Isolation of a Diylide-Stabilized Stannylene and Germylene: Enhanced Donor Strength through Coplanar Lone Pair Alignment

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Abstract: *The preparation of the first stable diylide-substituted stannylene and germylene (**Y_2E**, with E = Ge, Sn and Y = [PPh$_3$-C-SO$_2$Tol]$^-$) is reported. The synthesis is easily accomplished in one step from the sulfonyl-substituted metalated ylide **YNa** and the corresponding ECl$_2$ precursors. **Y_2Ge** and **Y_2Sn** exhibit unusual structures in the solid state and in solution, in which the three adjacent lone pairs in the C-E-C linkage are arranged coplanar to each other. As shown by DFT studies, this bonding situation is preferred over the typical π-donation from the ligands into the empty p-orbital at the metal due to the strong anion-stabilizing ability of the sulfonyl groups in the ylide backbone and their additional coordination to the metal. The alignment of the three lone pairs leads to a remarkable boost of the HOMO energy and thus of the donor strengths of the tetrylenes. Hence, **Y_2Ge** and **Y_2Sn** become stronger donors than their diamino or diaryl congeners and comparable to cyclic alkyl(amino)carbenes. First reactivity studies confirm the high reactivity of **Y_2Ge** and **Y_2Sn**, which for example undergo an intramolecular C–H activation reaction via metal–ligand cooperation.*

Compounds with Group 14 elements in low oxidation states have been the subject of intense research interest in the past years due to their applicability in element–hydrogen bond activations, which are important processes in many catalytic cycles normally only enabled by toxic transition metals.[1] The ability of tetrylenes to undergo bond activations is largely determined by the singlet–triplet gap, which in turn can be manipulated by the choice of substituents. Classical substituents that allow the stabilization and isolation of these usually reactive compounds are amino or bulky aryl groups.[2,3] However, several other functional groups have been employed successfully in this chemistry and have led to

a further tunability of the orbital setting at the central element and the propensity to undergo bond activation reactions.[4] For example, *N*-heterocyclic olefins[5] and imines,[6] boryl,[7] and even metallo substituents[8] have been reported for germylenes.[9]

More recently, the introduction of ylide substituents has also been recognized as a means for the stabilization and electronic manipulation of tetrylenes.[10] Comparable to amino groups, ylide substituents can act as strong π-donors. However, because carbon has lower electronegativity than nitrogen, ylide functionalization should result in more electron-rich tetrylenes with enhanced nucleophilicity. Despite significant effort, the number of isolated ylide-substituted carbenes and carbene analogues is extremely limited. No acyclic system has been reported to date and most synthetic efforts addressed mixed amino(ylide) tetrylenes to tame the expected high donor strength. Although the isolation of amino(ylide) carbenes (e.g. **A**) has been attempted, no stable system has been reported as yet (Figure 1).[11,12] In the case of
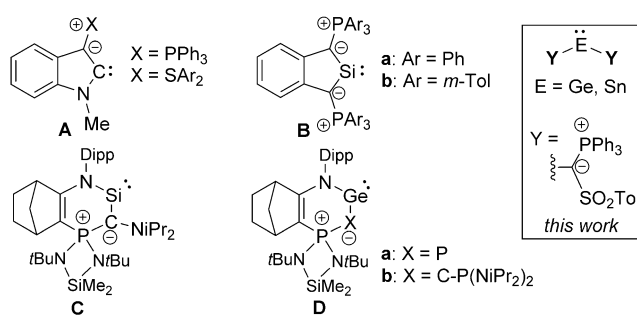
Figure 1. Ylide-stabilized tetrylenes reported so far (Dipp = 2,6-iPr$_2$C$_6$H$_3$).

the heavier analogues, Driess and co-workers succeeded in the isolation of cyclic silylenes of type **B**, which are the only diylide-substituted tetrylenes isolated so far.[13] The cyclic amino(ylide)silylene **C**[14] and germylenes **D**[15] reported by Kato and Baceiredo are the only isolated and also structurally characterized ylide-functionalized tetrylenes. These compounds exhibited strong donor properties, thus proving the strong donation from the ylide substituent.

Recently, we reported on the ready isolation of metalated ylides and their use in ylide functionalization,[16] which, for example, was used for the synthesis of stable boron cations and highly electron-rich phosphines.[17] We envisioned that metalated ylides should also be ideal reagents for the stabilization of tetrylenes via simple salt metathesis reactions.

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Thus, also the synthesis of the first acyclic ylide-substituted system and hence heavier tetrylenes with high nucleophilicity and stronger donor properties should be accessible. To test this hypothesis, we set out to isolate the diylidestannylene and germylene **Y₂Sn** and **Y₂Ge** based on the metalated ylide **YNa** (Scheme 1).[16a] Indeed, treatment of 2 equiv of **YNa** with
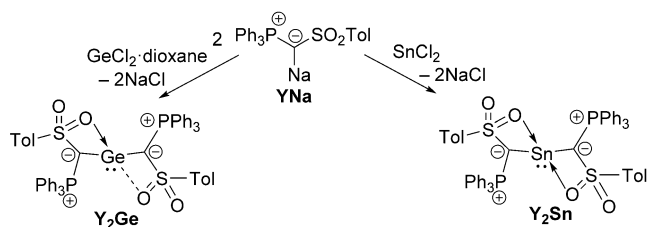
Scheme 1. Preparation of the diylide-substituted tetrylenes, **Y₂Sn** and **Y₂Ge**.

GeCl₂·dioxane or SnCl₂ selectively provided the corresponding tetrylenes **Y₂Sn** and **Y₂Ge**, which were isolated as pale-yellow solids in 68 and 63 % yield, respectively. **Y₂Sn** and **Y₂Ge** are characterized by singlets in the ³¹P{¹H} NMR spectrum at $\delta_P = 6.88$ ppm and 7.98 ppm, respectively, and a doublet for the ylide carbon atom at approx. $\delta_C = 52$ ppm in the ¹³C{¹H} NMR spectrum. In the case of the stannylene, the ¹¹⁷Sn NMR signal appears at $\delta_{Sn} = -122.2$ ppm. This highfield-shifted signal indicates additional coordination of the sulfonyl groups in solution.[18]

Single crystals of **Y₂Ge** and **Y₂Sn** were prepared to unambiguously confirm the nature of the compounds (see the Supporting Information). The structures prove the coordination of the two ylide groups as well as the additional coordination of the sulfonyl moieties to the tetrel (Figure 2 a).[19] While both sulfonyl groups symmetrically bind to the tin center in **Y₂Sn**, only one of the sulfonyl groups strongly interacts with the germanium center in **Y₂Ge** ($d_{Ge-O} = 2.299(1)$ and $3.269(4)$ Å), probably due to the increased ring strain. The most interesting feature, however, concerns the arrangement of the ylide groups relative to the central C-E-C moiety. In contrast to typical π-donor substituents, the ylide groups (P-C-S plane) in both tetrylenes arrange perpendicularly to the C-E-C linkage (Figure 2 b, conformer 1). This suggests that no π-donation from the ylide substituents into the empty p-orbital at Ge/Sn is possible and that the lone pairs remain localized at the ylide carbon atoms. This results in an unusual bonding situation, in which three lone pairs of electrons are in plane and located next to each other (canonical structure **a**, Figure 3 a). This is in clear contrast to typical diaminotetrylenes, in which the nitrogen atoms donate electron density into the empty p-orbital at the central atom (conformer 2). To the best of our knowledge, such an electronic situation has never been observed for any tetrylene. Due to the lack of π-donation, the Sn−C and Ge−C bond lengths (2.23 and 2.04 Å, respectively) are in the range of single bonds[20] and the P−C and C−S distances in the ylide groups are comparable to those in the free ylide **YH** (P−C: 1.646(2) Å and S−C: 1.626(2) Å).[16a] The C-E-C angles of 103.05(7) (for Sn) and
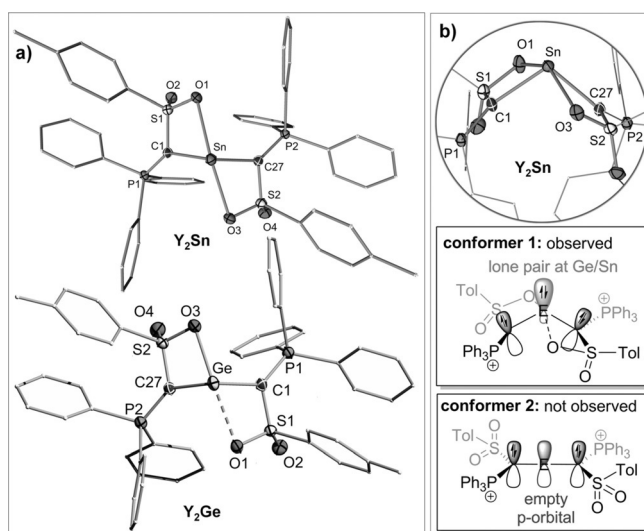
Figure 2. a) Molecular structures of **Y₂Sn** and **Y₂Ge** (ellipsoids at 50 % probability level, hydrogens and solvent molecules omitted for clarity). b) View on the C-E-C plane. Selected bond lengths [Å] and angles [°]: **Y₂Sn**: Sn–C1 2.224(2), Sn–C27 2.238(2), Sn–O1 2.428(1), Sn–O3 2.479(1), S2–C1 1.663(2), P2–C27 1.701(2), P1–C1 1.692(2), S2–C27 1.658(2); C1-Sn-C27 103.05(7), S1-C1-P1 120.8(1), S2-C27-P2 121.2(1); **Y₂Ge**: Ge–C1 2.035(2), Ge–C27 2.049(2), Ge–O3 2.299(1), S1–C1 1.662(2), S2–C27 1.662(2), P1–C1 1.688(2), P2–C27 1.687(2); C1-Ge-C27 105.94(7), S1-C1-P1 123.3(1), S2-C27-P2 123.5(1).
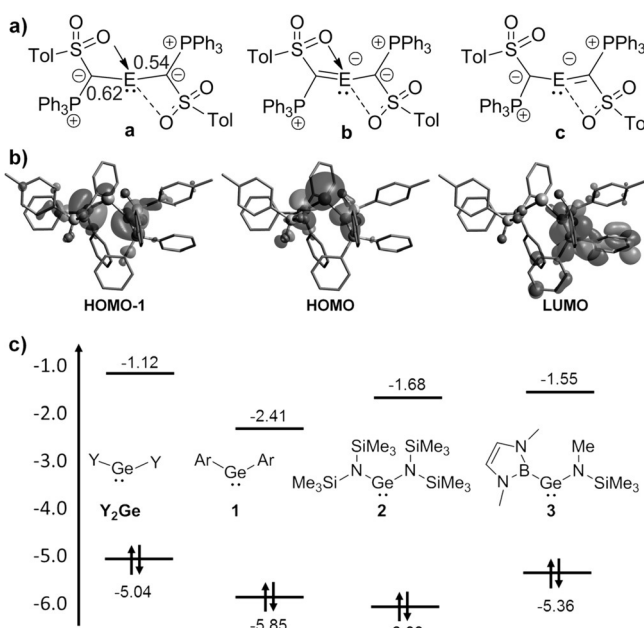
Figure 3. a) Possible canonical structures of **Y₂E** and calculated Wiberg bond indices for **Y₂Ge**, b) Kohn–Sham orbitals of **Y₂Ge** (isosurface value = 0.030 eÅ⁻³) and c) comparison of the HOMO–LUMO energies in eV of different germylenes (Ar = 2,6-dimethylphenyl).

105.94(7)° (for Ge) are comparable to those of other germylenes and stannylenes.[5–9,21]

The unsymmetrical coordination of both ylide substituents in **Y₂Ge** is inconsistent with the single signal observed in the ³¹P{¹H} NMR spectrum at room temperature, thus

indicating a fluxional behavior in solution. VT-NMR studies in [D$_8$]toluene revealed a broadening (no splitting) of the signal upon cooling, which is in line with a fast exchange process (see the Supporting Information). For **Y$_2$Sn**, which exhibits a sharp singlet in its ^{31}P{^{1}H} NMR spectrum, no broadening was observed. This agrees well with a symmetrical coordination by the two ylide substituents also in solution (cf. ^{119}Sn NMR shift). Thus, the NMR studies indicate that the structures are also retained in solution.

To gain further insight into the electronic properties of the tetrylenes, DFT calculations were performed at the PBE0-D3/def2-tzvp level of theory. The structural parameters closely matched those found in the crystal structures of **Y$_2$Ge** and **Y$_2$Sn** (e.g. different Ge–O distances in **Y$_2$Ge**). The Wiberg bond indices (Figure 3a) of the Ge–C bonds amount to only 0.54 and 0.62 (0.44 for **Y$_2$Sn**) and are thus lower than those calculated for Ar$_2$Ge **1** (Ar = 2,6-dimethylphenyl; WBI = 0.73). Natural bond orbital (NBO) analysis also only shows a single bond between Ge and C and two lone pairs residing at the ylidic carbon atoms. Thus, in line with the experimental data, the calculations show that the canonical structure **a** (Figure 3a) reflects best the electronic situation in **Y$_2$E**. This is in contrast to silylene **C**, in which strong π-interaction from the ylide to the silicon center was observed.[14] This difference probably arises from the different substituents in the ylide backbone. In contrast to the amino substituent in **C**, the sulfonyl group considerably stabilizes the negative charge at the ylidic carbon atoms in **Y$_2$E** and thus favors electrostatic and negative hyperconjugation effects over π-interactions in the Ge–C linkage. This demonstrates the dramatic impact of the substituents in the ylide backbone on the electronics and thus on the reactivity of the tetrylene.

To further study the electronic situation, the hypothetical conformer **2** was calculated, in which the ylide substituents are forced into a coplanar arrangement with the C-Ge-C linkage to allow for π-delocalization with the p-orbital at germanium. Accordingly, the WBIs of the Ge–C bond increase to approximately 0.8, which is comparable to the Ge–N bond in the amino/boryl germylene **3** reported by Aldridge,[4b] but still is considerably smaller than that found in the phosphanylide-stabilized germylene **Da**,[15b] thus further proving the tunability of the donor properties by the ylide substituents. It is also important to note that conformer 2 is clearly energetically disfavored over conformer 1 (ΔG = 35 kJ mol^{-1}), thus confirming the experimental observations.

We hypothesized that the unique electronic structure of **Y$_2$E** decisively impacts the orbital energies and thus the donor properties of the tetrylenes. The calculated HOMO of **Y$_2$Ge** and **Y$_2$Sn** mainly resides on the metal center, while the LUMO is distributed over one of the ylide ligands (Figure 3b).[22] The HOMO-1 is greatly localized at the ylidic carbon atoms, thus reflecting the two lone pairs at the C atoms. A comparison of the HOMO–LUMO energies with those of other acyclic germylenes showed that **Y$_2$Ge** is indeed a stronger donor and weaker acceptor than diaryl, diamino, or even the amino/boryl germylene **3** (Figure 3c). This is a consequence of the coplanar arrangement of the three lone pairs which raises the HOMO energy (by 0.17 eV relative to conformer 2). Thus, the HOMO energy of **Y$_2$Ge** is

boosted to the level of alkyl(amino)carbenes (see the Supporting Information). This is also confirmed by the pyramidalization of the GaCl$_3$ moiety in the energy-optimized **Y$_2$Ge·GaCl$_3$** complex, which was shown to correlate with the donor strength of a given ligand.[23,24] The calculated sum of Cl-Ga-Cl angles in **Y$_2$Ge·GaCl$_3$** amounts to 327°, which corresponds to a Tolman electronic parameter of 2032.3 cm^{-1}. Thus, **Y$_2$Ge** is a considerably stronger donor than germylenes **1–3** and comparable to cyclic alkyl(amino)carbenes. This makes **Y$_2$Ge** the germylene with the highest donor capacity known so far. The same holds true for stannylene **Y$_2$Sn**.

While the stannylene is stable in solution at room temperature for several days without showing evidence of decomposition reactions, the germylene decomposed slowly in THF in the course of one week to form a new product along with an equivalent amount of ylide **YH**. The same product is formed within 1 h when a toluene solution of **Y$_2$Ge** is heated to 90°C. XRD analysis revealed the new compound to be cyclotetragermane **4**. Compound **4** is presumably formed by C–H activation of one of the PPh$_3$ phenyl groups, thus generating the cyclometalated germylene **4-Int**, which eliminates the ylide ligand and tetramerizes to **4** (Scheme 2). DFT studies suggest that the C–H activation does not occur at the germanium center, but via addition across the Ge–C bond, which is in line with the lone pairs at the carbon atoms. This
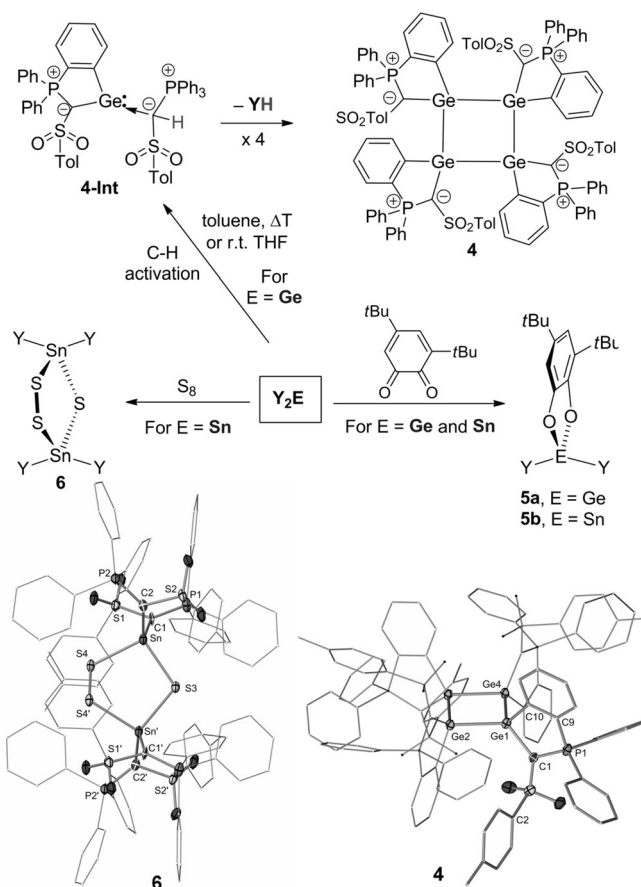
Scheme 2. Reactivity studies of **Y$_2$Ge** and **Y$_2$Sn** and molecular structures of compound **4** and **6** (thermal ellipsoids at the 50% probability level).

indicates that ylide functionalization does not only increase the donor strength of the germylene but may also result in reactivities via metal–ligand cooperation. Compound **4** could be isolated as a yellow solid in 33 % yield. The tetragermane is characterized by a signal at $\delta_P = 15.7$ ppm in the $^{31}P\{^1H\}$ NMR spectrum and a doublet at $\delta_C = 37.5$ ppm in the $^{13}C\{^1H\}$ NMR spectrum for the ylide carbon atom ($^1J_{PC} = 81.3$ Hz). In the solid state, **4** shows a fully planar Ge_4 core, at which the ylide substituents bind in an alternating fashion to minimize steric repulsion between the PPh_3 moieties. The Ge–Ge bonds (2.480(1)–2.493(1) Å) are in the range of other tetragermanes.[25]

Despite the instability of **Y₂Ge**, it can be applied in further transformations. **Y₂Ge** readily reacts within a couple of minutes with 3,5-di-*tert*-butyl-*o*-benzoquinone to form **5a**. The same [4+1] cycloaddition reaction was observed with **Y₂Sn** to generate **5b**. Both compounds could be isolated as colorless solids and were fully characterized. While the germylene shows no selective reaction with elemental sulfur, **Y₂Sn** selectively generates compound **6** with a non-planar, C_2-symmetric Sn_2S_3 five-membered ring. To the best of our knowledge, formation of such a five-membered Sn-S cycle has never been observed with any other stannylene.[26] In contrast to the structures of the tetrylenes, no coordination of the tin and germanium center, respectively, by the sulfonyl group is observed in the molecular structures of **4–5b** and only a weak interaction by one of the sulfonyl groups in **6**. This shows that—although important for the stabilization of **Y₂Ge** and **Y₂Sn**—the sulfonyl coordination is easily opened to facilitate substrate coordination and/or attack.

In conclusion, we have isolated the first diylide-stabilized germylene and stannylene synthesized via simple salt meta-thesis reactions using an α-metalated ylide. These tetrylenes feature an unusual electronic structure with three lone pairs arranged in a coplanar fashion. This arrangement results in a boost of the HOMO and LUMO energy levels and in a remarkable increase of the donor strength, thus making **Y₂Ge** a stronger donor than classical germylenes and comparable to cyclic alkyl(amino)carbenes. This electronic structure also leads to novel reactivity patterns, such as an intramolecular C−H activation by the Ge−C linkage. Thus, ylide substituents may be used as a tool to impart unique properties to low-valent main group compounds which were so far not accessible with other substituents. The forced alignment of lone pairs through a sophisticated molecular design may also be used to enhance the donor strengths of other ligands.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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