

Main Group Chemistry

Synthesis of Low-Valent Dinuclear Group 14 Compounds with Element–Element Bonds by Transylidation

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Dedicated to Professor Manfred Scheer on the occasion of his 65th birthday

Abstract: Dinuclear low-valent compounds of the heavy main group elements are rare species owing to their intrinsic reactivity. However, they represent desirable target molecules due to their unusual bonding situations as well as applications in bond activations and materials synthesis. The isolation of such compounds usually requires the use of substituents that provide sufficient stability and synthetic access. Herein, we report on the use of strongly donating ylide-substituents to access low-valent dinuclear group 14 compounds. The ylides not only impart steric and electronic stabilization, but also allow facile synthesis via transfer of an ylide from tetrylene precursors of type R^Y_2E to ECl_2 ($E = Ge, Sn$; $R^Y = TolSO_2(PR_3)_2$ with $R = Ph, Cy$). This method allowed the isolation of dinuclear complexes amongst a germanium analogue of a vinyl cation, $[(Ph^Y)_2GeGe(Ph^Y)]^+$ with an electronic structure best described as a germylene-stabilized Ge^{II} cation and a ylide(chloro)digermene $[C^Y(Cl)GeGe(Cl)C^Y]$ with an unusually unsymmetrical structure.

unusual bonding situations and structural properties.^[2] Heavier alkene and alkyne analogues were the first examples which demonstrated the unique reactivity of such compounds and thus paved way to the exploration of the transition-metal-like behavior of the main group elements.^[3] Cationic and low-valent species with E–E multiple bonds are only little investigated, particularly with Ge and Sn due to the decreasing E–E bond strength.^[4] Landmark examples in case of germanium are the stable germanium vinylidene **A** by Aldridge^[5] and Scheschkewitz's silagermenylidene **B** (Figure 1).^[6] However, often no multiple bonds but only single or dative bonds are formed^[7] such as in Driess' three coordinate $[Ge:]^{2+}$ complex **D**^[8] as well as in allene-like structures $R_2E=E-ER_2$,^[9] such as germylene **C**^[10] or the di(germylene)-substituted germene **E**.^[11]

The most common strategy to access such low-valent compounds is the reduction of halo precursors which upon treatment with strong reducing agents form a new element–element bond (e.g. to **A**, **B**, **E**). Alternatively, bonds between the heavier elements can also be formed by donor-acceptor interactions using heavier carbenes as Lewis base. For example, Rivard and co-workers used the NHC-coordinated $GeCl_2$ adduct

The ability of elements to form homonuclear bonds is most pronounced for carbon. This propensity is the basis of organic chemistry and the chemistry of life. However, compared to carbon, the heavier elements form weaker homonuclear bonds due to the weaker overlap of the orbitals and the increased Pauli repulsion.^[1] Low-valent compounds with an additional element–element bond are thus extremely rare species, but of special interest, since they typically exhibit unique reactivities such as towards small molecules and offer prospects to study

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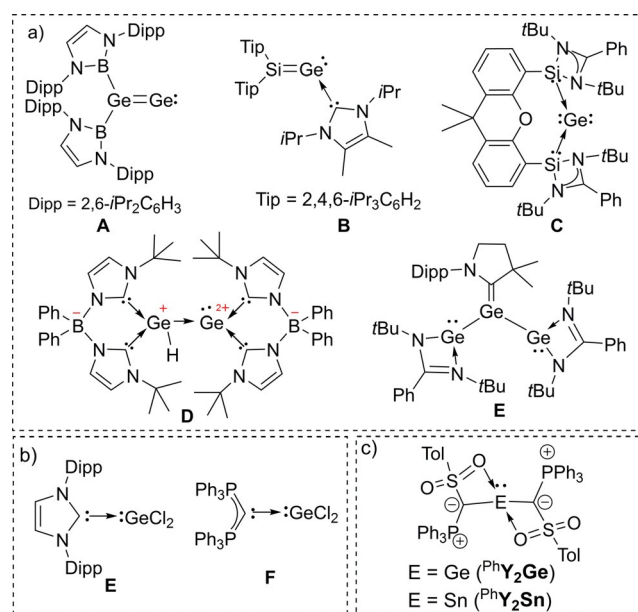


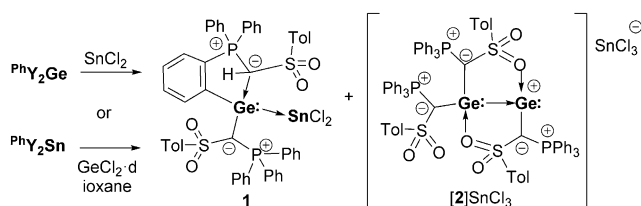
Figure 1. (a) Examples of low-valent germanium compounds with a Ge–Ge/Si bond, (b) donor-stabilized $GeCl_2$ and (c) diylidetetrylenes Ph^Y_2Ge and Ph^Y_2Sn .

E, which reacts with GeCl_2 to branched and linear germanes.^[12] The same strategy was applied by Alcarazo using the carbodiphosphorane adduct $\text{F}^{[13]}$ as well as by So using an amidinato germylene^[14] and by Driess in the synthesis of germylone **C** and **D**.^[10]

Recently, we reported on the isolation of the diylidgermylene PhY_2Ge and stannylene PhY_2Sn which exhibited high donor strengths due to the alignment of the three lone pairs in the C–E–C linkage.^[15] We hypothesized that this donor strength should be ideal for generating donor-acceptor complexes and hence for the formation of unique homo- and heterodimetallic compounds. Furthermore, the donor ability of the ylide-substituents^[16] should also be suited to access unusual cationic compounds which are difficult to isolate with other classes of substituents.

To test this hypothesis, germylene PhY_2Ge was treated with tin and germanium dichloride, respectively, with the intention to isolate germylene-coordinated ECl_2 complexes, which upon halide abstraction would give rise to heavier vinyl cations of type $\text{Y}_2\text{Ge}=\text{E}(\text{Cl})^+$. Reaction of PhY_2Ge with 1 equiv GeCl_2 :dioxane unfortunately gave a mixture of inseparable products. However, applying the same procedure with SnCl_2 yielded two products in an approx. 1:1 ratio along with free ylide. The two products could be separated by sequential precipitation and identified by XRD analysis as the germylene-coordinated SnCl_2 **1** and the digermanium cation $\mathbf{2}^+$ (Scheme 1). Both compounds could be isolated in 89 and 26% yield, respectively. Most interestingly, the same products are formed from the reaction of PhY_2Sn with GeCl_2 :dioxane. This suggests that the diylidtetrylenes readily transfer ylide substituents to other metals. Such transylidation processes are known for transition-metal complexes^[17] and hypervalent halonium compounds,^[18] but not to and from low-valent main group species.^[19]

Complex **1** is a rare example of a donor-stabilized monomeric SnCl_2 , which for example was reported by Rivard using an *N*-heterocyclic carbene,^[20,21] and by So using an amidinato silylene or germylene.^[14] **1** features two doublets at 22.4 and 27.1 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR and a singlet at 58.0 ppm in the ^{119}Sn NMR spectrum, which is significantly downfield-shifted compared to Rivard's $\text{IPr}\cdot\text{SnCl}_2$ (−68.7 ppm).^[20] XRD analysis revealed that one ylide ligand in the germylene underwent an intramolecular cyclometallation, which results in unsymmetrical NMR patterns in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Such a cyclometallation reaction has previously been observed for PhYGe and was found to proceed via C–H activation across the C_{ylide} linkage.^[15]



Scheme 1. Preparation of **1** and $\mathbf{2}[\text{SnCl}_3]$ (Tol = *p*- $\text{CH}_3\text{C}_6\text{H}_4$).

In the crystal (Figure 2a), **1** features a Ge–Sn distance of 2.7493(5) Å, which is considerably shorter than the $\text{Sn}^{\text{II}}\text{–Ge}^{\text{II}}$ bond length reported by So (2.8520(3) Å).^[14] Nonetheless, the Sn–Ge bond in **1** is longer than the Ge=Sn double bond reported by Weidenbruch (2.5065(5) Å),^[22] but similar to distances observed by Power and Driess for a $\text{Ge}^{\text{IV}}\text{–Sn}^{\text{II}}$ ^[23] and a $\text{Ge}^{\text{I}}\text{–Sn}^{\text{I}}$ bond.^[24] The Ge–C bonds to the ylide ligands in **1** are distinctly different, thus reflecting the different bonding situations (Ge–C1: 2.1245(3) and Ge–C2: 1.940(4) Å).

The digermanium(II) cation $\mathbf{2}^+$ crystallizes with SnCl_3^- as counter anion and was characterized by NMR spectroscopy as well as elemental and XRD analysis. The cation features two sets of signals in a 2:1 ratio in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, thus being in line with the different ylide substituents at the two Ge centers. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two broad signals at 9.9 and 13.1 ppm which suggest fluxional behavior in solution. The crystal structure confirms that the two Ge centers are coordinated by three ylide substituents and two sulfonyl groups. The unsymmetrical coordination of the two ylide ligands at Ge1 is probably the origin of the broadening of the signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. $\mathbf{2}^+$ features a $\text{Ge}^{\text{II}}\text{–Ge}^{\text{II}}$ bond distance of 2.489(1) Å. This bond is clearly longer than the Ge=Ge double bond in digermavinylidene **A** (2.312(1) Å)^[5] and other digermenes,^[25] but shorter than the Ge–Ge bond in Rivard's GeCl_2 adduct with **E** (2.630 Å),^[12] in Driess' cation **D** (2.556 Å) and in Jones's digermine with a Ge–

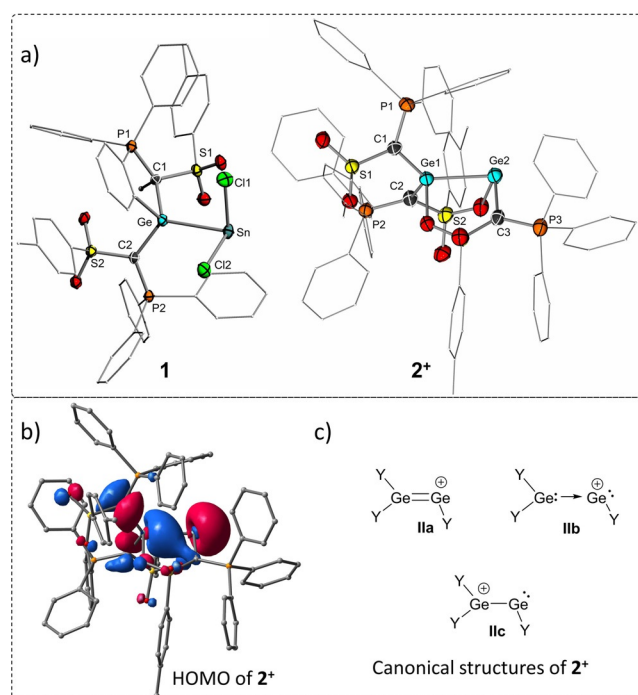


Figure 2. (a) Molecular structures of **1** and $\mathbf{2}^+$. Hydrogens, solvent molecules and SnCl_3^- omitted for clarity; ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: (**1**): Sn1–Cl1 2.4883(10), Sn–Cl2 2.5263(10), Sn–Ge 2.7493(5), Ge–C1 2.125(3), Ge–C2 1.940(4), Ge–C3 1.970(4), Cl1–Sn–Ge 90.64(3), Cl1–Sn–Cl2 92.64(3), Cl2–Sn–Ge 88.76(3). ($\mathbf{2}^+$): P1–C1 1.730(7), C1–C1 1.670(7), C1–Ge1 1.996(7), Ge1–Ge2 2.489(1), P1–C1–S1 116.148(3), C1–Ge1–Ge2 88.243(2), C27–Ge2–Ge1 104.530(2). (b) HOMO (isosurface value 0.4) and (c) possible canonical structures of $\mathbf{2}^+$.

Ge single bond (2.709 Å).^[26] The Ge–C bond distances vary between 1.918(6) and 1.996(6) Å and are thus shorter than in the free germylene PhY_2Ge (approx. 2.042 Å). This can be explained by a decreased repulsion between the lone pairs at the carbon atoms and germanium or an increased s-character in the Ge–C bond due to the involvement of the lone pair at Ge1 in the bonding to Ge2.

Several canonical structures can be formulated for 2^+ depending on the bonding situations between the two germanium centers (Figure 2c): a digermavinyl cation (**IIa**), a germylene-stabilized germanium(II) cation (**IIb**) and a germylene-substituted germylium ion (**IIc**).^[27] The rather long Ge–Ge distance found in the crystal structure suggests that 2^+ cannot be regarded as a true digermavinyl cation with a Ge=Ge double bond. This is also confirmed by computational studies (PW6B95D3/def2tzvp; see Supporting Information). The HOMO of 2^+ indicates the presence of a lone pair at Ge2 (in line with structures **IIb** and **IIc**), as well as a σ bond between the two germanium atoms polarized towards Ge1. The latter is indicative for a dative bond, which is also confirmed by natural bond orbital (NBO) analysis which describes the Ge–Ge bond as a single bond with a predominant contribution of Ge1 (62%). The Wiberg bond index of 0.861 is smaller than the one found for Ge=Ge double bonds (WBI=1.528 for $\text{Ph}_2\text{Ge}=\text{GePh}_2$; WBI=1.668 for **A**), but almost identical to the value calculated for the single bond in $\text{Ph}_3\text{Ge}-\text{GePh}_3$ (WBI=0.863). Thus, 2^+ is best described by resonance structures **IIb** and **IIc**. The shorter Ge-Ge distance in 2^+ compared to **D** with dicarbene ligands indicates that **IIc** is more important for 2^+ .^[28]

The unexpected formation of **1** and 2^+ from PhY_2Ge with SnCl_2 and from PhY_2Sn with GeCl_2 suggests that ylide transfer from the tetrylenes proceeds rapidly. However, the formation of **1** indicates that C–H activation of the phenyl group might be an additional driving force in this reaction. To better understand the transylidation process and to probe its generality we turned our attention towards PCy_3 -substituted analogues which should be less prone to C–H activation. CyY_2Ge and CyY_2Sn were obtained via salt metathesis from the metallated ylide $\text{CyY-M}^{[29]}$ and half an equiv $\text{GeCl}_2\cdot\text{dioxane}$ or SnCl_2 (Figure 3) as pale-yellow solids in good yields (71 and 75%). The important structural features (e.g. alignment of the lone pairs in the C–E–C) are almost identical to PhY_2Ge and PhY_2Sn ,

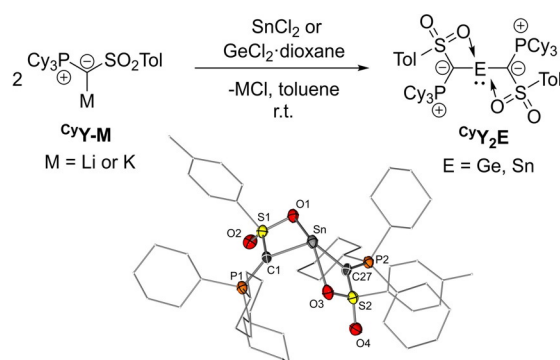
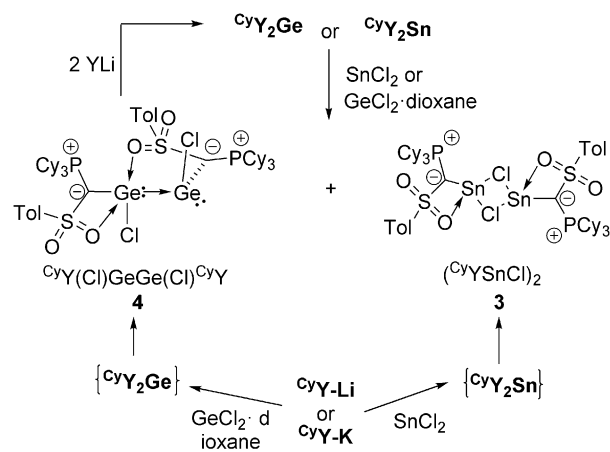


Figure 3. Synthesis of CyY_2Sn and CyY_2Ge and molecular structure of CyY_2Sn .

indicating no significant changes in the electronic properties upon replacement of PPh_3 by PCy_3 .

Next, the reactivity of the tetrylenes was tested. The reaction of CyY_2Ge with SnCl_2 in C_6D_6 revealed to be slow but could be accelerated by sonication. After 1 h, full consumption of CyY_2Ge and selective formation of a single new species in solution along with a colorless precipitate was observed. The precipitate was identified as chloro(ylide)stannylene **3** (Scheme 2). **3** forms a chloro-bridged dimer in the crystal but was found to be in equilibrium with stannylene CyY_2Sn and presumably SnCl_2 in THF solution (see below). In $^{31}\text{P}\{^1\text{H}\}$ and in the ^{119}Sn NMR spectrum, **3** exhibits broad singlets at $\delta_{\text{p}} = 24.0$ ppm and at $\delta_{\text{sn}} = -184.6$ ppm, respectively. The second product was isolated from the reaction solution as colorless crystals in 54% yield and identified as 1,2-dichlorodigermene **4**. XRD analysis (Figure 4) showed an unsymmetrical coordination of the two Ge centers by the two ylide-substituents, which thus results in two sets of signals in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Like-



Scheme 2. Formation of germylene $(\text{CyY}_2\text{SnCl}_2)$ (**3**) and $\text{CyY}(\text{Cl})\text{Ge}-\text{Ge}(\text{Cl})\text{CyY}$ (**4**) from CyY_2Ge and stannylene CyY_2Sn .

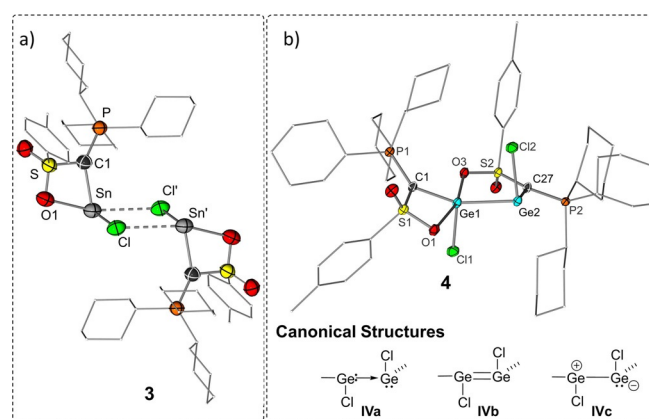


Figure 4. (a) Molecular structure of **3** and (b) molecular and canonical structures of **4**. Selected bond lengths [Å] and angles [°]: (**3**): P1–C1 1.735(5), S1–C1 1.659(5), Sn–C1 2.191(5), Sn–Cl 2.5681(12), Sn–Cl' 3.0695(11), C–Sn1–Cl 100.9(1); (**4**): P1–C1 1.743(2), P2–C27 1.742(2), S1–C1 1.685(2), S2–C27 1.660(2), Ge1–C1 1.923(2), Ge2–C27 2.030(2), Ge1–Ge2 2.4908(4), Ge1–O1 2.451(2), Ge1–O3 1.976(2), C1–Ge1–C27 143.5(1), C27–Ge2–Ge1 85.5(1), Cl1–Ge1–Ge2 103.8(2), Ge1–Ge2–Cl2 93.2(2).

wise, two signals at $\delta = 33.1$ and 24.1 ppm are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, thus suggesting a dimeric structure also in solution. In the solid state, the two Ge^{II} centers exhibit remarkably different coordination environments. Ge1 is five-coordinate due to the interaction with two sulfonyl groups and adopts a square-pyramidal geometry, whereas Ge2 is only three-coordinate. Thus, in contrast to conventional 1,2-halogermines^[25] no *trans*-bent structure is found in **4**. Instead, C1 is almost in plane with the Cl-Ge-Ge-Cl unit with an acute Cl1-Ge1-C1 angle of $109.6(1)^\circ$. This suggests that the lone pair at Ge1 is involved in the bonding to Ge2, which itself retains its lone pair. Hence, **4** is better described as a germylene-stabilized germylene (structure **IVa**, Figure 4), rather than a digermene with a Ge=Ge double bond (**IVb**). This is also in line with the Ge-Ge distance of $2.4908(4)$ Å, which is comparable to the one found in **2**⁺ and in the range of a single bond.^[30] In principle, also a dipolar structure (**IVc**) with a single rather than a dative bond between the two germanium centers is reasonable, but presumably less dominant. This is suggested by the facile cleavage of the Ge-Ge bond upon reaction of **4** with two equiv of the metallated ylide $^{\text{C}}\text{YLi}$ thus resulting in the formation of the germylene $^{\text{C}}\text{Y}_2\text{Ge}$. Nonetheless, **4** exhibits a remarkable stability and contrary to many other reported digermenes^[31] retains its dimeric structure even in coordinating solvents such as acetonitrile or THF.

It is noteworthy that tin prefers the formation of the symmetric dimeric chloro(ylide)stannylene **3**, while germanium forms the unsymmetrical digermylene **4**. This is due to the weaker metal-metal interaction of Sn compared to Ge, as was already noted by Power.^[25a] DFT calculations show that for Ge structure **4** is preferred over any other isomer (see Table S19 and S20) and 68.7 kJ mol⁻¹ more stable than a structure similar to **3**. For tin, however, both structures as well as the complex $^{\text{C}}\text{Y}_2\text{Sn} \rightarrow \text{SnCl}_2$ lie within only 6 kJ mol⁻¹ of energy. This small energy difference corroborates with the fact that no pure NMR spectra of **3** could be obtained. Even when dissolving crystals of **3**, mixtures of **3**, stannylene $^{\text{C}}\text{Y}_2\text{Sn}$ and presumably SnCl_2 are obtained indicating the existence of an equilibrium between all species in solution.

To test whether the chloro(ylide)tetrylenes **3** and **4** can directly be accessed from the metallated ylide, $^{\text{C}}\text{Y-M}$ was treated with one equiv SnCl_2 and GeCl_2 -dioxane, respectively. In both cases, the diylidetetrylenes formed initially but reacted further to **3** and **4**. While **4** was obtained in good yields of 75%, **3** could only be isolated in 50% yield since purification was complicated by the equilibrium between **3**, $^{\text{C}}\text{Y}_2\text{Sn}$ and SnCl_2 (Scheme 2). Overall, these observations clearly confirm the facile transfer of ylide substituents from Ge^{II} and Sn^{II} compounds. Even the reaction of $^{\text{C}}\text{Y}_2\text{Ge}$ with one equiv SnCl_2 was found to proceed via intermediate formation of the stannylene. This demonstrates that transylidation is a viable process in low-valent group 14 compounds which does not require an additional driving force through C-H activation and thus may be used as a general tool in this chemistry.

In conclusion, we reported on the formation of homo- and heterodinuclear low-valent germanium and tin compounds stabilized by ylide-substituents. These compounds are uniquely

formed by transfer of an ylide substituent from tetrylene precursors. Together with the propensity of ylide substituents to act as strong donor substituents, this migratory ability discloses new possibilities for the preparation and isolation of reactive main group compounds. This was demonstrated by the isolation of a germylene-stabilized Ge^{II} cation, a formal germanium-analogue of a vinyl cation, as well as a chloro(ylide)digermene with an unusual, unsymmetrical structure. These results clearly prove the aptitude of ylide substituents to access reactive main group compounds. Transylidation constitutes a mild synthetic method suggesting that more unusual species with unique reactivities should be isolable with these substituents.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cations · germanium · structure elucidation · tetrylenes · ylides

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