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,Ge, with E = Ge, Sn and Y = PPh3-C-SO2Tol) is reported. The synthesis is easily accomplished in one step from the sulfonyl-substituted metalated ylide YNa and the corresponding ECl2 precursors. Y,Ge and Y,Sn 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,Ge and Y,Sn become stronger donors than their diamino or diaryl congeners and comparable to cyclic alkyl(amino)carbene. First reactivity studies confirm the high reactivity of Y,Ge and Y,Sn, 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 germynes.[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 carbene 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) carbene (e.g. A) has been attempted, no stable system has been reported as yet (Figure 1).[11,12] In the case of 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 germylene 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.

Figure 1. Ylide-stabilized tetrylenes reported so far (Dipp = 2,6-iPr2C6H3).

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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 $Y_2Sn$ and $Y_2Ge$ based on the metalated ylide $YNa$ (Scheme 1). Indeed, treatment of 2 equiv of $YNa$ with

$$GeCl_2 \cdot $dioxane or SnCl$_2$ selectively provided the corresponding tetrylenes $Y_2Sn$ and $Y_2Ge$, which were isolated as pale-yellow solids in 68 and 63% yield, respectively. $Y_2Sn$ and $Y_2Ge$ are characterized by singlets in the $^{31}P[\text{H}]$ 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 $^{13}C[\text{H}]$ NMR spectrum. In the case of the stannylene, the $^{11}Sn$ NMR signal appears at $\delta_{Sn} = -122.2$ ppm. This high-field-shifted signal indicates additional coordination of the sulfonyl groups in solution.\(^{[18]}\)

Single crystals of $Y_2Ge$ and $Y_2Sn$ 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 2a).\(^{[19]}\) While both sulfonyl groups symmetrically bind to the tin center in $Y_2Sn$, only one of the sulfonyl groups strongly interacts with the germanium center in $Y_2Ge$ ($\delta_{Ge-O} = 2.299(1)$ 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 $\pi$-donor substituents, the ylide groups ($P-C-S$ plane) in both tetrylenes arrange perpendicularly to the C-E-C linkage (Figure 2b, conformer 1). This suggests that no $\pi$-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 3a). 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 $\pi$-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).\(^{[20a]}\) The C-E-C angles of 103.05(7) (for Sn) and 105.94(7)° (for Ge) are comparable to those of other germynes and stannylenes.\(^{[5-9,21]}\)

The unsymmetrical coordination of both ylide substituents in $Y_2Ge$ is inconsistent with the single signal observed in the $^{31}P[\text{H}]$ NMR spectrum at room temperature, thus

**Scheme 1.** Preparation of the diylide-substituted tetrylenes, $Y_2Sn$ and $Y_2Ge$.  

**Figure 2.** a) Molecular structures of $Y_2Sn$ and $Y_2Ge$ (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 [°]: $Y_2Sn$: 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); $Y_2Ge$: 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 $Y_2Ge$ and calculated Wiberg bond indices for $Y_2Ge$, b) Kohn–Sham orbitals of $Y_2Ge$ (isosurface value = 0.030 e Å$^{-1}$) and c) comparison of the HOMO–LUMO energies in eV of different germynes ($Ar = 2,6$-dimethylphenyl).
indicating a fluxional behavior in solution. VT-NMR studies in [D₈]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 Y₂Sn, which exhibits a sharp singlet in its ³¹P[¹H] NMR spectrum, no broadening was observed. This agrees well with a symmetrical coordination by the two ylide substituents also in solution (cf. ¹¹Sn 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 Y₂Ge and Y₂Sn (e.g. different Ge–O distances in Y₂Ge). The Wiberg bond indices (Figure 3a) of the Ge–C bonds amount to only 0.54 and 0.62 (0.44 for Y₂Sn) and are thus lower than those calculated for Ar₅Ge 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 Y₂E. 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 Y₂E 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,[25] but still is considerably smaller than that found in the phosphanylide-stabilized germylene DA₁[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 Y₂E decisively impacts the orbital energies and thus the donor properties of the tetrylenes. The calculated HOMO of Y₂Ge and Y₂Sn 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 germynes showed that Y₂Ge 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 Y₂Ge is boosted to the level of alkyl(aminocarbene) (see the Supporting Information). This is also confirmed by the pyramidalization of the GaCl₃ moiety in the energy-optimized Y₂Ge-GaCl₃ 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 Y₂Ge-GaCl₃ amounts to 327°, which corresponds to a Tolman electronic parameter of 2032.3 cm⁻¹. Thus, Y₂Ge is a considerably stronger donor than germelines 1–3 and comparable to cyclic alkyl(aminocarbene). This makes Y₂Ge the germylene with the highest donor capacity known so far. The same holds true for stannylene Y₂Sn.

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 Y₂Ge is heated to 90°C. XRD analysis revealed the new compound to be cyclotetramerane 4. Compound 4 is presumably formed by C–H activation of one of the PPh₃ 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 Y₂Ge and Y₂Sn 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 tetramerane is characterized by a signal at δp = 15.7 ppm in the 13P[1H] NMR spectrum and a doublet at δc = 37.5 ppm in the 13C[1H] NMR spectrum for the ylide carbon atom (1JPC = 83.1 Hz). In the solid state, 4 shows a fully planar Ge4 core, at which the ylide substituents bind in an alternating fashion to minimize steric repulsion between the PPh3 moieties. The Ge–Ge bonds (2.480(1)–2.493(1) Å) are in the range of other tetrameranes.[25]

Despite the instability of Y,Ge, it can be applied in further transformations. Y,Ge 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 Y,Sn 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, Y,Sn selectively generates compound 6 with a non-planar, C2-symmetric Sn3S5 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.[28] 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 Y,Ge and Y,Sn—the sulfonyl coordination is easily opened to facilitate substrate coordination and/or attack.

In conclusion, we have isolated the first diylide-stabilized germylene and stannyleny synthesized via simple salt metathesis 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 Y,Ge a stronger donor than classical germylenes and comparable to cyclic alkyl(aminocarbene). 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.

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Conflict of interest

The authors declare no conflict of interest.

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