

1-Arsa-3-germaallene Tip(*t*-Bu)Ge=C=AsMes*: The Heaviest Mixed Group 14 and 15 Heteroallenic Compound

Dumitru Ghereg,^{†,||} Nathalie Saffon,[‡] Jean Escudié,^{*,†} Karinne Miqueu,[§] and Jean-Marc Sotiropoulos[§]

[†]Université de Toulouse, UPS, LHFA, 118 Route de Narbonne, and CNRS, LHFA, UMR 5069, 31062 Toulouse cedex 09, France

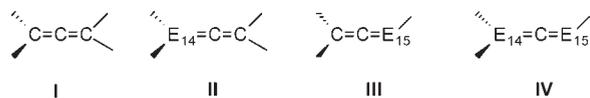
[‡]Structure Fédérative Toulousaine en Chimie Moléculaire, FR 2599, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse cedex 09, France,

[§]Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, UMR-CNRS, 5254, Université de Pau et des Pays de l'Adour, Hélioparc 2 Avenue du Président Angot, 64053 Pau cedex 09, France.

S Supporting Information

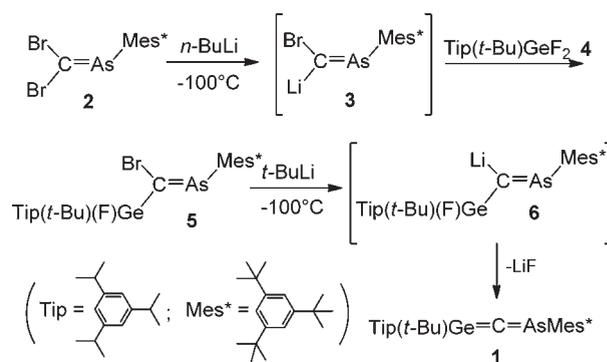
ABSTRACT: The 1-arsa-3-germaallene Tip(*t*-Bu)Ge=C=AsMes* (**1**, Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl), a stable heavier group 14 and 15 congener of allenes, has been synthesized by debromofluorination of Tip(*t*-Bu)Ge(F)—C(Br)=AsMes*. It reacts with methanol and 2,3-dimethyl-1,3-butadiene by the Ge=C double bond. The allenic-type structure of **1**, featuring cumulated Ge=C and C=As double bonds, has been evidenced by means of spectroscopic and single-crystal X-ray determination. The electronic properties involved in this new system were obtained from DFT calculations. The mechanism of the reaction between **1** and the dimethylbutadiene is also described to understand the observed regio- and chemoselectivity.

Allenes (**I**) are a well-known class of compounds and hold a central position in organic chemistry, being readily transformed into new organic functions by various reactions (additions, oxidations, etc.).¹ With regard to analogous cumulative doubly bonded derivatives containing a heavier group 14 (**II**) or 15 (**III**) element, several examples have also been prepared and isolated.² Such compounds have received much recent interest, not only from a structure/bonding viewpoint but also as potential precursors of heterocyclic systems and polymers. In sharp contrast to **I**, **II**, and **III**, little is known about the synthesis, structure, and chemistry of the less common mixed group 14 and 15 allenic systems, **IV**.



Within this field, we have succeeded in the synthesis of the transient 1-phospha-3-silaallene Tip(Ph)Si=C=PMes*³ and 1-phospha-3-germaallene Mes₂Ge=C=PMes*⁴ and thereafter in the isolation of the stable Tip(*t*-Bu)Ge=C=PMes*.⁵ By contrast, >E₁₄=C=N— (E₁₄ = Si,⁶ Sn⁷) species are generally better described as silylene- or stannyleno-isocyanide complexes, with the exception of the derivative reported by Kira,^{6c} which represents allenic silaketenimine (azasilaallene) rather than such

Scheme 1. Synthesis of 1-Arsa-3-germaallene **1**



a donor–acceptor complex. In view of this recent progress, the synthesis of stable heavier arsenic analogues of type **IV** is of great interest from the standpoint of systematic elucidation of the structure and properties of allenic derivatives containing main-group elements. Herein we report the synthesis, structure, and characterization of the stable 1-arsa-3-germaallene Tip(*t*-Bu)-Ge=C=AsMes*, the heaviest mixed group 14 and 15 heteroallenic compound reported to date, consisting of terminal germanium and arsenic atoms.

The reaction of *n*-butyllithium at $-100\text{ }^{\circ}\text{C}$ with Mes*As=CBr₂⁸ (**2**) followed by addition of Tip(*t*-Bu)GeF₂⁵ (**4**) in dry diethyl ether resulted in the formation of 1-arsa-3-germapropene **5**, which was isolated in good yield and fully characterized by NMR spectroscopy [$\delta^{13}\text{C}_{\text{C}=\text{As}} = 176.18\text{ ppm}$ (*d*, $^2J_{\text{CF}} = 7.2\text{ Hz}$), $\delta^{19}\text{F} = -175.04\text{ ppm}$] and X-ray analysis (Scheme 1, Figure 1). The As1–C1 [1.796(2) Å] and As1–C21 [1.968(2) Å] distances were found to be typical for double and single bonds, respectively; the three Ge–C bonds [Ge1–C1 1.947(3) Å, Ge1–C2 1.981(2) Å, and Ge1–C6 1.968(2) Å] also lie within standard values.⁹ The C1As1C21 bond angle [101.42(10) $^{\circ}$] is characteristic for an sp²-hybridized arsenic atom in arsaalkenes. The C=As double bond adopts a slightly twisted geometry with torsion angles C21As1C1Br1 of 1.58 $^{\circ}$ and C21As1C1Ge1 of -164.65° . This study also revealed the formation of only the *Z*-isomer of **5**, probably because the bromine–lithium exchange

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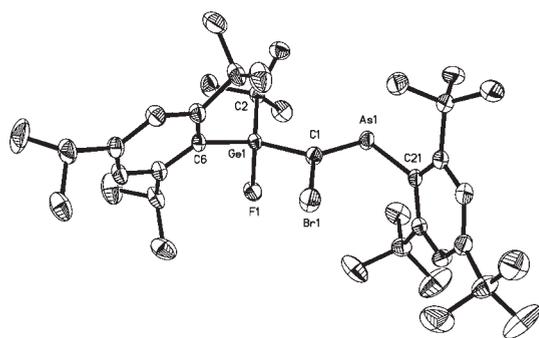


Figure 1. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (°): Ge1–C1 1.947(3), Ge1–C2 1.981(2), Ge1–C6 1.968(2), Ge1–F1 1.771(1), C1–As1 1.796(2), C1–Br1 1.905(2), As1–C21 1.968(2), Ge1–C1–As1 119.73(12), Ge1–C1–Br1 114.38(12), As1–C1–Br1 124.59(14), C1–As1–C21 101.42(10), F1–Ge1–C1–Br1 –81.09.

in **2** occurred from the less hindered side, to afford the intermediate *Z*-**3**. Treatment of **5** with 1 equiv of *tert*-butyllithium at –100 °C led to the formation of lithiated intermediate **6** ($\delta^{19}\text{F}$ –164.93 ppm), which gave 1-arsa-3-germaallene **1** in nearly quantitative yield by elimination of lithium fluoride (Scheme 1).

The allenic structure of **1** was first suggested by ^{13}C NMR spectroscopy, which shows a very low-field shift (305.2 ppm) for the central *sp* carbon atom, close to those reported for 1-arsa-3-phosphaallene $\text{Mes}^*\text{P}=\text{C}=\text{AsMes}^*$ ¹⁰ (299.5 ppm) and 1,3-diarsaallene $\text{Mes}^*\text{As}=\text{C}=\text{AsMes}^*$ ¹¹ (297.5 ppm). This is, to the best of our knowledge, the highest value ever reported for an allenic structure of type $\text{E}=\text{C}=\text{E}'$ ($\text{E}, \text{E}' = \text{main group elements}$). Less deshielded *sp* carbon atoms were observed for 1-phospha-3-germaallenes $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$ ^{5a} (280.8 ppm) and $\text{Mes}_2\text{Ge}=\text{C}=\text{PMes}^*$ ⁴ (280.9 ppm), 1-germaallenes $\text{Tip}_2\text{Ge}=\text{C}=\text{C}(t\text{-Bu})\text{Ph}$ ¹² (235.1 ppm) and $\text{Tbt}(\text{Mes})\text{Ge}=\text{C}=\text{CR}_2$ ¹³ (243.5 ppm), or arsaallene $\text{R}_2\text{C}=\text{C}=\text{AsMes}^*$ ¹⁴ (255.8 ppm).

The ^1H NMR spectrum of **1** at room temperature displays broad signals for each aliphatic *o*- CHMe_2 (2.86 and 3.43 ppm) and aromatic *m*- CH (7.04 and 7.07 ppm) protons of the Tip group, suggesting a hindered rotation around the $\text{Ge}-\text{C}_{\text{ipso}}$ single bond on the NMR time scale due to a significant overcrowding around the germanium atom. Thus, the important steric congestion in **1** explains its kinetic stabilization.

The molecular structure of **1** was undoubtedly determined by single-crystal X-ray analysis¹⁵ (Figure 2). The Ge1–C1 and the C1–As1 double bonds [1.759(2) and 1.746(2) Å, respectively] are the shortest reported to date.¹⁶ These bond lengths are about 10–12% shorter than corresponding standard single bonds [1.94–1.98 Å for $\text{Ge}-\text{C}^9$ and 1.97–2.00 Å for $\text{C}-\text{As}$]. Other $\text{Ge}-\text{C}$ [Ge1–C2 1.973(2) Å and Ge1–C6 1.948(2) Å] or $\text{C}-\text{As}$ [C21–As1 2.006(2) Å] single bonds lie in the normal range and correspond to typical values. The shortening of the C1–As1 bond in comparison with that of **5** [1.796(2) Å] is partly due to the higher *s*-character of the orbital used to form the $\text{C}-\text{As}$ bond because of the *sp*-type hybridization of the central C atom in the allenic structure of **1**. The geometry around the germanium atom is trigonal planar ($\sum\theta_{\text{Ge}} = 359.64^\circ$). The 1-arsa-3-germaallene unit deviates somewhat from linearity, but the bond angle Ge1C1As1 [$158.29(15)^\circ$] remains reasonable for a heteroallenic structure and comparable with literature values for germa- or arsaallenes [$\text{Tbt}(\text{Mes})\text{Ge}=\text{C}=\text{CR}_2$ ¹³ 168.0° ,

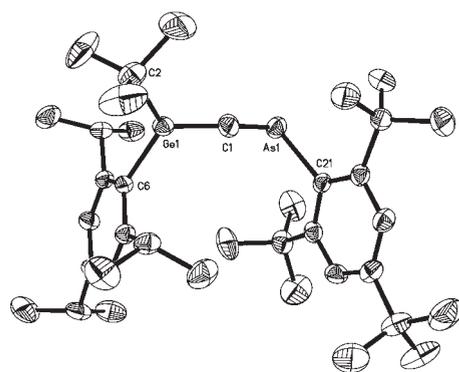


Figure 2. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (°): Ge1–C1 1.759(2), Ge1–C2 1.973(2), Ge1–C6 1.948(2), C1–As1 1.746(2), C21–As1 2.006(2), C2–Ge1–C6 122.73(10), C2–Ge1–C1 124.58(11), C6–Ge1–C1 112.33(10), Ge1–C1–As1 158.29(15), C1–As1–C21 100.33(10).

$\text{R}_2\text{C}=\text{C}=\text{AsMes}^*$ ¹⁴ $169.72(19)^\circ$, $\text{Mes}^*\text{As}=\text{C}=\text{AsMes}^*$ ¹¹ $175.6(6)^\circ$]. As expected, the bond angle is smaller than in its phosphorus analogue $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$ ^{5b} [$166.57(14)^\circ$] in agreement with the fact that the bending generally increases going down the periodic table.¹⁷ The bending is the result of an interaction between two singlet fragments ($>\text{Ge}$ and $\text{C}=\text{As}-$) leading to a double π -donor–acceptor interaction.¹⁷ The angle between the mean planes C1Ge1C2C6 and C1As1C21 (81.8°) is not far from the ideal 90° , and this value is in good agreement with those reported for other heteroallenes. The C21As1C1 bond angle [$100.33(10)^\circ$] is 2.82° smaller than the corresponding C21P1C1 angle in $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$ ^{5b} [$103.15(11)^\circ$], which is consistent with the expected change as one moves to a heavier pnictogen.

Bond lengths calculated using DFT at the B3LYP/6-31G** level of theory (real molecule) are in good agreement with experimental data. However, the GeCAs bond angle in the gas phase (143°) is found to be underestimated in relation to that in the solid state (-15°). The electronic properties of **1** are rather close to those of the phosphorus analogue $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$ previously described.^{5b} The HOMO is found to be the antibonding combination between the $\pi_{\text{Ge}=\text{C}}$ and the arsenic lone pair orbital, while the HOMO–1 can be described as the $\pi_{\text{As}=\text{C}} - \pi^1_{\text{Mes}^*}$ combination and the HOMO–2 as the $\pi_{\text{As}=\text{C}} + \pi^1_{\text{Mes}^*}$ one. In fact, the π_{Mes^*} MO plane is not perfectly perpendicular to the $\pi_{\text{As}=\text{C}}$ one ($\sim 80^\circ$), allowing a small overlap. The $\pi^2_{\text{Mes}^*}$ is found to be the HOMO–3. From the energetics point of view, the HOMO is found to be quasi energetic compared to the HOMO calculated for the phosphorus analogous, consistent with the compensation between the lower electronegativity and the higher *s* character of arsenic in relation to that of the phosphorus atom. Finally, the $\pi_{\text{As}=\text{C}}$ orbital in **1** is destabilized compared to the $\pi_{\text{P}=\text{C}}$ one (0.4 eV) in $\text{Tip}(t\text{-Bu})\text{Ge}=\text{C}=\text{PMes}^*$, which is coherent with a more diffuse character in the case of arsenic derivatives.

1-Arsa-3-germaallene **1** was found to undergo addition reactions only on the $\text{Ge}=\text{C}$ double bond (Scheme 2). Thus, the reaction of **1** with methanol at ambient temperature afforded the corresponding adduct **7** in 69% yield, in accordance with the expected $\text{Ge}^{\delta+}=\text{C}^{\delta-}$ polarity. **1** reacted smoothly with 2,3-dimethyl-1,3-butadiene (DMB) as a dienophile to give the [2+4] cycloadduct **8**.

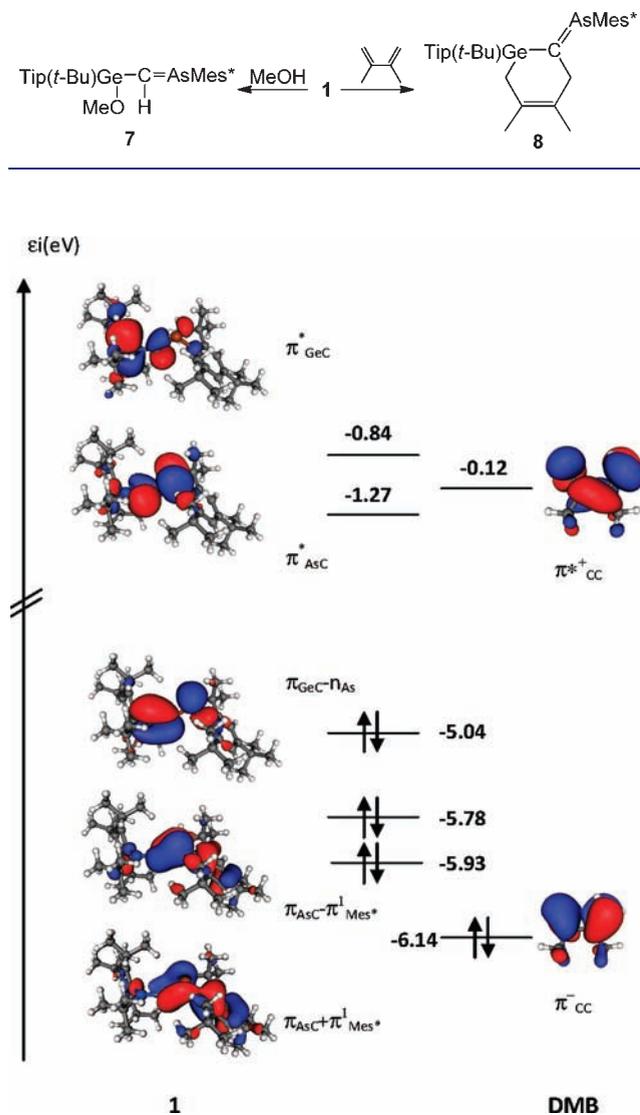
Scheme 2. Reactions of **1** with MeOH and DMB

Figure 3. Nature (main contribution) and energetic positions (Kohn–Sham energies) of the main molecular orbitals for **1** and DMB.

Figure 3 presents the main MOs of **1** and of DMB reagent. From a simple molecular orbital consideration, it is clear that if we consider the heteroallene as a nucleophile, the reaction with the DMB must proceed via the $\pi_{\text{Ge}=\text{C}}$, which is the HOMO, and not via the $\pi_{\text{As}=\text{C}}$ (HOMO–1). In contrast, if we consider **1** as an electrophile, the difference between the $\pi_{\text{C}=\text{C}}^{\text{DMB}}$ (HOMO) and the $\pi_{\text{As}=\text{C}}^*$ (LUMO) is found to be the same as in the previous case (4.92 and 4.87 eV, respectively). Thus, to gain more insight into the regioselectivity of this reaction, we calculated the two pathways involving the Ge=C or As=C double bonds of the arsa-germaallene parent compound **1H** and the DMB π system (see Supporting Information).

The [2+4] cycloaddition with the Ge=C moiety is supra–supra facial (C1GeCC2 dihedral angle $\sim 20^\circ$), concerted, and asynchronous. The geometry around the germanium atom deviates from planarity ($\sum \theta_{\text{Ge}} = 346^\circ$), indicating an interaction between the germanium atom and the carbon C1 of the DMB, while the new C–C2 bond is not yet been formed (see Figure 4). The

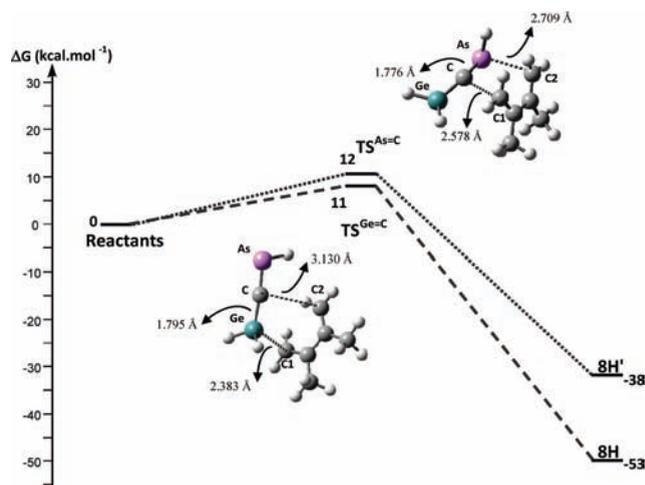


Figure 4. Two possible pathways in the reaction between **1** and DMB.

cycloaddition involving the As=C double bond of the allene is also a concerted reaction, clearly supra–supra facial (C1AsC2 dihedral angle $\sim 7^\circ$) and more synchronous than the latter approach. The difference in synchronicity can probably be explained by the electronegativity (EN) differences between the atoms involved. In front of the carbon atom (2.5), the EN of the germanium is lower than that of the arsenic atom (2.0 vs 2.2). The two calculated barriers have roughly the same magnitude, slightly in favor of the Ge=C cycloaddition (10.9 versus 12.1 kcal·mol⁻¹). However, both reactions are exergonic: **8H** (cycloaddition on Ge=C) is 15 kcal·mol⁻¹ more thermodynamically stable than **8H'** (cycloaddition on As=C), in agreement with the experimental result. It is noteworthy that calculations show higher repulsion energies for both $\text{TS}^{\text{As}=\text{C}}$ and **8H'** than for $\text{TS}^{\text{Ge}=\text{C}}$ and **8H**, respectively, which point out the importance of steric effects.

Taking into account the steric hindrance of the substituent on the germanium and arsenic atoms for the real molecule, it is clear that the approach in the $\pi_{\text{As}=\text{C}}$ plane to obtain **8H'** is not favored. This is probably why, experimentally, the attack occurs only on the Ge=C bond.

In summary, we have succeeded in the synthesis and characterization of the first 1-arsa-3-germaallene, a heavy allenic compound containing arsenic and germanium, both elements from the fourth row of the periodic table. Spectroscopic (low-field shift for the central carbon atom in ¹³C NMR) and structural data (very short Ge=C and C=As bonds, trigonal planar germanium atom, wide Ge=C=As bond angle, and almost mutually orthogonal CGeC and CAsC planes) are strongly consistent with an allenic structure. The electronic structure is comparable with that of the phosphorus analogue. The $\pi_{\text{Ge}=\text{C}}-\pi_{\text{As}}$ MO corresponds to the HOMO and the $\pi_{\text{As}=\text{C}}$ to the HOMO–1. The Ge=C double bond of **1** appears (on first investigation) to dominate its chemistry with the conservation of the GeCAs unit. A first study on the pathway of this reaction seems to indicate the importance of the steric effect on the regio- and chemoselectivity. Further theoretical and experimental investigations on the reactivity of this new species are currently in progress.

■ ASSOCIATED CONTENT

S Supporting Information. Theoretical results (Z-matrix files); experimental procedures and spectral data for **1**, **5**, **7**, and **8**,

and structural data for **1** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

escudie@chimie.ups-tlse.fr

Notes

[†]Deceased.

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