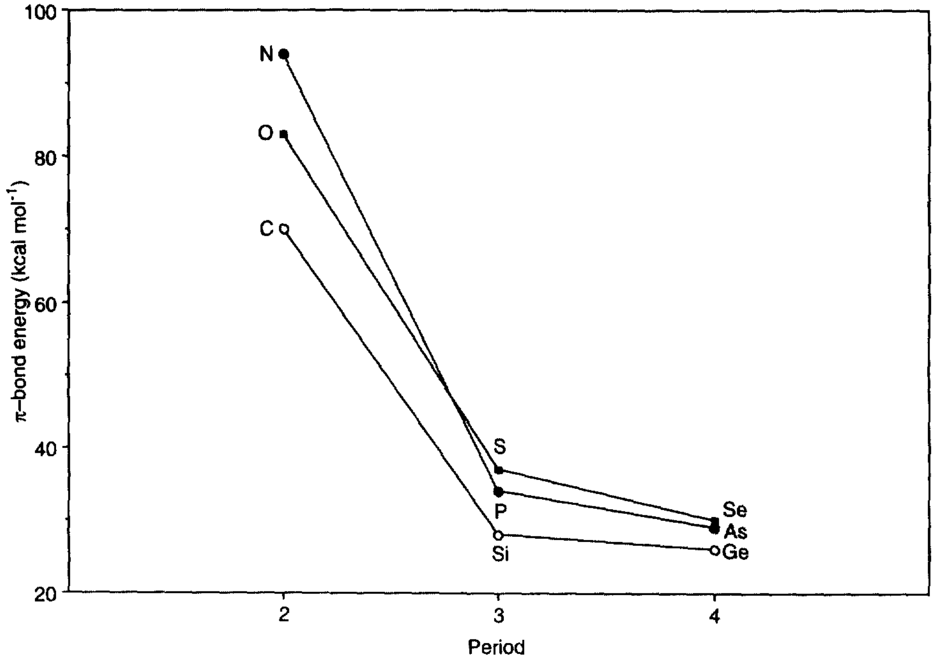

Fig. 2. Variation in π-bond energies for some homonuclear interactions (data taken from Kutzelnigg [8]).

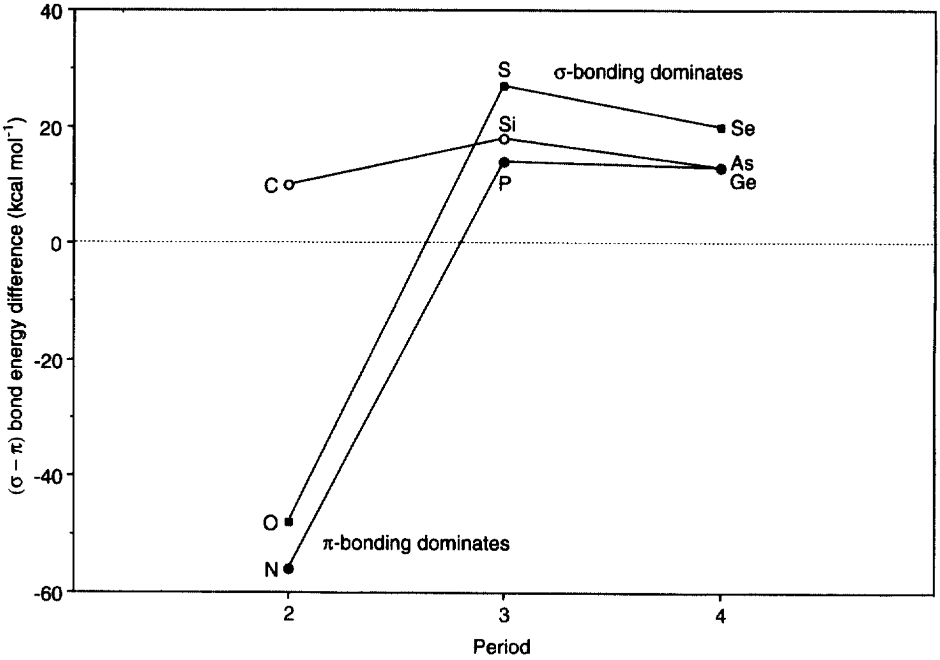

Fig. 3. Difference in σ and π-bond energies for some homonuclear interactions (data taken from Kutzelnigg [8]).

clear interactions are illustrated in Figs. 1 and 2, with the difference between these components summarized in Fig. 3. Of most interest, the σ-bond energies do not vary in a simple manner, whereas the π-bond energies of the X_2 molecules vary monotonically down a group (as is also observed for $[M{=}CH_2]$ and $[M{=}S]$; see Table 2). As a result of these different trends, the π-bonds for nitrogen and oxygen are significantly stronger than their corresponding σ-bonds (with the π and σ-bond energies for carbon being comparable),[9] while for the heavier elements, the opposite is true, namely that the strengths of the σ-bonds are greater than their π-bonds, in some cases by a factor of approximately two. Consequently, for the lighter p-block elements, a σ and π-bonding combination is energetically favored over two σ-bonds, whereas for the heavier congeners the opposite is true, i.e. two σ-bonds are favored over a σ and π combination.[10] As indicated above, this trend is exemplified by a comparison of the elemental forms of the Group 15 elements nitrogen and phosphorus. Thus, while nitrogen exists as a diatomic

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[9] The low σ-bond energies for N–N, O–O, and F–F are normally attributed to lone-pair/lone-pair repulsions.

[10] Two σ-bonds are favored over a σ and π combination when the $(\sigma - \pi)$ bond energy difference is greater than zero; see Fig. 3.

Table 2
π-Bond energies for $[M{=}CH_2]$ and $[M{=}S]$

$[M{=}CH_2]$[a]	π-Bond energy (kcal mol^{-1})	$[M{=}S]$[b]	π-Bond energy (kcal mol^{-1})
$[C{=}CH_2]$	65	$[C{=}S]$	56
$[Si{=}CH_2]$	38	$[Si{=}S]$	46
$[Ge{=}CH_2]$	31	$[Ge{=}S]$	40
$[Sn{=}CH_2]$	19	$[Sn{=}S]$	32

[a] Data for $[H_2M{=}CH_2]$ taken from Grev [16].
[b] Data cited in Matsuhashi et al. [232].

molecule (N_2) with a nitrogen–nitrogen triple bond, white phosphorus exists as a tetranuclear species (P_4) constructed by phosphorus–phosphorus single bonds.

1.1.2. Stability of the subvalent state

Another factor that influences the stability of a multiply bonded [M=X] interaction is the stability of the subvalent ($N-2$) state. In this regard, it is well-known that the stability of the subvalent state for the Group 13 and 14 elements increases upon descending the periodic table (i.e. the so-called 'inert pair' effect) [49–52]. For example, the divalent state stabilization energies (DSSE) for a series of Group 14 hydride complexes are listed in Table 3, illustrating the magnitude by which the subvalent ($N-2$) state becomes more stable upon descending a group. It is, therefore, evident that the increasing stabilization of the subvalent state upon descending the periodic table is a factor which also serves to decrease the stability of a multiply bonded [M=X] moiety, with respect to dissociation, for the heavier congeners.

1.2. Terminal chalcogenido complexes

In considering terminal chalcogenido complexes, it is important to make a distinction between those with a valence single bond and those with a valence multiple bond. Within this review, we will use the term 'multiply bonded' to refer

Table 3
Divalent state stabilization energies[a]

$[H_2M]$	DSSE (kcal mol^{-1})
H_2C	−5.6
H_2Si	19.3
H_2Ge	25.8

[a] Data taken from Grev [16]. The DSSE is defined as the difference in first and second bond dissociation energies of MX_4, i.e. $D(X_3M{-}X) - D(X_2M{-}X)$. As such, it is equivalent to the enthalpy of disproportionation of $[MX_3]$ to $[MX_2]$ and MX_4.

$$\overset{+}{M}-\overset{-}{E} \longleftrightarrow M=E \longleftrightarrow \overset{-}{M}\equiv\overset{+}{E}$$

$ML_lX_xZ_z$ classification	MZ	MX_2	MLX_2
valence number of M	2	2	2

Scheme 1.

to interactions for which a *neutral* resonance structure of the type [M=E] (E = O, S, Se, Te) can be drawn. In general, a multiply bonded terminal chalcogenido interaction may be represented as a composite of the three resonance structures shown in Scheme 1, which differ in the degree of π-interaction between the metal and the terminal chalcogenido ligand. Such a bonding scheme is similar to that used to describe species such as tertiary phosphine oxides, with the exception that for R_3PO, with C_{3v} symmetry,[11] the [M=E] resonance structure is not strictly applicable because the [M–E] π-type interactions must occur in a pairwise manner [54–60].[12]

The relative contributions of the three resonance structures, [$\overset{+}{M}-\overset{-}{E}$], [M=E] and [$\overset{-}{M}\equiv\overset{+}{E}$], will be expected to be a sensitive function of the nature of both M and E. For example, interactions in complexes with low-coordinate metal centers are more likely to be better represented by the multiply bonded resonance structures [M=E] and [$\overset{-}{M}\equiv\overset{+}{E}$], than are analogous interactions in complexes with high-coordinate metal centers, for which the resonance structure [$\overset{+}{M}-\overset{-}{E}$] may provide the better description. In essence, since the p-orbitals on M are also used for binding additional ligands, the availability of vacant p-orbitals for π-bonding with the chalcogen consequently decreases as the coordination number of M increases. Furthermore, the [$\overset{+}{M}-\overset{-}{E}$] resonance structure would be expected to play a more significant role for oxo derivatives due to the greater electronegativity of oxygen which stabilizes the negative charge. In addition, since the M–E bond length is shortest for the oxo derivative, the [$\overset{+}{M}-\overset{-}{O}$] resonance structure would also experience a greater Coulombic stabilization than would either [$\overset{+}{M}-\overset{-}{S}$], [$\overset{+}{M}-\overset{-}{Se}$], or [$\overset{+}{M}-\overset{-}{Te}$].[13] In fact, theoretical studies [65–67] on three-coordinate $H_2M{=}O$[14] have indicated that for Ge, Sn and Pb, *both* the σ and π-bonds are *strongly* polarized towards oxygen, to the extent that even the representation [$H_2\overset{+}{M}-\overset{-}{O}$] is misleading.[15] Calculations on $H_2Ge{=}S$ indicate that the Ge=S bond is also polarized, but to a lesser degree than the Ge=O bond. [66]

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[11] Likewise, the [M=E] resonance structure would not be appropriate for a molecule with C_{4v} symmetry.

[12] For an excellent review of the bonding in R_3PE which critically discusses the various bonding descriptions, see Gilheany [53].

[13] For a further discussion on this subject with respect to $Cp^*_2Zr(E)(NC_5H_5)$, see references [61–64].

[14] It is worth noting that H_2MO is calculated to be more stable than divalent HM(OH) for carbon, whereas silicon, germanium, tin and lead favor the tautomer HM(OH).

[15] For further theoretical calculations on $H_2M{=}O$ (M = Si, Ge, Sn, Pb) and $H_2M{=}MH_2$, see reference [68].

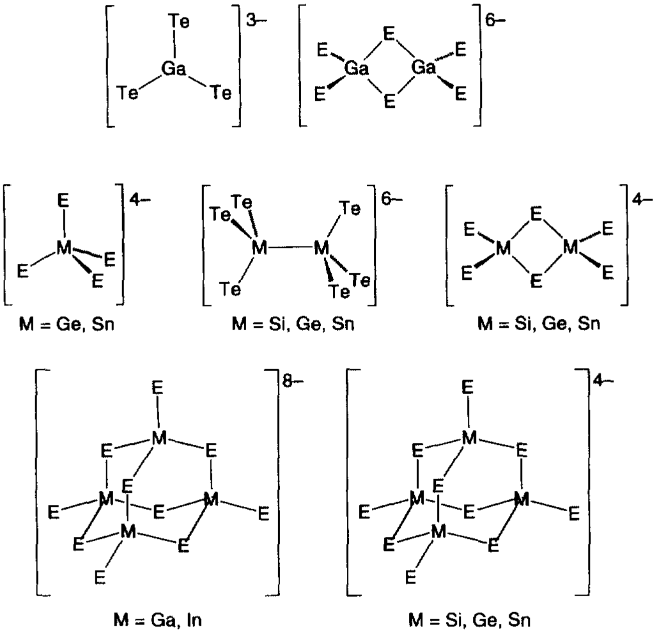

Fig. 4. Representative examples of polyanionic terminal chalcogenido complexes of the Group 13 and 14 elements.

Despite the fact that the resonance structure $[\overset{+}{M} - \overset{-}{E}]$ implies no π-bonding, it is important to emphasize that it should *not* be considered to depict a single bond, but should rather be viewed to represent a valence double bond. Such interactions have been termed 'semipolar' double bonds and may be considered to be composed of both covalent and ionic contributions [69,70]. Furthermore, although the formal covalent bond order may vary for each of the resonance structures shown in Scheme 1, each of these structures correspond to a valence *double* bond, as judged by the valence number of the metal according to the $ML_lX_xZ_z$ classification.[16] For this reason, and for simplicity, we will use the representation [M=E] to describe generally the interactions of the terminal chalcogenido complexes with valence double bonds, recognizing that there is no implication with respect to the degree of π-interaction. In this regard, it is important to emphasize that not all terminal chalcogenido complexes of the Group 13 and 14 elements contain [M=E] valence double bonds. For example, there are many polyanionic complexes, as illustrated by $[GaTe_3]^{3-}$, $[Ga_2E_6]^{6-}$, $[M_4E_{10}]^{8-}$ (M = Ga, In), $[M_4E_{10}]^{4-}$ (M = Si, Ge, Sn) and $[ME_4]^{4-}$ (M = Ge, Sn), which contain terminal chalcogenido ligands

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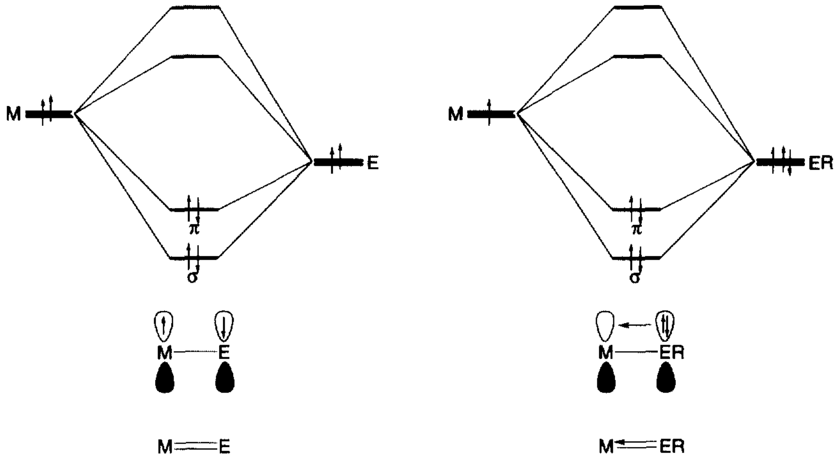
[16] The valence number of M in a complex classified as $ML_lX_xZ_z$ is $(x + 2z)$ [71,72].



normal π-bond

dative π-bond

Fig. 5. Distinction between a valence multiple bond and a multiple bond associated with a dative π-interaction.

(Fig. 4) [73,74], but in these cases the metal–chalcogen interactions are formally valence single bonds of the type $[M-\bar{E}]$.[17–20]

Finally, with respect to multiple bonding of the chalcogens, it is also appropriate to distinguish between a valence multiple bond and a multiple bond associated with a dative π-interaction, as illustrated in Fig. 5. The importance of this distinction is concerned with the fact that dative covalent bonds are typically considerably weaker than normal covalent bonds.[21] As a cogent illustration of this notion, the rotation about a $[M{=}CR_2]$ valence double bond has a significantly higher barrier than does rotation about an $[M \overset{\leftarrow}{-} ER]$ double bond, with the latter often being facile on the NMR timescale [118,119].[22]

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[17] For two reviews on this topic see: [73,74].

[18] Specific examples of gallium and indium chalcogenido polyanions include: $Na_6Ga_2S_6$, $Na_6Ga_2S_6$, $Sr_2[Ga_2S_5]$, $K_6Ga_2S_6$, $K_8Ga_4S_{10} \cdot 16H_2O$, $Cs_{10}Ga_6Se_{14}$, $Na_6Ga_2Se_6$, $K_6Ga_2Se_6$, $K[K([18]crown\text{-}6)]_3[GaTe_3] \cdot 2MeCN$, $[(Ph_4P)]GaTe_2(en)_2$, $K_6Ga_2Te_6$, $\{Ba_2[In_2Se_5]\}_\infty$ and $K_8[In_4Se_{10}] \cdot 16H_2O$ [75–84].

[19] Specific examples of germanium chalcogenido polyanions include: $PbGeS_3$, Na_2GeS_3, M_2GeS_4 (M = Ba, Sr, Ca), $Na_4Ge_2S_6$, $Ba_2Ge_4S_{10}$, $M_4Ge_4S_{10}$ (M = Tl, Cs), M_2GeSe_4 (M = K, Rb), Na_4GeSe_4, $Cs_4Ge_2Se_8$, $M_4Ge_4Se_{10}$ (M = Tl, Cs, Rb), $M_2Ge(Te_2)Te_2$ (M = Cs, K), $K_6Ge_2Te_6$, $(Et_4N)_4Ge_4Te_{10}$, $Na_8Ge_4Te_{10}$ and $[K(2.2.2\text{-cryptand})]_2[\mu\text{-O})\{\mu\text{-O}_2Si(CH_3)_2\}_2(GeSe)_2]$ [85–99].

[20] Specific examples of tin chalcogenido polyanions include: K_2SnS_3, Na_4SnS_4, $Na_4Sn_2S_6$, $Na_6Sn_2S_7$, $Na_4Sn_3S_8$, Na_4SnSe_4, $M_4Sn_2Se_6$ (M = Na, Cs, Tl, Rb), $[(K)_2(18\text{-crown-6-K})_2][Sn_2Se_6]$, $K_4Sn_3Se_8$, $[Na]_4[SnTe_4]$, $[Me_4N]_4[Sn_2Te_6]$, $[Et_4N]_4[Sn_2Te_6]$, $[Cs]_2[SnTe_4]$, $[K]_6[Sn_2Te_6]$ and $[Cs]_4[Sn_2Te_7]$ [100–116].

[21] For a distinction between covalent and dative bonds, see Haaland [117].

[22] It should be noted that NMR exchange experiments do not distinguish between a process involving rotation about an $[M \overset{\leftarrow}{-} ER]$ bond and a process involving linear inversion at E. However, calculations suggest that linear inversion is a higher energy process, especially for the heavier chalcogens [119].

2. Terminal chalcogenido complexes of the Group 13 elements (B, Al, Ga, In, Tl)

2.1. Multiple bonding of the Group 13 elements

In contrast to the many examples of Group 13 element complexes which exhibit multiple bonding due to the presence of dative π-interactions [120,121,133][23–26], complexes with valence multiple bonds are exceptionally rare. In fact, until very recently, such complexes were known exclusively for the lightest element, boron, for which complexes with B=B, B=C, B≡C, B=N, B=P and B=As multiple bond character exist [120,121,126,134–146]. With respect to gallium, a very interesting two-coordinate gallium complex $[\mathrm{Na}]_2[\mathrm{ArGaGaAr}]$ ($\mathrm{Ar}=2,4,6\text{-}\mathrm{Pr}^i_3\text{-}\mathrm{C_6H_2}$) has recently been synthesized by the reduction of $\mathrm{ArGaCl_2}$ with Na, and has been proposed to be a 'gallyne' derivative with a Ga ≡ Ga triple bond [147]. There is, however, some debate concerning the precise nature of the bonding in this complex (which has a distinctly non-linear R–Ga–Ga moiety), with a lower bond order structure possessing lone pair electrons on Ga, i.e. $[\mathrm{R\overline{Ga}{-}R\overline{Ga}}]$, having been proposed as an alternative description [148,149,262,263].[27]

2.2. Syntheses of Group 13 terminal chalcogenido complexes

Stable multiply bonded terminal chalcogenido complexes of the Group 13 elements are extremely uncommon.[28] For example, boron and aluminum are known to form molecules such as HB=O [158], HB=S [159,160], $\mathrm{CH_3B{=}S}$ [161,162], ClB=S [163,164] and X–Al=O (X = F, Cl) [165,166], which have been generated and characterized as unstable species in the gas phase or in matrices, but structurally authenticated terminal chalcogenido derivatives are unknown to our knowledge. It is, therefore, interesting that terminal chalcogenido complexes of gallium and indium have been isolated and structurally characterized.

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[23] For a comprehensive review of Group 13 multiple bonding with particular emphasis on three coordinate complexes with dative multiple bonding and anionic species with homonuclear metal–metal multiple bonds, see Brothers and Power [122].

[24] For theoretical studies of dative multiple bonding see: [123,124].

[25] Such interactions are well-known in boron complexes of the types $\mathrm{R_2BER'}$ (E = O,S) [125], $[\mathrm{RBNR}]_n$ [126], $\mathrm{R_2BPR_2}$ [127], $\mathrm{R_2BAsR_2}$ [127] and $[\mathrm{RBPR}]_3$ [127,128].

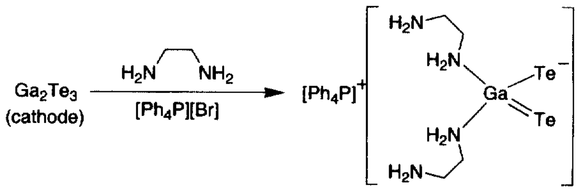
[26] Examples of multiple bond interactions involving dative π-donation to Al and Ga include $[\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_2\mathrm{Al}]_2\mathrm{O}$ [129], $[\mathrm{RAlNR}]_3$ [130,131], and $[\mathrm{ArGaPR}]_3$ [132].

[27] Power and Robinson have recently described $[\mathrm{Li}([12]\mathrm{crown\text{-}4})_2]\{[(\mathrm{Pr}^i_3\mathrm{C_6H_2})_2\mathrm{Ga}\}_2]$ [150] and $\mathrm{M_2}[(\mathrm{Mes_2C_6H_3})\mathrm{Ga}]_3$ (M = Na, K) [151–153], respectively, which are interesting examples of gallium complexes with Ga–Ga multiple bond character. A complex with a Ga–Fe multiple bond, $(\mathrm{Pr}^i_3\mathrm{C_6H_2})_2\mathrm{GaFe(CO)_4}$ has also been reported [154]. Interestingly, the bonding in related indium complexes, $[\mathrm{Tp}^{\mathrm{Me_2}}]\mathrm{InFe(CO)_4}$ and $[\mathrm{Tp}^{\mathrm{Me_2}}]\mathrm{InW(CO)_5}$, has been suggested to involve a single dative bond from In to M (M = Fe, W), rather than a In–M multiple bond [155]. Furthermore, recent theoretical calculations on $(\mathrm{Pr}^i_3\mathrm{C_6H_2})_2\mathrm{GaFe(CO)_4}$ also suggest that the bonding between the gallium and iron atoms is analogous and that there is no basis for proposing an iron-gallium triple bond [264].

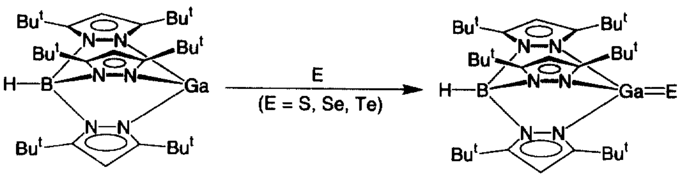
[28] For recent reviews which include singly bonded chalcogenolate complexes of the Group 13 elements, see reference [156,157].

The anionic gallium complex $[Ga(Te)_2(en)_2][PPh_4]$ (en = 1,2-ethylenediamine), synthesized by the cathodic dissolution of a Ga_2Te_3 electrode in a 1,2-ethylenediamine solution of $[Ph_4P][Br]$, was the first multiply bonded terminal chalcogenido complex of a heavy Group 13 element to be isolated (Scheme 2) [167]. With two terminal tellurido ligands, each of the Ga–Te inteactions of anionic $[Ga(Te)_2(en)_2]^-$ may be assigned a formal bond order of 1.5 (cf. the C–O bond order in HCO_2^-).

The only examples of doubly bonded terminal chalcogenido complexes of the heavy Group 13 elements are the gallium and indium complexes supported by the bulky tris(3,5-di-*tert*-butyl)pyrazolyl hydroborate ligand [168],[29] $[Tp^{Bu^t_2}]GaE$ (E = S, Se, Te) [171,172] and $[Tp^{Bu^t_2}]InSe$ [173]. These complexes were synthesized by oxidative addition of the elemental chalcogens to the monovalent precursors, $[Tp^{Bu^t_2}]M$ (M = Ga, In), [174][30] of which $[Tp^{Bu^t_2}]Ga$ is the sole example of a monomeric, monovalent, gallium complex to be structurally characterized in the solid state (Schemes 3 and 4).



Scheme 2.



Scheme 3.

The reactions of low oxidation state Group 13 compounds with elemental chalcogens and related reagents is precedented. However, the products of such reactions typically yield bridging chalcogenido complexes. For example, the dinuclear gallium complex $[\{(Me_3Si)_2CH\}_2Ga]_2$ reacts with Et_3PE (E = S, Se, Te) to give $[\{(Me_3Si)_2CH\}_2Ga]_2(\mu\text{-}E)$ [177,178], while elemental selenium reacts with

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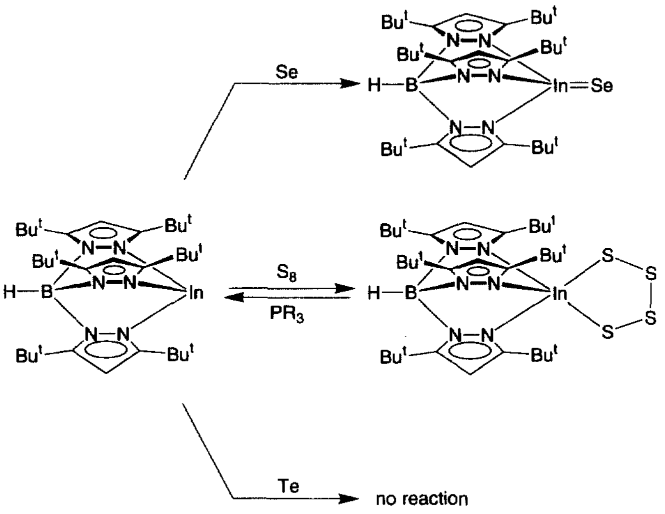
[29] For nomenclature (i.e. $[Tp^{R,R'}]$) and a review of tris(pyrazolyl) hydroborate complexes see Trofimenko [169] and Parkin [170].

[30] Related monovalent $[Tp^{R,R'}]In$ complexes have been reported. See references [175,176].

$[\{(Me_3Si)_3C\}In]_4$, to give $[\{(Me_3Si)_3C\}In(\mu_3\text{-}Se)]_4$ [179]. Structurally related chalcogenido clusters that have been obtained for the Group 13 elements include $[\eta^1\text{-}Cp^*Ga(\mu_3\text{-}Se)]_4$ [180], $[\eta^1\text{-}Cp^*Ga(\mu_3\text{-}Te)]_4$ [181], $[Bu^tGa(\mu_3\text{-}Se)]_4$ [182], $[(Me_2EtC)Ga(\mu_3\text{-}E)]_4$ (E = S, Se, Te) [183] and $[\eta^5\text{-}Cp^*Al(\mu\text{-}E)]_4$ (E = Se, Te) [184]. The fact that classical bulky ligands, such as Cp* and $[R_3C]$, do not enable the isolation of terminal chalcogenido complexes of the Group 13 elements highlights the importance of the use of the $[Tp^{Bu^t_2}]$ ligand in synthesizing such complexes. The successful isolation of the terminal chalcogenido complexes, $[Tp^{Bu^t_2}]ME$, is undoubtedly a consequence of the sterically demanding environment that is provided by the bulky $[Tp^{Bu^t_2}]$ ligand, as illustrated for $[Tp^{Bu^t_2}]GaTe$ in Fig. 6.



Scheme 4.

It is worth emphasizing that there is an important distinction in the above gallium and indium systems, $[Tp^{Bu^t_2}]ME$, namely that whereas the terminal sulfido, selenido and tellurido complexes have been isolated for gallium, only the selenido derivative has so far been isolated for indium. Specifically, the indium complex $[Tp^{Bu^t_2}]In$ reacts with sulfur to give the tetrasulfide, $[Tp^{Bu^t_2}]In(\eta^2\text{-}S_4)$,[31] while no reaction is observed with elemental tellurium (Scheme 4). Furthermore, the thallium analog $[Tp^{Bu^t_2}]Tl$ is unreactive towards both elemental selenium and tel-

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[31] It is also noteworthy that the tetrasulfide complex $[Tp^{Bu^t_2}]In(\eta^2\text{-}S_4)$ readily regenerates the indium(I) complex $[Tp^{Bu^t_2}]In$ upon treatment with PR_3 (R = Me, Ph). Thus, if a terminal sulfido complex were to be an intermediate for the latter reaction, it is evident that the sulfido ligand would also be abstracted by PR_3 (see Section 4.1).

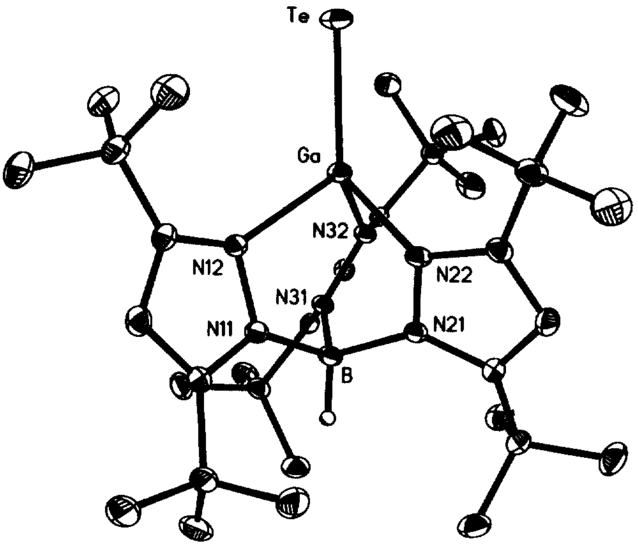

Fig. 6. Molecular structure of $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{GaTe}$.

lurium. These observations are in accord with two notions associated with the heavy *p*-block elements, namely that (i) the tendency to engage in multiple bonding and (ii) the stability of the N vs. $(N-2)$ valence state decreases upon descending a group.

2.3. d(M = E) bond length data and bonding for Group 13 terminal chalcogenido complexes

The metal–chalcogen bond length data for the structurally characterized multiply bonded terminal chalcogenido complexes of gallium and indium are compiled in Table 4. For comparison purposes, M–E single bond and M=E double bond length data for Group 13 element complexes are presented in Table 5 and Fig. 7. Notably, the M=E bond lengths in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{ME}$ are significantly shorter than the corresponding M–E single bond lengths that have been reported; for example, the Ga–E bond lengths in $\mathrm{K}_6[\mathrm{Ga}_2\mathrm{E}_6]$ species are summarized in Table 6. Furthermore, the Ga=Te bond length in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{GaTe}$ [2.422(1) Å] is shorter than that in the anion $[\mathrm{Ga(Te)}_2(\mathrm{en})_2]^-$ [2.509(1) Å] with a formal Ga–Te bond order of 1.5 [167]. The shortness of the M=E bonds in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{ME}$ is, therefore, consistent with multiply bonded character. Although precise details of the bonding in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{ME}$ are unknown, it is likely that the polar form $[\overset{+}{\mathrm{M}}-\overset{-}{\mathrm{E}}]$ provides an important contribution to the overall description, in which case the multiple bond is best viewed as being a composite of both covalent and ionic interactions, i.e. a semipolar double bond (see Section 1.2).

Table 4
d(M=E) bond length data for gallium and indium complexes

Compound	d(M=E) (Å)	Reference
$[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{GaS}$	2.093(2)	[172]
$[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{GaSe}$	2.214(1)	[171]
$[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{GaTe}$	2.422(1)	[171]
$[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InSe}$	2.376(1)	[173]

Table 5
M–E single and M=E double bond length data for Group 13 element complexes

	d(M–E)[a] (Å)	d(M=E)[b] (Å)
B–O	1.439	–
B–S	1.849	–
B–Se	2.046	–
B–Te	–	–
Al–O	1.808	–
Al–S	2.304	–
Al–Se	2.390	–
Al–Te	2.578	–
Ga–O	1.943	–
Ga–S	2.290	2.093
Ga–Se	2.324	2.214
Ga–Te	2.515	2.422
In–O	2.189	–
In–S	2.528	–
In–Se	2.612	2.376
In–Te	2.814	–
Tl–O	2.530	–
Tl–S	2.801	–
Tl–Se	2.815[c]	–
Tl–Te	2.955	–

[a] d(M–E) is the mean single bond length (restricting the coordination number of E to 2) extracted from the Cambridge Structural Database (CSD Version 5.13. *3D Search and Research Using the Cambridge Structural Database*; F.H. Allen, O. Kennard, *Chemical Design Automation News* 8 (1) (1993) 1, 31–37).
[b] d(M=E) are the values of the M=E bond lengths listed in Table 4.
[c] The value reported is that without restricting the coordination number of Se to 2, since only two compounds with an anomalous average of 2.652 Å satisfy the two-coordinate criterion.

Table 6
Ga–E bond lengths in $[\mathrm{Ga}_2\mathrm{E}_6]^{6-}$

Complex	$d(\mathrm{Ga{-}E})_{\mathrm{av}}$ (Å)	Reference
$\mathrm{K}_6\mathrm{Ga}_2\mathrm{S}_6$	2.249_{term}, 2.342_{br}	[78]
$\mathrm{K}_6\mathrm{Ga}_2\mathrm{Se}_6$	2.374_{term}, 2.465_{br}	[82]
$\mathrm{K}_6\mathrm{Ga}_2\mathrm{Te}_6$	2.591_{term}, 2.680_{br}	[84]

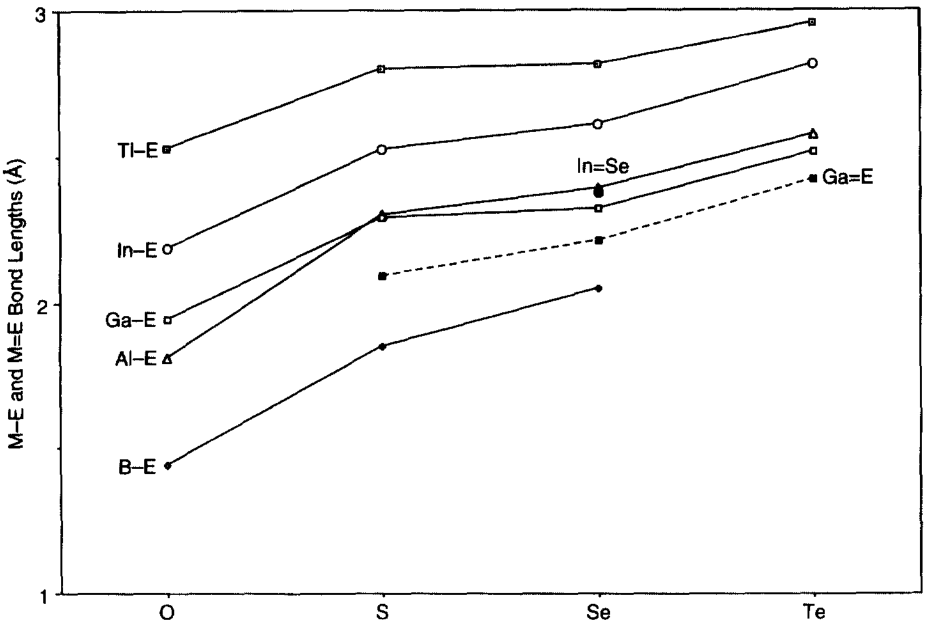

Fig. 7. M-E single bond and M=E double bond length data for Group 13 element complexes.

3. Terminal chalcogenido complexes of the Group 14 elements (C, Si, Ge, Sn, Pb)

3.1. *Multiple bonding of the Group 14 elements*

Multiple bonding of the Group 14 elements is considerably more common than that of the Group 13 elements, as illustrated by the fact that it plays a much more prominent role in the chemistry of carbon compared to that of boron. It is, therefore, not surprising that terminal chalcogenido complexes of the heavier Group 14 elements (and especially silicon and germanium) have been actively studied for approximately 20 years. Until recently, however, this work was exclusively limited to the investigation of transient [M=E] species, an area that has been extensively reviewed [20-27,66,185-195][32] and will not be considered further in this review, except where comparisons to stable multiply bonded terminal chalcogenido complexes are relevant.

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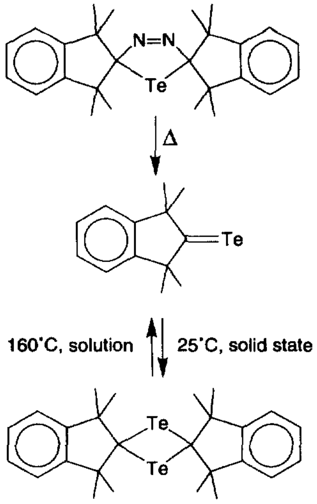
[32] The majority of these studies have been concerned with tetravalent derivatives. However, the divalent multiply-bonded germanium and silicon complexes, $Ge=CH_2$ and $Si=CH_2$, have recently been detected, see reference [195].



Scheme 5.

3.2. Syntheses of Group 14 terminal chalcogenido complexes

3.2.1. Carbon

In contrast to the ubiquitous carbonyl functionality, stable compounds which possess C=S,[33] C=Se,[34] and C=Te[35] double bonds, and especially the latter, are rather limited. Recently, however, Okazaki synthesized the first telluroketone [$C_6H_4(CMe_2)_2CTe$] that is sufficiently stable in solution to allow spectroscopic characterization (see Scheme 5) [200,201]. Although stable in solution, the telluroketone exists as a dimer in the solid state. The synthesis of [$C_6H_4(CMe_2)_2CTe$] completes the series of chalcogen derivatives [$C_6H_4(CMe_2)_2CE$] (E = O, S, Se, Te). In this regard, Bildstein has also synthesized a series of ferrocenyl chalcogenoketones, $(Fc)_2CE$ (E = S, Se, Te), by reaction of the ketone $(Fc)_2CO$ with P_4S_{10}, $(Me_2Al)_2Se$ and $(Me_2Al)_2Te$, respectively [202]. Finally, several exam-

X = OR, NR$_2$

Scheme 6.

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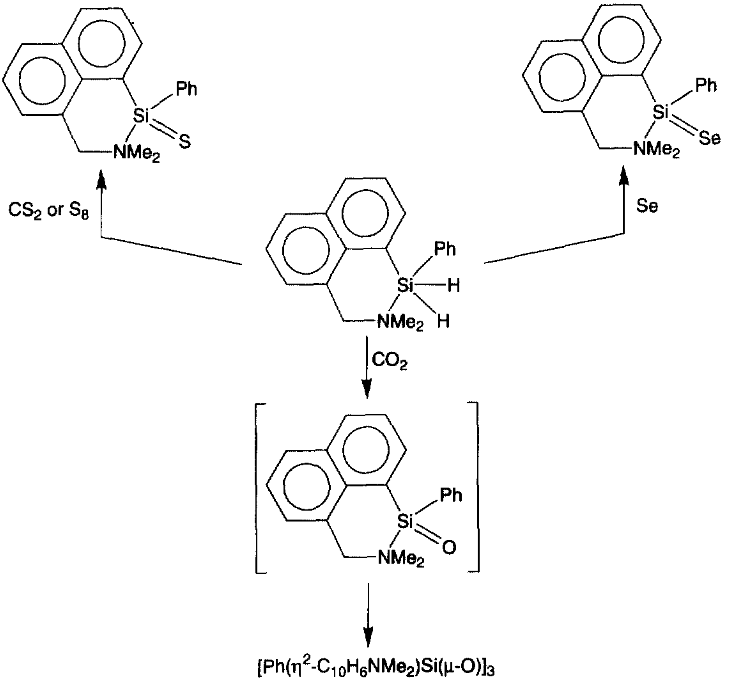
[33] For a review on thiocarbonyls, see reference [196].

[34] For a review which includes selenocarbonyls, see reference [197].

[35] For examples of telluroaldehydes and telluroketones that been generated and trapped in situ by dienes and other substrates, see references [198,199].

ples of stable telluroesters and telluroamides have been reported and structurally characterized, but these complexes are stabilized by resonance structures of the types $\overset{-}{\mathrm{Te}}-\mathrm{C}=\overset{+}{\mathrm{X}}$, as illustrated in Scheme 6 [203,204].

In addition to studying chalcogenoketones, Okazaki has also synthesized thio [205] and selenoaldehyde [206] derivatives using bulky substituents, namely TbtC(E)H (E = S, Se; Tbt = $2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$).



Scheme 7.

3.2.2. Silicon

Terminal oxo complexes of silicon, i.e. silanones, have not yet been isolated and their existence is limited to that of reactive intermediates; for example, Me_2SiO has been synthesized in a matrix at low temperatures by reaction of in situ generated Me_2Si[36] with either N_2O or ethylene oxide [6–28].[37] Until recently, the chemistry of silanethiones was likewise restricted to that of transient species. A significant advance, however, occurred in 1989 when Corriu reported the synthesis

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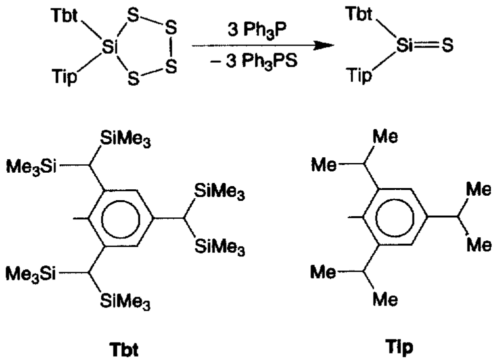
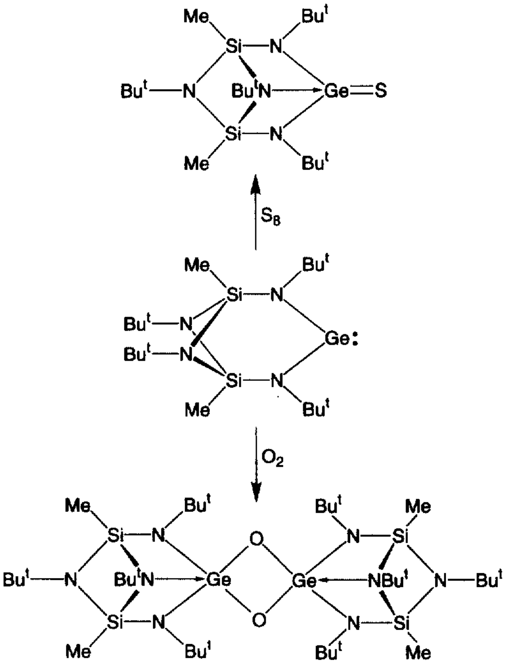
[36] Me_2Si is generated by photolysis of either dodecamethylcyclohexasilane or diazidodimethylsilane.

[37] For theoretical calculations on $H_2M{=}O$ complexes (M = Si, Ge, Sn, Pb), see reference [65].



Scheme 8.

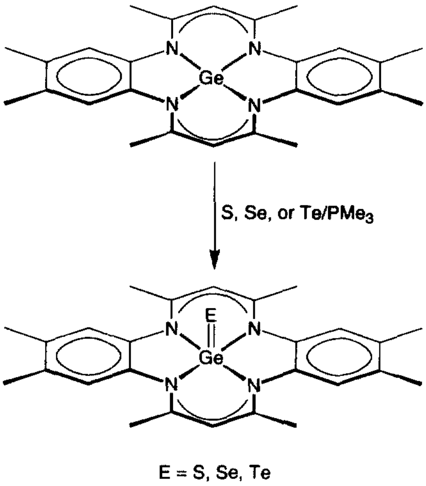
of the four-coordinate sulfido complex Ph(η^2-$C_{10}H_6NMe_2$)SiS by the reaction of the parent silane, Ph(η^2-$C_{10}H_6NMe_2$)SiH_2, with either carbon disulfide (CS_2) or elemental sulfur (Scheme 7) [207]. Corriu was also able to prepare the selenido counterpart Ph(η^2-$C_{10}H_6NMe_2$)SiSe by reaction of Ph(η^2-$C_{10}H_6NMe_2$)SiH_2 with selenium, but attempts to synthesize the silanone Ph(η^2-$C_{10}H_6NMe_2$)SiO resulted in the generation of a trimer possessing a six-membered [Si_3O_3] ring.



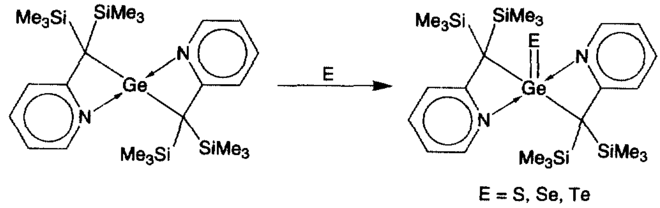
Scheme 9.

More recently, in 1994, Okazaki synthesized the first three-coordinate silanethione complex. Specifically, by making use of bulky aryl substituents, namely 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$ (Tbt) and 2,4,6-$Pr^i_3C_6H_2$ (Tip), Okazaki isolated Tbt(Tip)SiS by abstraction of sulfur from the tetrathiasilolane complex, Tbt(Tip)Si(η^2-S_4), via reaction with three equivalents of triphenylphosphine (Scheme 8) [208].

Terminal selenido complexes of silicon are not stable. For example, Et_2SiSe has



Scheme 10.

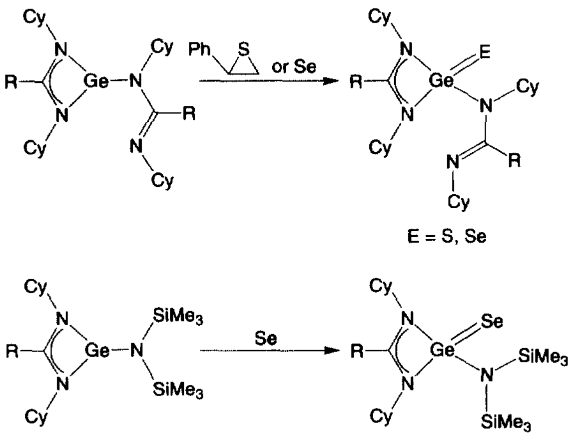


Scheme 11.

been generated as a transient species by photolysis of trimeric $[Et_2Si(\mu\text{-}Se)]_3$ [189]. Furthermore, the room temperature reaction between Cp^*_2Si and Bu^n_3PSe has been reported to generate $[Cp^*_2SiSe]$ which has been trapped by a [2 + 4] cycloaddition reaction with 2,3-dimethylbutadiene; in the absence of a trapping agent, the bridging selenido complex $[Cp^*_2Si(\mu\text{-}Se)]_2$ is isolated [8].

3.2.3. Germanium

After carbon, the most significant advances in terminal chalcogenido complexes



Scheme 12.

of the Group 14 elements have been obtained for germanium, with some of the earliest work being concerned with the identification of simple germanone (R_2GeO) and germanethione (R_2GeS) species as reactive intermediates [20–25]. More recently, as the result of efforts by several research groups, a variety of terminal chalcogenido complexes of germanium have been synthesized and isolated. Thus, in 1989, Veith was the first to isolate and structurally characterize a terminal chalcogenido complex of germanium, namely the sulfido derivative $[\eta^3\text{-}\{(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2\}]\text{GeS}$, by oxidative addition of elemental sulfur to the divalent precursor $[\eta^2\text{-}\{(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2\}]\text{Ge}$ (Scheme 9) [209]. In contrast, however, the reaction of $[\eta^2\text{-}\{(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2\}]\text{Ge}$ with O_2 yields a bridging, rather than terminal, oxo derivative.

The first multiply bonded terminal selenido and tellurido complexes of germa-

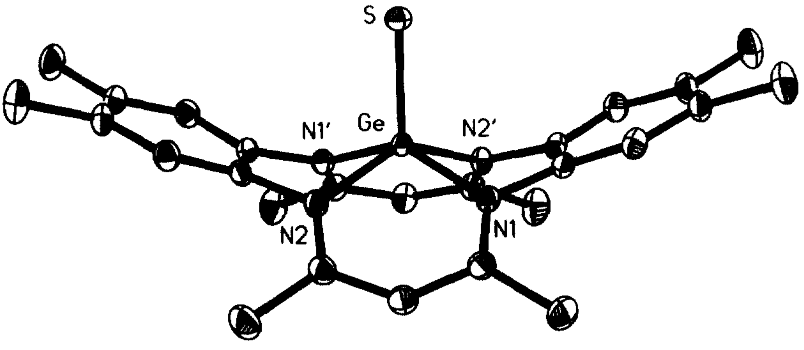


Fig. 8. Saddle-shaped structure of $[\eta^4\text{-Me}_8\text{taa}]\text{GeS}$ (the structure of $[\eta^4\text{-Me}_8\text{taa}]\text{GeSe}$ is similar).

nium are the five-coordinate macrocyclic derivatives, [η^4-Me$_8$taa]GeE, synthesized by addition of the elemental chalcogen to [η^4-Me$_8$taa]Ge (Scheme 10) [210]. The sulfido complex, [η^4-Me$_8$taa]GeS, has also been reported, so that [η^4-Me$_8$taa]GeE (E = S, Se, Te) represent the first series of heavy terminal chalcogenido complexes of germanium.[38] An interesting aspect of the structures of the germanium complexes, [η^4-Me$_8$taa]GeE (E = S, Se, Te), is associated with the configuration of the [η^4-Me$_8$taa] ligand, as illustrated in Figs. 8 and 9. Specifically, although the [η^4-Me$_8$taa] ligand adopts a saddle shape in all three complexes, the form of saddles are not all the same. Thus, whereas the sulfido and selenido complexes adopt an identical configuration of the saddle-shaped [η^4-Me$_8$taa] ligand, in which the benzo groups are directed from the macrocyclic N$_4$ plane *towards* the chalcogen ligand, the tellurido complex exhibits the inverted configuration in which the benzo groups are directed *away* from the chalcogen ligand. Interestingly, ^{1}H NMR spectroscopic studies indicate that solutions of each of the complexes [η^4-Me$_8$taa]GeE (E = S, Se, Te) contain both 'up/down' pairs of isomers; furthermore, magnetization transfer experiments demonstrate that isomer interconversion is facile [215].

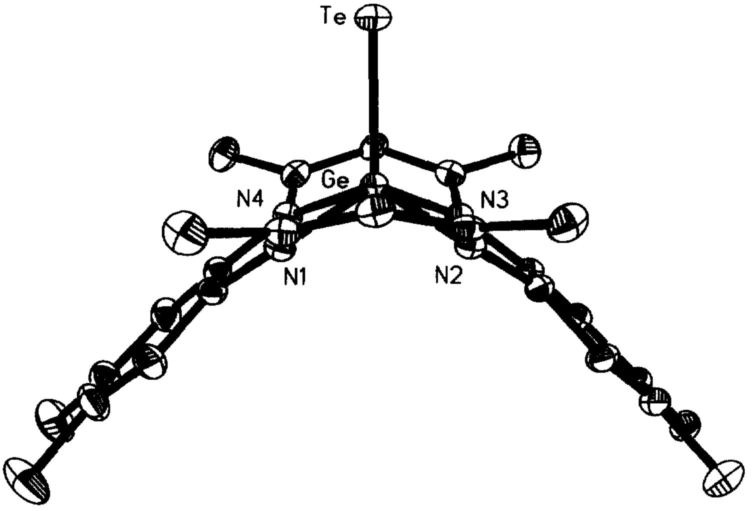


Fig. 9. Saddle-shaped structure of [η^4-Me$_8$taa]GeTe.

A second series of terminal chalcogenido complexes of germanium are the four-coordinate complexes {η^2-[2-(Me$_3$Si)$_2$CH]C$_5$H$_4$N}$_2$GeE (E = S, Se, Te) reported by Meller [216], although this series lacks the structure of the sulfido

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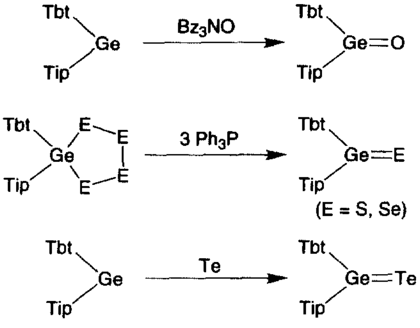
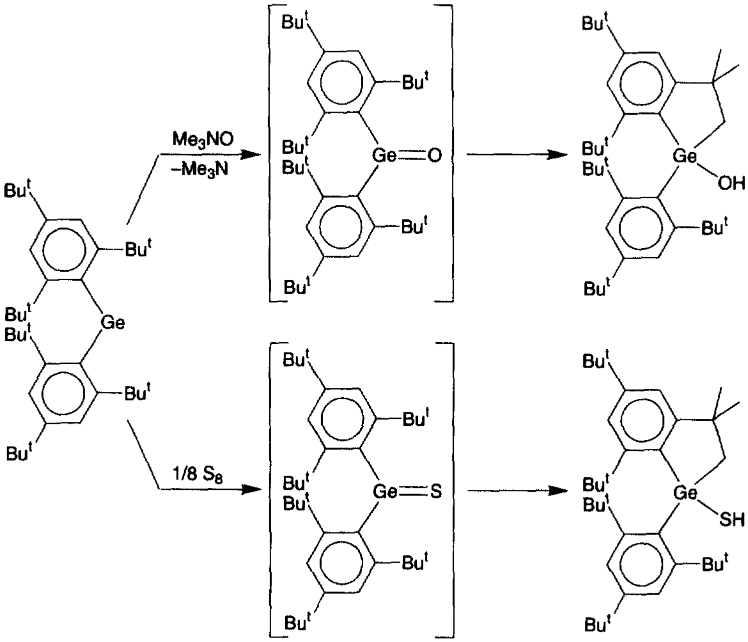
[38] It is noteworthy that [η^4-Me$_8$taa] and [η^4-Me$_4$taa] ligands have also been used to stabilize terminal chalcogenido complexes of tetravalent titanium [211–214] and vanadium [214].

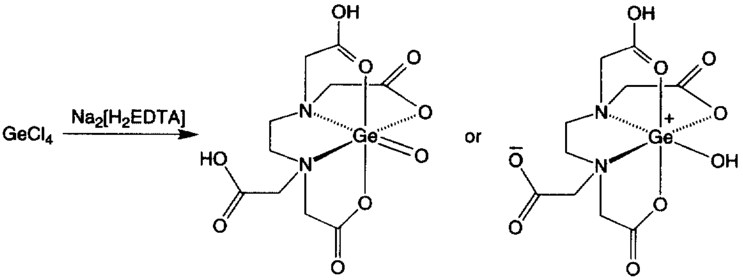


Scheme 13.

derivative. As with [η^4-Me_8taa]GeE, the terminal chalcogenido complexes {η^2-[2-$(Me_3Si)_2CH]C_5H_4N\}_2$GeE are prepared by direct addition of the chalcogen to the divalent precursor (Scheme 11). Other four-coordinate terminal chalcogenido complexes of germanium include Richeson's amidinate derivatives $[CyNC(R)NCy]_2GeE$ and $[CyNC(R)NCy][(Me_3Si)_2N]GeE$ (R = Me, Bu^t; E = S, Se), as illustrated in Scheme 12 [217]. Interestingly, in contrast to the tin analogs



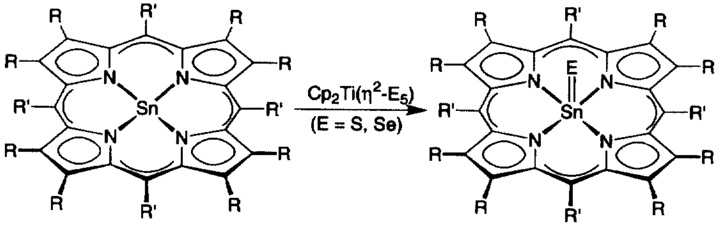
Scheme 14.



Scheme 15.

described below, $[CyNC(R)NCy]_2GeE$ contain both unidentate and bidentate amidinate ligands.

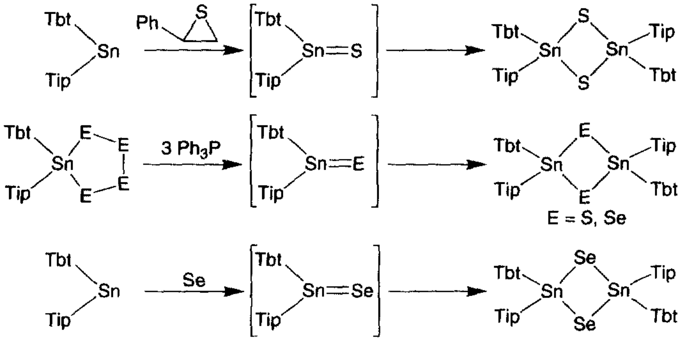
Okazaki has synthesized a very significant series of terminal chalcogenido complexes of germanium, namely the three-coordinate complexes (Tbt)(Tip)GeE (E = O [218,219], S [220], Se[221,222], Te [223]), the syntheses of which are illustrated in Scheme 13; in addition, the $Tbt[(Me_3Si)_2CH]GeTe$ derivative has also been synthesized. The importance of the very bulky Tbt, Tip and $[(Me_3Si)_2CH]$ ligands in stabilizing three-coordinate terminal chalcogenido complexes is highlighted by the fact that monomeric Tbt(Tip)GeS may be isolated in the solid state, whereas the closely related complex $[Tbt(Mes)Ge(\mu\text{-}S)]_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) exists as a dimer [224]. Interestingly, whereas the Tbt and Tip combination is



Scheme 16.

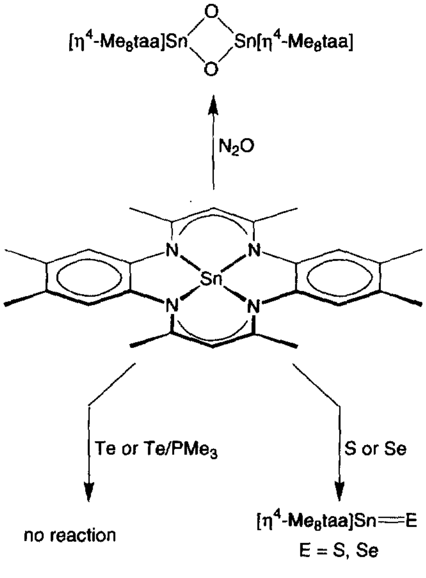
sufficient to allow isolation of the sulfido, selenido, and tellurido derivatives Tbt(Tip)GeE in the solid state, the oxo complex Tbt(Tip)GeO has not been isolated and its characterization is based on trapping reactions. The germanone complex Tbt(Tip)GeO may also be generated by cycloreversion of $Tbt(Tip)Ge(\eta^2\text{-}ONCMes)$ [219].

Jutzi has also generated a three-coordinate germanone, Mes^*_2GeO (Mes^* = $2,4,6\text{-}Bu^t_3C_6H_2$), by the reaction of Mes^*_2Ge with Me_3NO [225]. As with Tbt(Tip)GeO, Mes^*_2GeO is unstable in solution; the latter complex decomposes via reaction with a C–H bond of one of the ortho *t*-butyl substituents (Scheme 14),



Scheme 17.

while decomposition of Tbt(Tip)GeO involves migration of a Me_3Si group to oxygen. Furthermore, du Mont has reported that the sulfido intermediate [Mes^*_2GeS] (generated by reaction of Mes^*_2Ge with S_8) decomposes via reaction with a C–H bond of one of the *ortho* *t*-butyl substituents (Scheme 14) [226]. There is a single report of a structurally characterized germanium oxo complex, namely (H_2EDTA)GeO [227]. The latter complex is obtained by the reaction of $Na_2[H_2EDTA]$ with $GeCl_4$ (Scheme 15) and is characterized by $\nu(Ge{=}O) = 815$ cm^{-1} and $d(Ge{=}O) = 1.77(1)$ Å; however, it was noted that the X-ray diffraction was insufficiently accurate to unambiguously distinguish that the complex was an



Scheme 18.

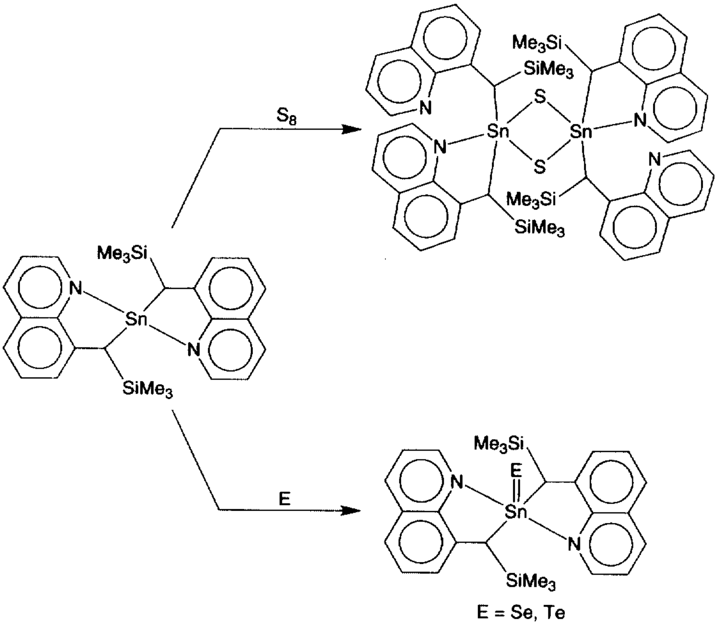
Table 7
IR data for (POR)SnE complexes[a]

	$\nu(Sn{=}E)$ (cm^{-1})
(TPP)SnS	437
(TMTP)SnS	433
(TTP)SnS	432
(TMP)SnS	434
(OEP)SnS	426
(TPP)SnSe	300
(TMTP)SnSe	298
(TTP)SnSe	298
(TMP)SnSe	297
(OEP)SnSe	292

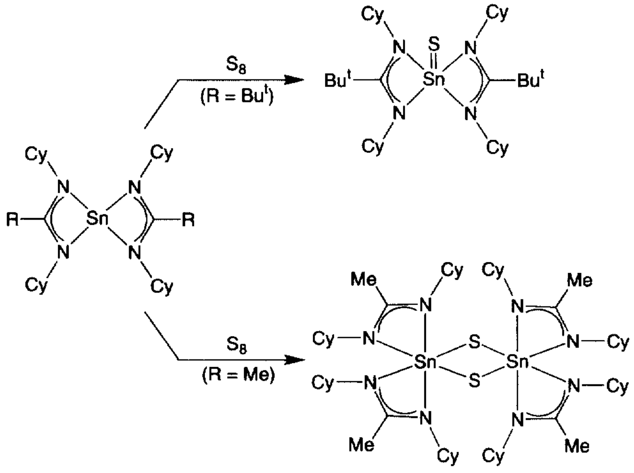
[a] Data taken from refs. [232,233].

oxo derivative, and not, for example, a hydroxy complex of the type illustrated in Scheme 15.

Finally, a bulky aryloxide ligand has been employed in the synthesis of the sulfido complex, $(ArO)_2GeS$ [Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$], by addition of sulfur to divalent $(ArO)_2Ge$; $(ArO)_2GeS$ has not, however, been structurally authenticated by X-ray diffraction [228].



Scheme 19.



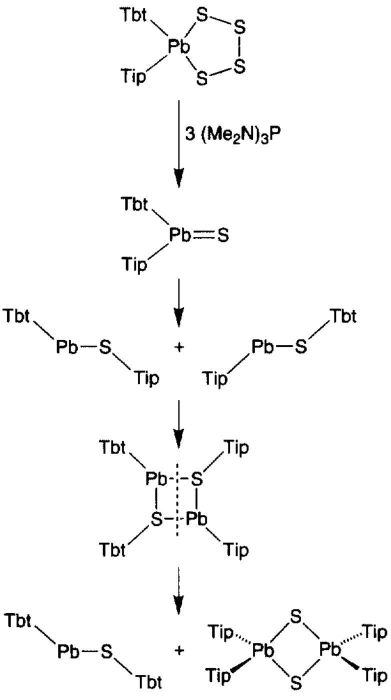
Scheme 20.

3.2.4. Tin

Several examples of multiply bonded terminal chalcogenido complexes of tin have been isolated, with the first examples having been reported in 1991 by Guilard et al. Specifically, the five-coordinate sulfido and selenido porphyrin complexes (POR)SnE (POR = TPP, TMTP, TTP, TMP, OEP) were synthesized by reactions of divalent (POR)Sn with the chalcogen transfer reagents $Cp_2Ti(\eta^2\text{-}E_5)$ (E = S, Se), as illustrated in Scheme 16 [229]. However, although spectroscopic evidence was obtained for (POR)SnE (see, for example Table 7), the complexes were not structurally characterized.

Okazaki was the first to report three-coordinate terminal chalcogenido complexes of tin. For example, the three-coordinate stannanethione complex Tbt(Tip)SnS was synthesized by the room temperature reaction of Tbt(Tip)Sn with styrene sulfide (Scheme 17) [230,231]. The corresponding stannaneselenone, Tbt(Tip)SnSe, has also been described [232,233]. On the basis of spectroscopic and reactivity studies, Tbt(Tip)SnE (E = S, Se) have been proposed to exist as monomeric species in solution; however, X-ray diffraction studies revealed both *cis* and *trans* chalcogen bridged dimeric structures for $[(Tbt)(Tip)Sn(\mu\text{-}Se)]_2$ and $[(Tbt)(Mes)Sn(\mu\text{-}E)]_2$ (E = S, Se) in the solid state [232]. The latter observation is particularly significant when it is considered that the germanium counterparts (Tbt)(Tip)GeE are monomeric in the solid state (see Section 3.2.3). As such, it provides a clear indication that germanium is more capable of supporting a multiple bond than is its heavier congener, tin.

The first structurally characterized examples of multiply bonded terminal chalcogenido tin complexes, namely $[\eta^4\text{-}Me_8taa]SnE$ (E = S, Se), were reported in 1995. These tin complexes were synthesized by the same method used for the germanium analogs, i.e. oxidative addition of elemental sulfur and selenium to the divalent



Scheme 21.

macrocyclic complex [η^4-Me_8taa]Sn (Scheme 18) [234].[39] Divalent [η^4-Me_8taa]Sn also reacts with N_2O to give an oxo complex, but in contrast to the terminal sulfido and selenido derivatives, the oxo complex exists as an oxo bridged dimer, {[η^4-Me_8taa]Sn(μ-O)}$_2$, in the solid state [235].[40] As such, it provides a further illustration of the observation noted in Section 3.2.3 that Group 14 oxo complexes show a greater tendency to bridge than do the heavier chalcogenido derivatives. It is also notable that [η^4-Me_8taa]Sn is unreactive towards tellurium to yield the tellurido complex [η^4-Me_8taa]SnTe. Since the germanium counterpart [η^4-Me_8taa]GeTe has been isolated using similar conditions, the inability to isolate the tin complex [η^4-Me_8taa]SnTe provides yet a further indication that germanium is more capable of supporting a terminal valence multiple bond than is tin.

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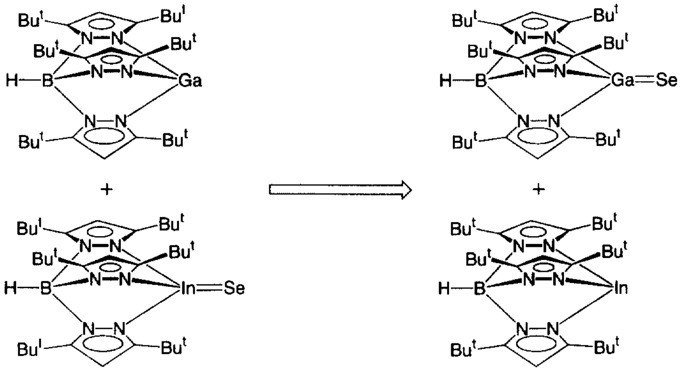
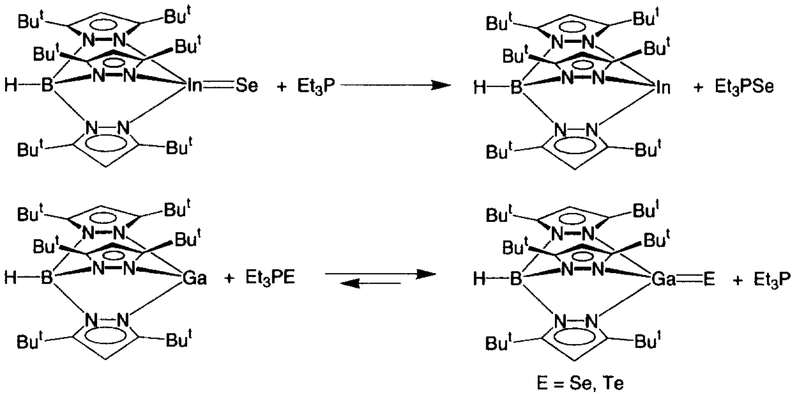
[39] The configurations of [η^4-Me_8taa]SnE (E = S, Se) in the solid state are similar to those of the germanium analogs. However, whereas two isomers are observed in solution for the germanium system, only one set of ligand resonances are observed for each of the tin analogs. Such an observation suggests that either there is only one ligand conformation in solution or that interconversion of the two ligand conformations is rapid on the NMR timescale.

[40] Another example of the formation of an oxo-bridged dinuclear tin complex by oxidation of a divalent tin precursor involves the oxidation of $[(Me_3Si)_2CH]_2Sn$ with Me_3NO to give $\{[(Me_3Si)_2CH]_2Sn(\mu\text{-}O)\}_2$ [236].

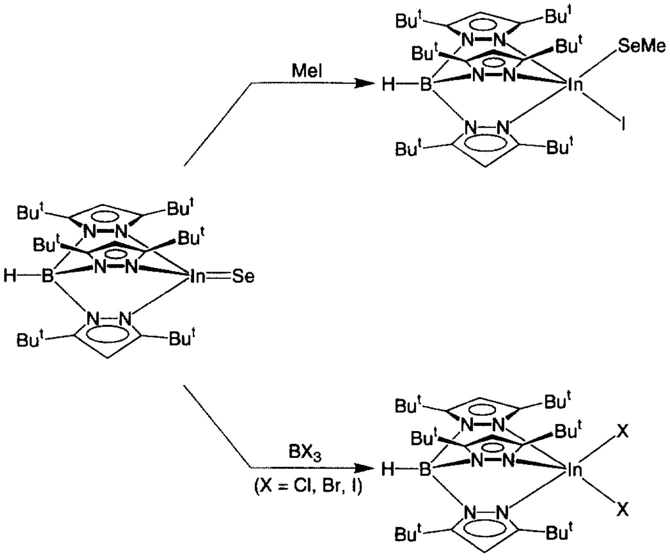


Scheme 22.

In view of the inability to isolate [η^4-Me$_8$taa]SnTe, it is significant that, in 1996, Leung reported the synthesis of {η^2-[(C$_9$H$_6$N)(Me$_3$Si)CH]}$_2$SnTe, the sole example of a multiply bonded terminal tin tellurido complex (Scheme 19) [237]. The selenido complex {η^2-[(C$_9$H$_6$N)(Me$_3$Si)CH]}$_2$SnSe has also been isolated and structurally characterized by X-ray diffraction. Somewhat surprisingly, however, the sulfido analog has been shown to exist as a sulfido-bridged dimer [{(C$_9$H$_6$N)(Me$_3$Si)CH}$_2$Sn(μ-S)]$_2$ in the solid state. Such an observation provides yet a further example of a situation in which a lighter chalcogen favors bridging more than does its heavier congeners (note, however, that the supporting ligands adopt different coordination modes in these particular examples). In this regard, it is important to note that Richeson has described some interesting results which indicate that the difference in the ability of a sulfido ligand to bridge or remain terminal is a very sensitive function of the supporting ligand environment. Specifi-

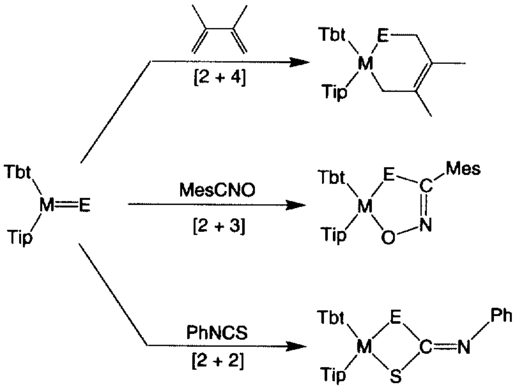


Scheme 23.



Scheme 24.

cally, Richeson has observed that the terminal sulfido complex $[\eta^2\text{-CyNC(Bu}^t\text{)NCy}]_2\text{SnS}$ is obtained by the reaction of $[\eta^2\text{-CyNC(Bu}^t\text{)NCy}]_2\text{Sn}$ with styrene sulfide (Scheme 20), whereas use of the related ligand [CyNC(Me)NCy], which differs from $[\text{CyNC(Bu}^t\text{)NCy}]$ only in the nature of the alkyl group occupying the remote 2-position of the amidinate ligand, yields a sulfido bridged dimer, $[(\text{CyNC(Me)NCy})_2\text{Sn}(\mu\text{-S})]_2$ [238].



Scheme 25.

3.2.5. Lead

Structurally characterized multiple bonds between lead and the chalcogens are presently unknown. However, Okazaki and Tokitoh have reported the generation of several plumbanethiones R(R′)PbS by the reactions of the tetrathiaplumbanes R(R′)Pb(η^2-S_4) with three equivalents of either Ph_3P or $(Me_2N)_3P$ at −78°C (Scheme 21) [26,239]. The terminal sulfido complexes are, however, unstable and decompose upon warming to room temperature; as a result of this instability, trapping studies (e.g. a [2 + 2] cycloaddition with PhNCS and a [3 + 2] cycloaddition with MesCNO) were used to establish the presence of a terminal sulfido ligand (see Section 4.2.1). In the case of $(Tip)_2PbS$, the dinuclear bridging sulfido complex $[(Tip)_2Pb(\mu\text{-}S)]_2$ is formed upon warming to room temperature. More interestingly, generating Tbt(Tip)PbS at 50°C (rather than −78°C) results in the formation of a mixture of divalent (Tbt)Pb(STbt) and tetravalent $[(Tip)_2Pb(\mu\text{-}S)]_2$, in which *each* complex contains only a *single* type of aryl group [240]. The formation of these complexes has been rationalized in terms of a mechanism that involves an initial 1,2-aryl migration (Scheme 21). Okazaki and Tokitoh have interpreted this observation as suggesting that the plumbylene derivative R(RS)Pb is more stable than the isomeric terminal sulfido complex $R_2Pb{=}S$. In this regard, it is noteworthy that Schleyer has calculated that R(RO)M is more stable than $R_2M{=}O$ for M = Ge, Sn and Pb, whereas for M = C and Si, the converse is true [65].

3.3. d(M = E) bond length data and bonding for Group 14 terminal chalcogenido complexes

Metal–chalcogen bond length data for the structurally characterized multiply bonded terminal chalcogenido complexes of Group 14 terminal chalcogenido complexes are compiled in Tables 8–10. For further comparison, M–E single bond and M=E double bond length data for Group 14 element complexes are presented in Table 11 and Fig. 10. In accord with their multiple bond character, the M=E bond lengths for each of these complexes are substantially shorter than the mean M–E single bond lengths. It is also notable that, for a given M=E functionality, the shortest M=E bond lengths are observed for Okazaki's structurally characterized three-coordinate complexes R(R′)ME. As with the gallium and indium complexes described in Section 2.3, it is most likely that the [M=E] interactions of the majority of the complexes listed in Tables 8–10 (and especially the four- and five-coordinate complexes) are best represented as a composite of the resonance

Table 8
d(M=E) bond length data for silicon complexes

Compound	*d*(Si=S) (Å)	Reference
Tbt(Tip)SiS	1.948(4)	[208]
α-Np(η^2-$C_{10}H_6NMe_2$)SiS	2.013(3)	[207]

Table 9
d(M=E) bond length data for germanium complexes

Compound	d(Ge=E) (Å)	Reference
$(H_2EDTA)GeO$	1.77(1)[a]	[227]
Tbt(Tip)GeS	2.049(3)	[220]
$[\eta^3\text{-}\{(\mu\text{-}Bu^tN)_2(SiMeNBu^t)_2\}]GeS$	2.063(3)	[209]
$[\eta^4\text{-}Me_8taa]GeS$	2.110(2)	[210]
Tbt(Tip)GeSe	2.180(2)	[221]
$[CyNC(Bu^t)NCy]_2GeSe$	2.196(4)	[217]
$[CyNC(Me)NCy][(Me_3Si)_2N]GeSe$	2.2212(3)	[217]
$[\eta^4\text{-}Me_8taa]GeSe$	2.247(1)	[210]
$\{\eta^2\text{-}[2\text{-}(Me_3Si)_2CH]C_5H_4N\}_2GeSe$	2.2472(7)	[216]
Tbt(Dis)GeTe	2.384(2)	[223]
Tbt(Tip)GeTe	2.398(1)	[223]
$[\eta^4\text{-}Me_8taa]GeTe$	2.466(1)	[210]
$\{\eta^2\text{-}[2\text{-}(Me_3Si)_2CH]C_5H_4N\}_2GeTe$	2.4795(5)	[216]

[a] The identification of this compound as a terminal oxo complex is uncertain (see text).

forms [M=E] and [$\overset{+}{M}-\overset{-}{E}$]. In support of this notion, Steiner has noted that the terminal chalcogenido complexes $[\eta^4\text{-}Me_8taa]GeE$ (E=S, Se, Te) and $[\eta^4\text{-}Me_8taa]SnE$ (E = S, Se) exhibit $E \cdots H{-}CCl_3$ hydrogen-bonding interactions with $CHCl_3$ molecules in the crystal lattice (Figs. 11 and 12) [241]. Furthermore, calculations on species such as H_2GeE (E = O, S), as described in Section 1.2, suggest that the [Ge=E] bonding is highly polarized [66].[41]

Table 10
d(M=E) bond length data for tin complexes

Compound	d(Sn=E) (Å)	Reference
$[\eta^4\text{-}Me_8taa]SnS$	2.274(3)	[234]
$[\eta^2\text{-}CyNC(Bu^t)NCy]_2SnS$	2.280(5)	[238]
$[\eta^4\text{-}Me_8taa]SnSe$	2.394(1)	[234]
$\{\eta^2\text{-}[(C_9H_6N)(Me_3Si)CH]\}_2SnSe$	2.398(1)	[237]
$\{\eta^2\text{-}[(C_9H_6N)(Me_3Si)CH]\}_2SnTe$	2.618(1)	[237]

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[41] Furthermore, given the notion that π-bonding is not prominent for the heavy p-block elements, it seems unlikely that there exists a significant contribution from the triply bonded resonance form [$\overset{-}{M}\equiv\overset{+}{E}$].

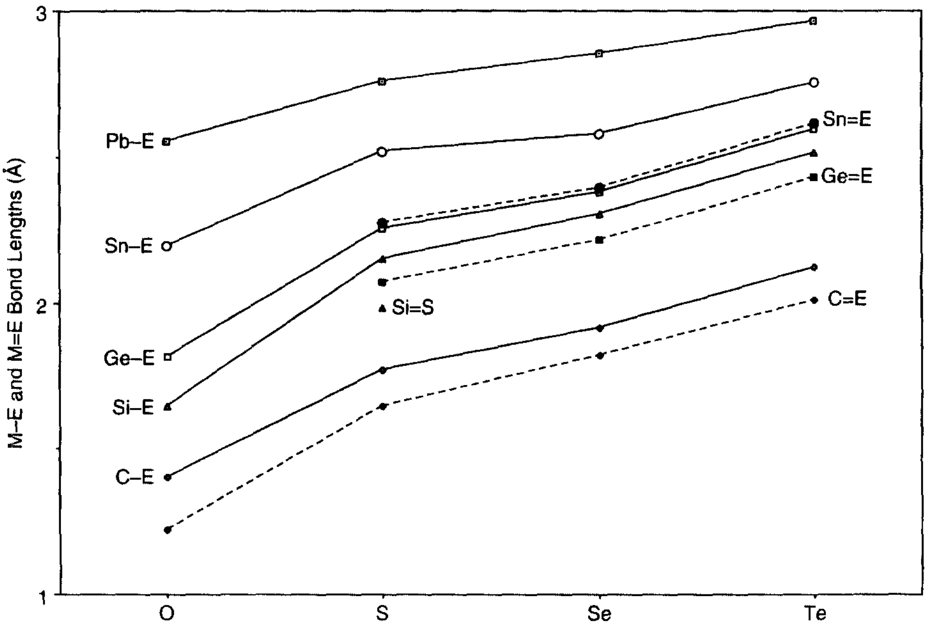


Fig. 10. M–E single bond and M=E double bond length data for Group 14 element complexes.

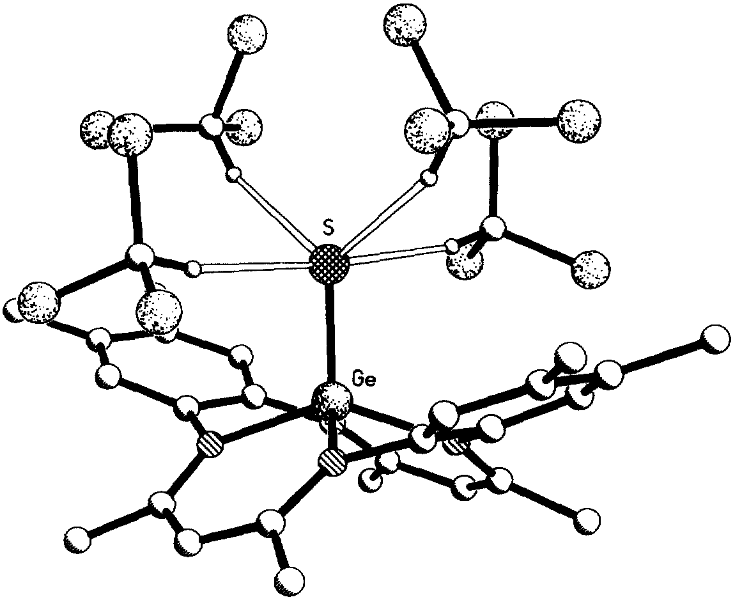


Fig. 11. E ··· H–CCl$_3$ hydrogen-bonding interactions in [η^4-Me$_8$taa]ME (M = Ge, Sn; E = S, Se).

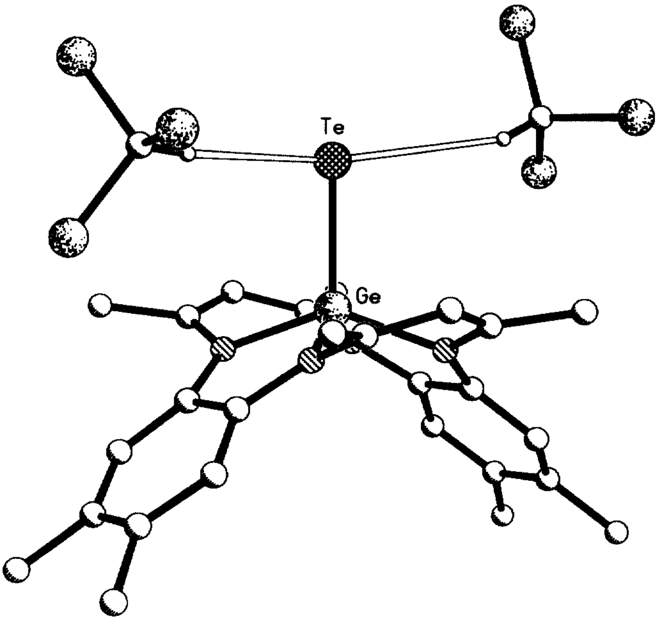
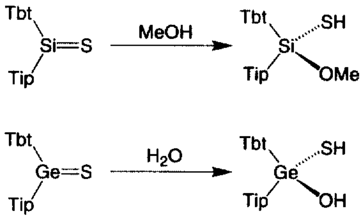


Fig. 12. E ··· H–CCl_3 hydrogen-bonding interactions in [η^4-Me_8taa]GeTe.

4. Reactivity of multiply bonded terminal chalcogenido complexes

4.1. Reactivity of Group 13 terminal chalcogenido complexes

Reactivity studies on Group 13 terminal chalcogenido complexes have been exclusively concerned with the gallium and indium complexes [$Tp^{Bu^t_2}$]GaE (E = S, Se, Te) and [$Tp^{Bu^t_2}$]InSe and have focused on: (i) reactions which involve the simple transfer of chalcogen atoms to other metal centers; and (ii) reactions which involve attack at the [M=E] moiety by polar substrates.



Scheme 26.

Table 11
M–E single and M=E double bond length data for Group 14 element complexes

	d(M–E) (Å) mean[a]	d(M=E) (Å) mean[b] (calc)[c]
C–O	1.401	1.217 (1.32)
C–S	1.767	1.641 (1.61)
C–Se	1.911	1.817 (1.74)
C–Te	2.120	2.005 (1.94)
Si–O	1.644	– (1.62)
Si–S	2.151	1.981 (2.01)
Si–Se	2.305	– (2.14)
Si–Te	2.516	– (2.34)
Ge–O	1.814	1.77[d] (1.67)
Ge–S	2.255	2.074 (2.06)
Ge–Se	2.384	2.218 (2.19)
Ge–Te	2.595	2.432 (2.39)
Sn–O	2.199	– (1.85)
Sn–S	2.522	2.277 (2.24)
Sn–Se	2.583	2.396 (2.37)
Sn–Te	2.758	2.618 (2.57)
Pb–O	2.555	–
Pb–S	2.760	–
Pb–Se	2.857[e]	–
Pb–Te	2.967	–

[a] d(M–E) is the mean single bond length (restricting the coordination number of E to 2) extracted from the Cambridge Structural Database (CSD Version 5.13. *3D Search and Research Using the Cambridge Structural Database*; F.H. Allen, O. Kennard, *Chemical Design Automation News* 8 (1) (1993) 1, 31–37).
[b] d(M=E) are the mean values of the M=E bond lengths listed in Table 10. For carbon, d(M=E) is the mean double bond length extracted from the Cambridge Structural Database.
[c] The calculated d(M=E) values listed in parentheses are the sum of the M and E covalent radii listed in L. Pauling, *The Nature of The Chemical Bond, 3rd ed.*, Cornell University Press, Ithaca, 1960, p. 224, except for the value for O (0.55 Å) which was taken from W.L. Jolly, *Modern Inorganic Chemistry*, McGraw-Hill, New York, 1984, p. 53.
[d] The value for d(Ge=O) is questionable (see text and Table 10).
[e] In view of the paucity of complexes with Pb–Se interactions, the search was expanded to all interactions, without restricting the coordination number of Se to 2.

4.1.1. Chalcogen atom transfer reactions

Chalcogen atom transfer reactions are particularly important because they provide considerable insight into the relative energies of the [M=E] bonding interaction within terminal chalcogenido complexes.[42] For example, the observation that the selenido ligand transfers from indium to gallium in the reaction of $[\mathrm{Tp}^{\mathrm{Bu^t_2}}]$InSe with $[\mathrm{Tp}^{\mathrm{Bu^t_2}}]$Ga (Scheme 22) provides a clear indication that the

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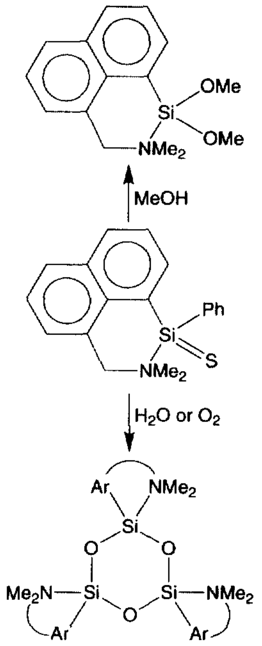
[42] For a review of chalcogen exchange reactions of this type, see reference [242].



Scheme 27.

Ga=Se interaction is stronger than the corresponding In=Se interaction. Chalcogen atom transfer between {$[Tp^{Bu^t_2}]M$} and {PR_3} also supports such a notion. For example, Et_3P readily abstracts the selenido ligand from $[Tp^{Bu^t_2}]InSe$ giving $[Tp^{Bu^t_2}]In$ and Et_3PSe, whereas it is the reverse reaction, namely chalcogen atom transfer from Et_3PE (E = Se, Te) to $[Tp^{Bu^t_2}]Ga$, which occurs in the gallium system (Scheme 23). Interestingly, however, despite the observation of selenium transfer between gallium and phosphorus, sulfur transfer is not observed in *either* direction under comparable conditions, clearly indicating that sulfur atom transfer is kinetically inhibited [243]. Such an observation is in accord with Woo's report that sulfur atom transfer between two tin centers is approx. 200 times slower than selenium atom transfer [244].

For the case of selenium atom transfer between Ga and P, the reaction is reversible and addition of excess Et_3P to $[Tp^{Bu^t_2}]GaSe$ generates low equilibrium concentrations of $[Tp^{Bu^t_2}]Ga$ and Et_3PSe. The temperature dependence of the equilibrium constant established values of $\Delta H° = 6.8(7)$ kcal mol^{-1} and $\Delta S° = 9(2)$ e.u. for selenium atom transfer from Ga to P, so that the [Ga=Se] interaction is approx. 7 kcal mol^{-1} stronger than the [P=Se] interaction of Et_3PSe. On the basis of the above chalcogen transfer reactions, it is apparent that [X=E] bond strengths decrease in the sequence $[Tp^{Bu^t_2}]GaE > Et_3PE > [Tp^{Bu^t_2}]InE$.

4.1.2. Reactivity of the [M = E] moiety towards polar substrates

To date, only the reactivity of the indium selenido complex $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InSe}$ has been studied in any detail. For example, the selenido ligand of $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InSe}$ is rapidly alkylated at room temperature by methyl iodide giving the methylselenolate-iodide complex, $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{In(SeMe)I}$ (Scheme 24) [245]. Alkylation of terminal chalcogenido moieties by alkyl halides is precedented and has been observed for both main group (also see Section 4.2)[43] and transition metal complexes. As a consequence of alkylation, the In–Se bond lengthens considerably from 2.376(1) Å in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InSe}$ to 2.52(1) Å in $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{In(SeMe)I}$. Such a lengthening is in accord with lowering the formal [In–Se] bond order from two to one.

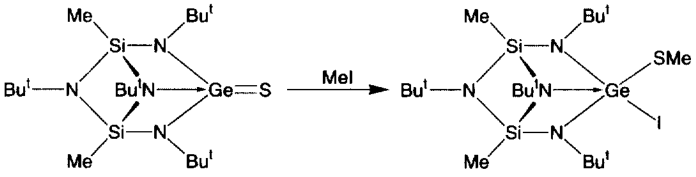
In contrast to alkylation by methyl iodide, the reactions of $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InSe}$ with the boron halides BX_3 (X = Cl, Br, I) result in abstraction of the selenido ligand, thereby yielding the indium dihalide complexes $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InX}_2$ (Scheme 24) [245]. The diiodide $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{InI}_2$ has also been obtained by oxidative addition of I_2 to $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]\mathrm{In}$ [248].

4.2. Reactivity of Group 14 terminal chalcogenido complexes

In view of the rather extensive chemistry of the [C=E] functionality, only the reactivity of silicon, germanium, tin and lead derivatives will be discussed.

4.2.1. Three-coordinate Tbt(Tip)ME complexes

Okazaki has extensively studied the reactivity of the three-coordinate silicon, germanium, tin and lead 'heavy ketone' complexes, Tbt(Tip)ME, described in Section 3.2. Transformations that are common to these derivatives include [2 + 2], [2 + 3], and [2 + 4] cycloadditions of the [M=E] moiety, as illustrated by the reactions with PhNCS, MesCNO and 2,3-dimethyl-1,3-butadiene, respectively (Scheme 25).[44] The M=E functionalities in these three-coordinate complexes Tbt(Tip)ME are also reactive towards protic reagents. For example, Tbt(Tip)SiS reacts with MeOH to give Tbt(Tip)Si(SH)(OMe), while Tbt(Tip)GeS reacts with $\mathrm{H_2O}$ to give Tbt(Tip)Ge(OH)(SH), as illustrated in Scheme 26.



Scheme 28.

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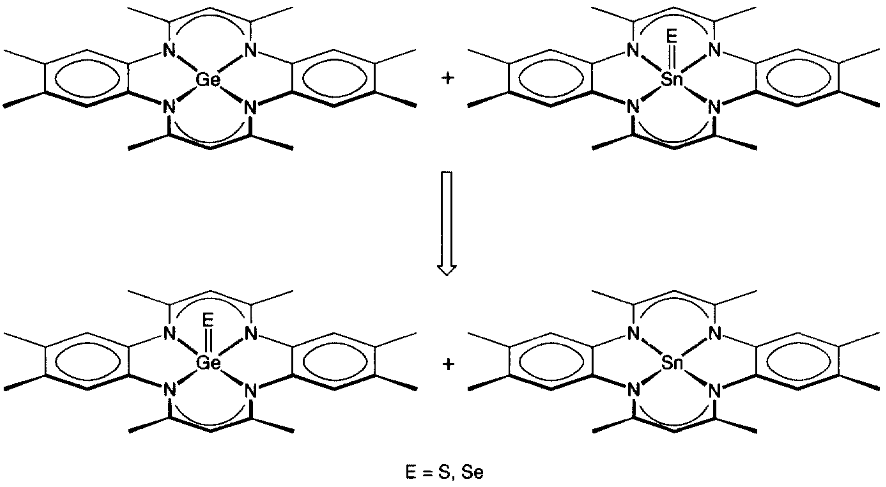
[43] For some examples of alkylation of terminal chalcogenido ligands in transition metal complexes, see refs. [61,246,247].

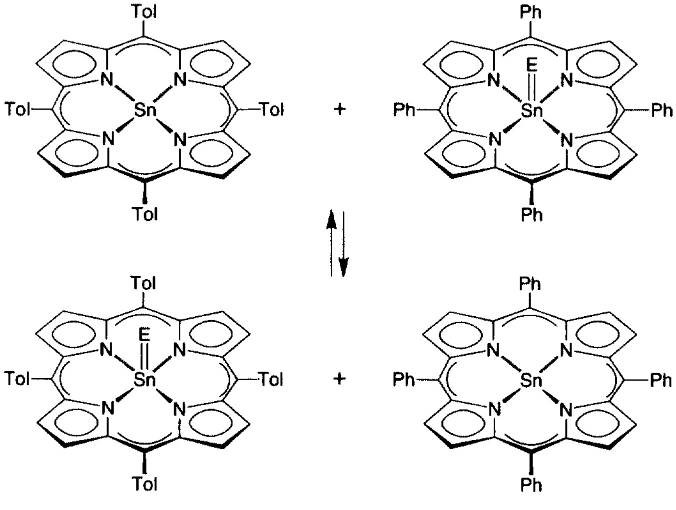
[44] It should be noted that transient [Ge=E] species also undergo analogous [2 + 3] cycloaddition reactions with MesCNO and related 1,3-dipolar substrates. See refs. [249,250].



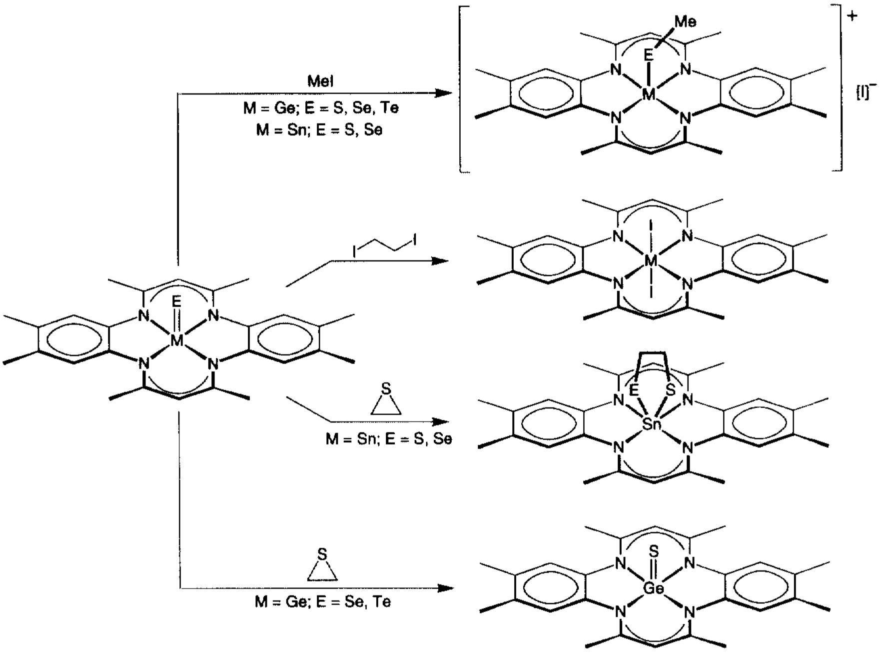
Scheme 29.

4.2.2. Four-coordinate L_nME complexes

In contrast to the above three-coordinate Tbt(Tip)ME complexes, the four-coordinate silicon sulfido complex Ph(η^2-$C_{10}H_6NMe_2$)SiS exhibits little reactivity. For example, Ph(η^2-$C_{10}H_6NMe_2$)SiS is inert towards both electrophiles and nucleophiles such as methyl iodide, hydrogen chloride, ethylene oxide, acetone, Et_3SiH, Me_3SiOMe, Bu^n_3P and $P(OMe)_3$ [207]; Ph(η^2-$C_{10}H_6NMe_2$)SiS does, however, react with excess methanol giving Ph(η^2-$C_{10}H_6NMe_2$)Si(OMe)$_2$ and is hydrolyzed



Scheme 30.



Scheme 31.

to the trimeric complex, $[Ph(\eta^2\text{-}C_{10}H_6NMe_2)Si(\mu\text{-}O)]_3$ (Scheme 27). Veith has reported that $[\eta^3\text{-}\{(\mu\text{-}Bu^tN)_2(SiMeNBu^t)_2\}]GeS$ reacts with methyl iodide resulting in alkylation of the terminal chalcogenido moiety giving $[\eta^3\text{-}\{(\mu\text{-}Bu^tN)_2(SiMeNBu^t)_2\}]Ge(SMe)I$ (Scheme 28) [251].

4.2.3. *Five-coordinate L_nME complexes*

4.2.3.1. Chalcogen atom transfer reactions. Chalcogen atom transfer between tin and germanium centers was first demonstrated for the macrocyclic complexes $[\eta^4\text{-}Me_8taa]SnE$ (E = S, Se) and $[\eta^4\text{-}Me_8taa]Ge$ (Scheme 29) [234]. Importantly, the transfer proceeds to completion, thereby demonstrating that the terminal [Ge=E] interaction is considerably stronger than the corresponding [Sn=E] interaction. In contrast, for situations in which there is little difference in [M=E] bond energies, the chalcogen atom transfer would be expected to be reversible. For example, Woo has reported the reversible transfer of sulfur and selenium between the tin centers of the porphyrin complexes (TPP)Sn and (TTP)Sn (Scheme 30) [244]. Interestingly, selenium atom transfer was shown to be significantly faster (by a factor of approx. 200) than sulfur atom transfer, an observation that was interpreted as indicating that the Sn=Se interaction is weaker than the Sn=S interaction.

In addition to the observation of sulfur and selenium transfer from tin to

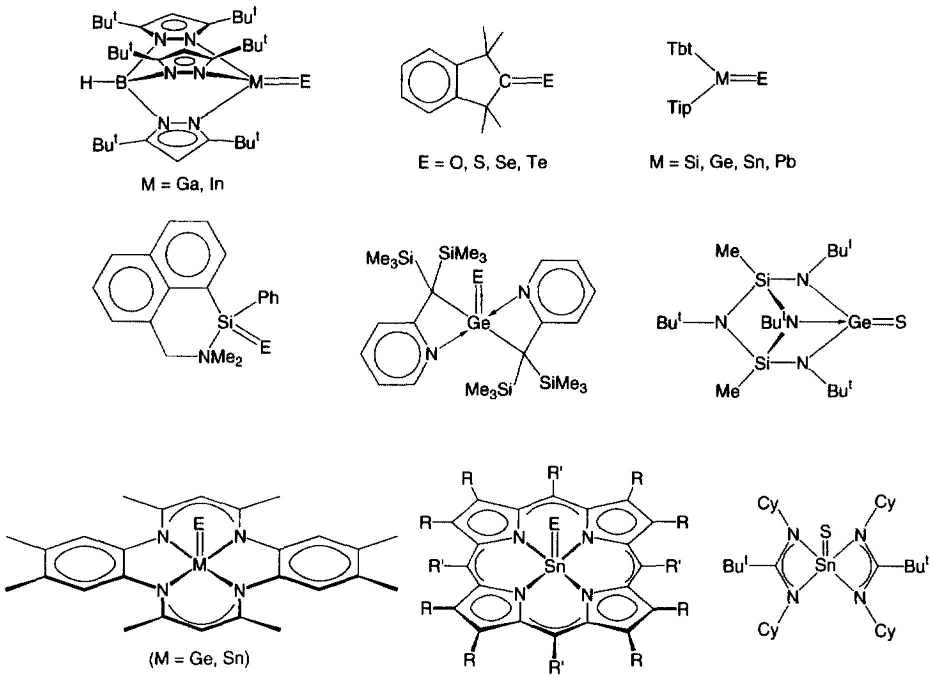


Fig. 13. Illustrative examples of structurally characterized terminal chalcogenido complexes of the Group 13 and 14 elements.

germanium, the inability to generate the tin tellurido complex [η^4-Me$_8$taa]SnTe under conditions which yield the germanium analog [η^4-Me$_8$taa]GeTe (see Section 3.2.3) also suggests that the [Ge=Te] interaction is stronger than the hypothetical [Sn=Te] interaction. It is, therefore, inferred that [Ge=E] bonds are expected to be stronger than the corresponding [Sn=E] bonds. In accord with this notion, calculations on the [M=S] functionalities (M = C, Si, Ge, Sn) indicate that π-bond energies decrease upon descending Group 14 (see Table 2). As noted in Section 2.2 for the Group 13 elements, these observations are consistent with the general concepts that (i) the tendency for elements of the p-block to engage in multiple bonding and (ii) the stability of the N vs. $(N-2)$ valence state decreases for the heavier congeners.

4.2.3.2. Reactivity of the [M=E] moiety towards polar substrates. In addition to chalcogen atom transfer, both [η^4-Me$_8$taa]GeE and [η^4-Me$_8$taa]SnE undergo reactions which result in functionalization of the chalcogenido ligands. In particular, a reaction that is common to each of the complexes [η^4-Me$_8$taa]ME (M = Ge, E = S, Se, Te; M = Sn, E = S, Se) involves alkylation of the terminal chalcogenido ligand by methyl iodide giving the methyl-chalcogenolate complexes, {[η^4-Me$_8$taa]M(EMe)}[I], as shown in Scheme 31 [252]. 1,2-Diiodoethane also reacts

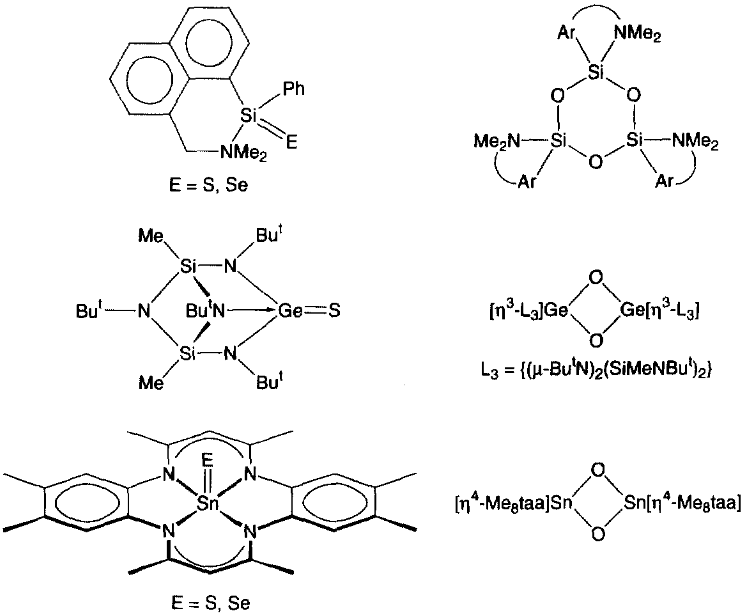


Fig. 14. Terminal sulfido vs. bridging oxo interactions in Group 14 chalcogenido complexes.

with each of the [η^4-Me_8taa]ME complexes; however, in contrast to the reactions with MeI, the products are the diiodide complexes, *trans*-[η^4-Me_8taa]MI_2, rather than chalcogenolate derivatives (Scheme 31).

While the reactions with alkyl halides are common to both the germanium and tin chalcogenido complexes, an interesting distinction is observed in the reactions with ethylene sulfide (Scheme 31). In the case of the tin complexes, the reactions with ethylene sulfide involve ring opening of the episulfide affording the five-membered 1,3-dichalcogenido-2-stannacyclopentane derivatives, [η^4-Me_8taa]Sn(η^2-ECH_2CH_2S) (E = S, Se). Such a reaction is similar to the previously reported trapping of transient [M=E] (M = Ge, Sn) containing species with epoxides and episulfides to yield five-membered ring products [230–233,253–258]. In contrast, the germanium chalcogenido complexes [η^4-Me_8taa]GeE (E = Se, Te) do not react with ethylene sulfide to yield stable five-membered 1,3-dichalcogenido-2-germanacyclopentane derivatives [η^4-Me_8taa]Ge(η^2-ECH_2CH_2S). Rather, chalcogen exchange giving the terminal sulfido complex [η^4-Me_8taa]GeS results (Scheme 31). Nevertheless, although [η^4-Me_8taa]Ge(η^2-ECH_2CH_2S) is not observed to be a product of these reactions, it is possible that such a species may be an intermediate: specifically, chalcogen exchange may be a result of decomposition of [η^4-Me_8taa]Ge(η^2-ECH_2CH_2S) by cycloreversion to [η^4-Me_8taa]GeS and the epichalcogenide. It should be noted that a by-product of these reactions is ethylene, which most likely derives from decomposition of ethylene selenide and

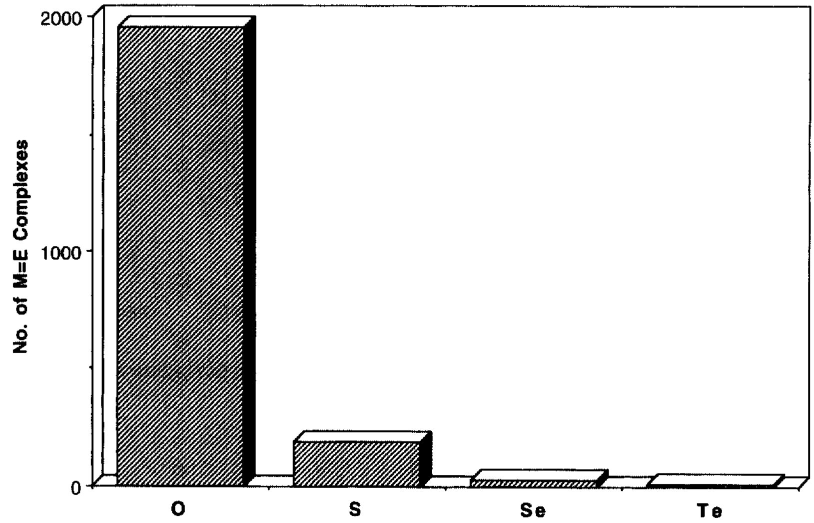


Fig. 15. Distribution of terminal chalcogenido complexes for the transition metals.

telluride; episelenides and epitellurides are known to be unstable [259].

The different stabilities 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 governed in part by the differences in the respective values of the M=S and M–S bond energies, and is a further illustration of the aforementioned trend that germanium favors multiple bonding more than does tin.

5. Concluding remarks

The chemistry of terminal chalcogenido complexes of the Group 13 and 14 elements has developed significantly over recent years, and continues to do so at a rapid pace. In contrast to multiply bonded $L_n\text{M}=\text{CR}_2$ and $L_n\text{M}=\text{NR}$ derivatives, whereby the use of bulky substituents (R) on carbon and nitrogen may be used to inhibit bridging, the successful isolation of terminal chalcogenido complexes has relied exclusively on the appropriate selection of supporting ligand (L_n). Specifically, (i) bulky alkyl and aryl ligands, e.g. $2,4,6\text{-}[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{C}_6\text{H}_2$ (Tbt), $2,4,6\text{-Pr}^i_3\text{C}_6\text{H}_2$ (Tip) and $[(\text{Me}_3\text{Si})_2\text{CH}]$ (Dis), and (ii) polydentate ligands which incorporate nitrogen donor Lewis base functionalities, e.g. $[\text{Tp}^{\text{Bu}^t_2}]$, $[\eta^4\text{-Me}_8\text{taa}]$, $[\eta^3\text{-}\{(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2\}]$ and $[\eta^2\text{-CyNC(R)NCy}]$, have found extensive use in enabling the isolation of multiply bonded terminal chalcogenido complexes of the Group 13 and 14 elements. Illustrative examples of terminal chalcogenido complexes that have been structurally characterized are summarized in Fig. 13. In each case, the ability to isolate these complexes is associated with the presence of bulky substituents and/or intramolecular Lewis base coordination, both of which serve to disfavor the formation of chalcogenido bridged structures. It is frequently assumed that the stabilization imparted by bulky alkyl and aryl groups is kinetic in origin, while the stabilization due to intramolecular Lewis base coordination is thermodynamic in origin. However, it should be recognized that in the absence of evidence, experimental or theoretical, which relates the energies of the various terminal chalcogenido complexes $L_nM{=}E$ with respect to those of the corresponding chalcogenido bridged complexes $[L_nM(\mu\text{-}E)]_2$, it is imprudent to assume that the isolation of a particular terminal chalcogenido complex has either a kinetic or thermodynamic origin. Thus, it is possible that both kinetic and thermodynamic factors may be responsible for the isolation of certain terminal chalcogenido complexes.

Perhaps one of the most notable features of the Group 13 and 14 terminal chalcogenido complexes that have been discovered to date is that they are almost exclusively, with the exception of carbon, limited to sulfido, selenido, and tellurido derivatives, so that definitive examples of terminal oxo complexes have yet to be isolated. A clear illustration of the difficulty in isolating terminal oxo complexes of these elements is provided by the observation that in systems where terminal sulfido or selenido complexes have been isolated, the corresponding oxo derivative exists as an oxo bridged complex (Fig. 14). Such behavior is in marked contrast to the chemistry of the transition metals, where the occurrence of terminal oxo derivatives vastly outweighs that of the heavier congeners, as illustrated in Fig. 15. A possible rationalization for this difference between the transition elements and the Group 13 and 14 *p*-block elements resides with the polarity of the M–O bonds. Specifically, as described in Section 1.2, oxo ligands attached to Group 13 and 14 elements may be anticipated to bear a substantial negative charge, i.e. $[\overset{+}{M}-\overset{-}{O}]$, and the existence of such a dipole may promote oxo bridging. In contrast, transition metal oxo complexes do not normally exhibit such a high degree of polarity due to favorable $d_\pi - p_\pi$ overlap resulting in a significant contribution from the resonance structure $[\overset{-}{M}\equiv\overset{+}{O}]$, which thereby serves to reduce the $[\overset{\delta+}{M}-\overset{\delta-}{O}]$ polarity of the transition metal-oxo bond.[45] The isolation of well-characterized terminal oxo complexes of the Group 13 and 14 elements, therefore, represents an important challenge to the synthetic chemist.

6. Abbreviations

Dis	$(Me_3Si)_2CH$
Fc	$CpFe(C_5H_4)$
Mes	mesityl, 2,4,6-$Me_3C_6H_2$
Mes*	supermesityl, 2,4,6-$Bu^t_3C_6H_2$
$[Me_8taa]H_2$	octamethyldibenzotetraaza[14]annulene

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[45] Certain transition metal oxo complexes are, however, believed to be best represented by the $[\overset{+}{M}-\overset{-}{O}]$ resonance structure, e.g. $Cp^*_2Zr(O)(NC_5H_5)$ [260] and (dppp)(L)PtO [261].

OEP	octaethylporphyrinate(2-)
POR	a variously substituted porphyrinate(2-) derivative
Tbt	2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$
Tip	2,4,6-$Pr^i_3C_6H_2$
TMP	*meso*-tetrakis(mesityl)porphyrinate(2-)
TMTP	*meso*-tetrakis(*m*-tolyl)porphyrinate(2-)
$[Tp^{Bu^t_2}]$	tris(3,5-di-t-butylpyrazolyl)hydroborate(1-),$[\eta^3$-HB(3,5-Bu^t_2pz$)_3]$
$[Tp^{Me_2}]$	tris(3,5-dimethypyrazolyl)hydroborate(1-),$[\eta^3$-HB(3,5-Me_2pz$)_3]$
TPP	*meso*-tetraphenylporphyrinate(2-)
TTP	*meso*-tetrakis(*p*-tolyl)porphyrinate(2-)

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Noted added in proof

For an excellent review of homonuclear multiple bonding in heavier main group elements which was published during the period that this manuscript was in press, see P.P. Power, J. Chem. Soc., Dalton Trans. (1998) 2939. Also, for recent theoretical calculations on $[H_2M = E]$ species (M = C, Si, Ge, Sn, Pb; E = O, S, Se, Te), see H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, J. Am. Chem. Soc. 120 (1998) 11096.

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