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2-Heteraallenes

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Mini Review

2-Heteroallenes[‡]Koh Sugamata^{a,*} and Takahiro Sasamori^{b,c}Received 00th January 20xx,
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While analogues of allenes with heavier main-group elements (group 14–16) have been extensively studied, 2-heteroallenes are rare chemical species whose properties are mostly unknown. It is also notable that the synthesis and isolation of allene-type molecules are not widespread, despite the extensive study of two-coordinated low-valent chemical species.

1. Introduction

The use of higher-period elements in the 14–16 groups to replace atoms that form multiple bonds has been a popular research topic in main group element chemistry. This is because these heavier compounds have unique structures and properties that differ from their carbon analogues. In particular, their larger atom size and lower electronegativity can lead to changes in bond angles, bond lengths, and reactivity. These differences can be exploited in various applications, such as in

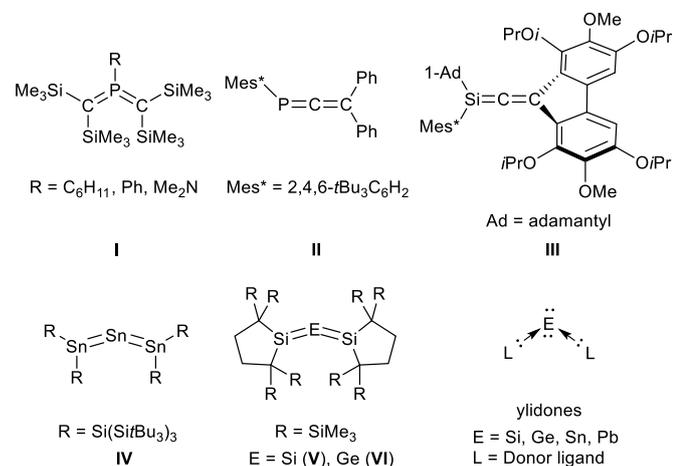


Figure 1. Heteroallenes and their related compounds.

^a Department of Chemistry, College of Science, Rikkyo University, 3-34-1 Nishi-ikebukuro, Toshima-ku, Tokyo 171-8501, Japan

^b Graduate School of Science and Technology, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

^c Department of Chemistry, Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Sciences (TREMS), University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

[†] Footnotes relating to the title and/or authors should appear here.

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[‡] Dedicated to Mr. Toshiaki Noda on the occasion of his 77th birthday

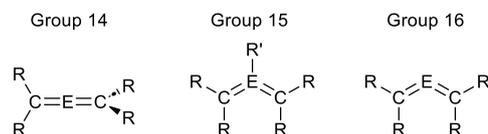


Figure 2. 2-Heteroallenes

catalysis, materials science, and electronics.¹ A number of heavier analogues of alkenes, alkynes, ketones, and aromatic compounds have been reported, revealing their unique structures and properties.² As for the cumulated double bond compounds, allenes, their heavier analogues have also been extensively studied. The first synthesis of bis(methylene)- λ^5 -phosphane (**I**), a 2-heteroallene type molecule with a phosphorus atom, was reported by Appel in 1982 (Figure 1).³ The structure of **I** showed the bent structure due to the steric repulsion by substituents on the central phosphorus atoms, on the basis of our preliminary results of theoretical calculations, showing that the parent molecule exhibits planar structure. The synthesis of 1-phosphapropadiene (**II**) was reported by Yoshifuji and co-workers in 1984.⁴ 1-Heteroallenes, in which the carbon atom in the terminal position of the allenes is replaced by heavier main group elements, have many analogues reported. For group 14 elements, the synthesis of 1-silapropadiene (**III**) have been reported by West and co-workers in 1993.⁵ These structures differed from linear allenes, which consisted only of carbon, with a bent C=C=E moiety. It is the same reason for the trans-bent structure often seen in higher-period analogues of alkenes.⁶ Furthermore, a molecule in which all the carbon atoms constituting an allene were replaced with tin (**IV**), a highly periodic typical element, was reported in 1999, revealing its unique structure and properties.⁷ Similarly, the synthesis of heavy allenes with all silicon (**V**) and germanium (**VI**) atoms substituted was reported by Kira and co-workers in 2003 and attracted much attention.⁸ In contrast, 2-heteroallenes are very rare chemical species whose properties are almost unknown.

Since 2010, the synthesis of zero-valent chemical species, ylidenes, which are considered isomers of 2-heteraallenes, has been reported extensively.⁹ These chemical species can be considered as heavier analogues of carbodicarbenes and are characterized by a bent structure. All group 14 element analogues from Si to Pb have been synthesized and isolated.¹⁰ While two-coordinated low-valent chemical species have been widely studied, there are few examples of synthesis and isolation of allene-type molecules. According to calculations of the allene molecules by Apeloig $\text{H}_2\text{C}=\text{M}=\text{CH}_2$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) were predicted to have a near linear structure, and their C-M bond lengths were also considered C=M double bonds.¹¹ Its characteristics are significantly different from the reported structures of zero-valent chemical species. Since several reviews of zero-valent group 14 chemical species have already been reported, this review will focus primarily on the type of $>\text{C}=\text{E}=\text{C}<$, 2-heteraallenes and their analogues, mainly of the higher period group 14-16 elements, and summarize their synthesis, structure, and properties (Figure 2).

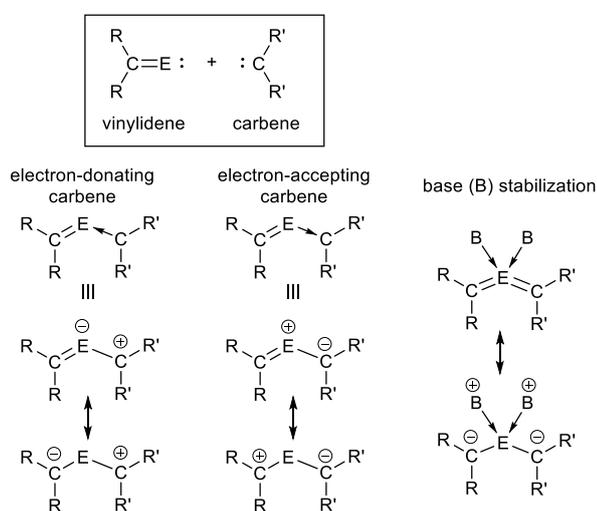


Figure 3. Resonance structures of 2-heteraallenes.

2. Group 14

2-1. Structural Features

All the zero-valent group-14 tetrylones ($>\text{C}\rightarrow\text{E}(\text{O})\leftarrow\text{C}<$, $\text{E} =$ group-14 elements) whose central E atoms retains all four valence electrons as two lone pairs, reported so far exhibit a bent structure.¹² The terminal carbons of tetrylones are electron-donating, which means that the electrons are localized on the central atom. The optimized structure of e.g., a 2-silapropadiene with amino groups is highly bent, indicating the characteristic structure for a zero-valent compound of this type (Figure 4). The corresponding 2-silalallene with methyl groups also exhibits a bent structure, albeit that the C-Si-C angles are wider and the C-Si bonds shorter than those of the amino-substituted 2-silapropadiene. The optimized structure of the 2-silapropadiene with electron-accepting silyl groups exhibits a

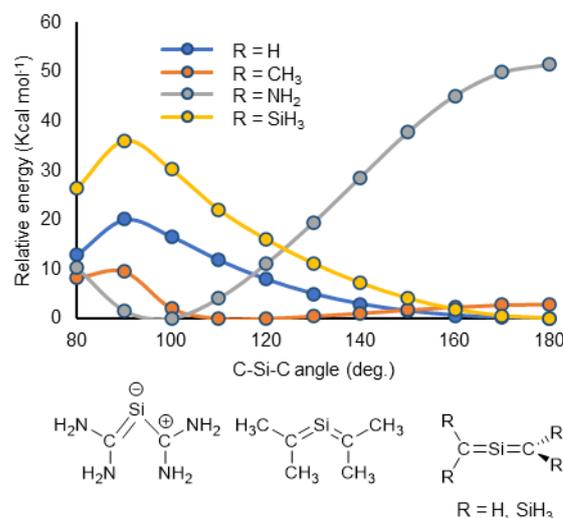
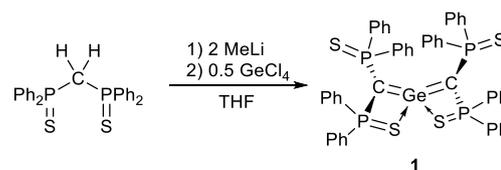


Figure 4. Optimized structures of 2-silapropadienes calculated at the B3LYP-D3/6-311G(2d,p) level.

linear allene structure similar to that of H_2C :. Thus, these chemical species are strongly influenced by the electron-donating nature of their substituents. NBO calculations on the corresponding H_2N -substituted 2-silapropadiene revealed an s-type lone pair on Si, which was considered to be the structure most strongly affected by the contribution of the ylidenic structure. In contrast, no lone pairs were observed on the Si atom of a H_3Si -substituted 2-silapropadiene with two equivalent C-Si double bonds. The two C-Si bonds contain formally sp-hybridized silicon atoms and should be considered to exhibit the same bonding mode as all-carbon allenes. The negative charges are also strongly delocalized on the terminal carbons, which avoids electron repulsion around the central silicon atom, and results in a linear structure. The molecule with the H_3C groups would be considered a bent allene-type structure; even though it is similar to the bonding mode of the H_3Si -substituted compound, it is bent due to the contribution of a resonance structure with a lone-pair on Si. The C-M-C bond angles of the 2-metallapropadienes narrow for progressively heavier group-14 elements, indicating a gradual change from an allene- to an ylidenic- or ylidenic-type electronic structure. In contrast, the silyl-substituted compounds show linear allene-type structures for all elements from Si to Pb. Thus, these chemical species are interesting because the substituents change the electronic state of the central element, resulting in subtle conformational changes.

2-2. Synthesis and Properties



Scheme 1. Synthesis of a base-stabilized 2-germapropadiene 1.

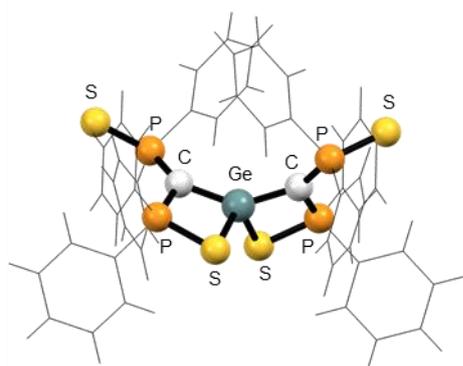
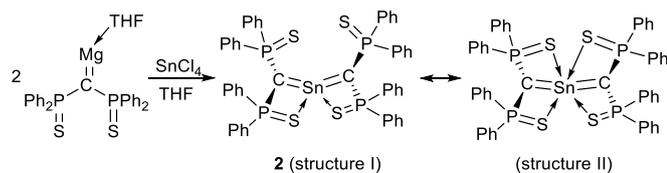


Figure 5. Molecular structure of a base-stabilized 2-germapropadiene **1**.

In 2009, So and co-workers reported the synthesis of a base-stabilized 2-germapropadiene **1** using $\text{Ph}_2\text{P}(=\text{S})-$ groups.¹³ Bis(phosphinoyl)methane was lithiated with MeLi and treated with germanium tetrachloride to give a base-stabilized 2-germapropadiene **1** (Scheme 1). The central moiety of **1** exhibits a bent structure with a C–Ge–C bond angle of $142.6(1)^\circ$ on account of the coordination of the sulfur atoms to the central germanium atom (Figure 5). The C–Ge bonds ($1.882(2) \text{ \AA}$) are longer than other reported C–Ge double bonds.¹⁴ The sum of the bond angles of the terminal carbons (358.3°) corresponds to a near-planar geometry, indicating that these carbons are sp^2 -hybridized. The structure of **1** in solution has not been reported in detail, probably due to the effects of coordination exchange. However, DFT calculations have been used to evaluate the properties of the double bonds in this base-stabilized 2-germapropadiene **1**; the results have shown that the coordination of the sulfur donor to the germanium atom delocalizes the p electrons and increases the length of the Ge–C double bond. An NBO analysis on **1** showed that the Ge–C bond is formed by $\text{sp}^{1.85}$ hybrids on the germanium atom and $\text{sp}^{2.22}$ hybrids on the carbon atoms, whereby the carbon atoms contribute 71.8% of the electron density.



Scheme 2. Synthesis of a base-stabilized 2-stannapropadiene.

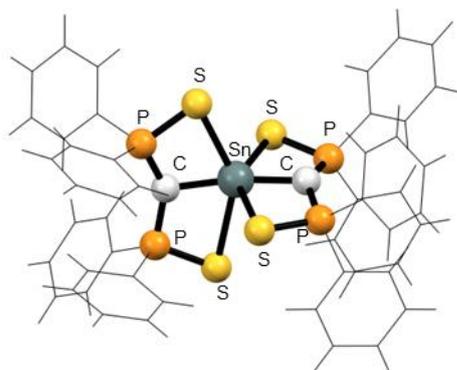


Figure 6. Molecular structure of a base-stabilized 2-stannapropadiene.

In 2011, the synthesis of 2-stannapropadiene analogues **2** was reported by Leung *et al.*, who used the same bis(phosphinoyl)methane carbene.¹⁵ The reaction of the magnesium complex with tin tetrachloride afforded the

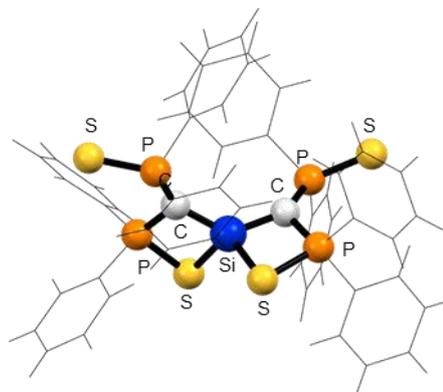
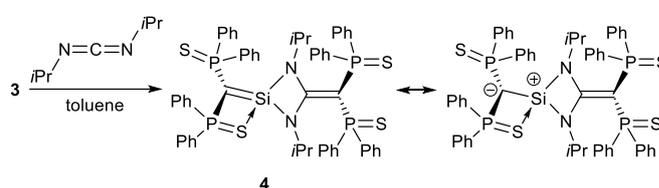


Figure 7. Molecular structure of a base-stabilized 2-silapropadiene **3**.



Scheme 3. Reaction of a base-stabilized 2-silapropadiene **3** with a carbodiimide.

corresponding base-stabilized 2-stannapropadiene **2** as a yellow solid (Scheme 2). Its C–Sn–C bond angle shows a slight bend ($171.1(1)^\circ$) due to the coordination of six sulfur atoms to the central tin atom (Figure 6). The two equivalent C–Sn bonds ($2.063(2) \text{ \AA}$) are slightly more elongated than other reported C–Sn double bonds.¹⁶ As in **1**, the sum of the bond angles of the terminal carbons in **2** indicates that it is close to planar, suggesting that these carbon atoms are sp^2 -hybridized. These results indicate that the structure of the tin complex in the solid state is close to that of allenes. In contrast, the ^{119}Sn NMR spectrum of the base-stabilized 2-stannapropadiene **2** in solution at room temperature featured only one broad signal at $\delta -401$ ppm, while that of the 2-stannapropadiene **2** at -80°C displayed two signals at $\delta -192$ and -445 ppm, which indicates that two different tin environments are present; this notion is also consistent with the low-temperature ^{31}P NMR spectrum. In the ^{119}Sn NMR spectrum, the signal at $\delta -192$ ppm corresponds to structure I, while the signal at $\delta -445$ ppm corresponds to the more shielded tin atom in structure II (Scheme 2).

In 2013, a silicon analogue of a base-stabilized 2-metallaallene **3** was reported by So and co-workers.¹⁷ The reaction of bis(phosphinoyl)methane with 2 equivalents of MeLi in Et_2O followed by the addition of 0.5 equivalent of SiCl_4 afforded the corresponding base-stabilized 2-silapropadiene **3**, whose structure consists of two bidentate bis(thiophosphinoyl)methanediide ligands bound to the silicon center in a spirocyclic arrangement, similar to that of base-stabilized 2-germapropadiene (Figure 7). The C–Si bond lengths (average 1.810 \AA) are comparable with those of typical C–Si

single bonds (1.87–1.91 Å).¹⁸ The C–Si–C bond angle in **3** is highly bent (134.9(8)°). The ¹³C NMR spectrum shows a triplet at δ 42.3 ppm (¹J_{P–C} = 67.1 Hz) corresponding to the terminal C atoms of the allene moiety. This result stands in sharp contrast to the ¹³C NMR spectra of the heavier analogues [(PPh₂S)₂C=M=C(PPh₂S)₂] (M = Ge, Sn), in which no signal was observed for the terminal C atoms. Furthermore, the room-temperature ²⁹Si NMR spectrum displays a quintet at δ –28.9 ppm (²J_{Si–P} = 7.6 Hz), which shows an upfield shift in comparison to that of the 1-silapropadienes (δ 13.1–58.6 ppm).¹⁹ These results indicate that the Si–C bonds in 2-silapropadiene **3** do not have multiple-bond character. They also show that the base-stabilized 2-metallapropadienes comprise a C[–]–M²⁺–C[–] ylidic skeleton with negative charge at the terminal C atoms of the allene moieties and two positive charges at the central M atoms (Figure 8).

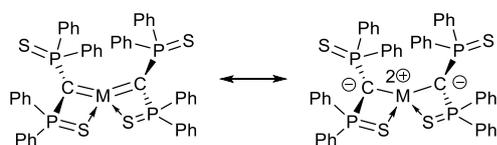
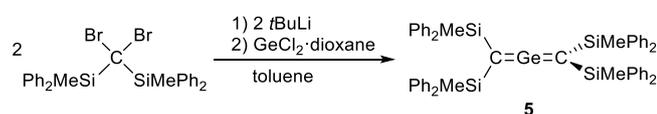


Figure 8. Resonance structures of base-stabilized 2-metallapropadienes.

Moreover, the reaction of a base-stabilized 2-silapropadiene **3** with a carbodiimide has been reported. Treatment of base-stabilized 2-silapropadiene with an excess of *i*PrN=C=N*i*Pr afforded the base-stabilized silene **4** (Scheme 3). The formation of a base-stabilized silene in the reaction of 2-silapropadiene is consistent with an ylidic skeleton in the base-stabilized 2-silapropadiene.



Scheme 4. Synthesis of a linear 2-germapropadiene.

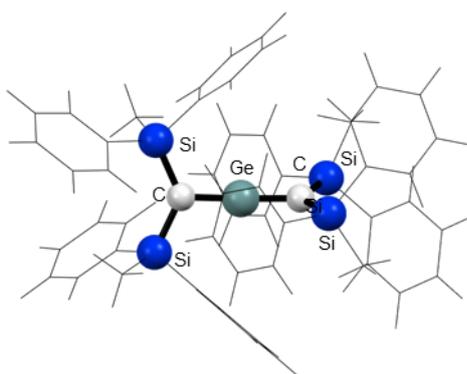


Figure 9. Molecular structure of the linear 2-germapropadiene.

The synthesis and isolation of a 2-germapropadiene **5** with a linear structure using bulky silyl groups (MePh₂Si), was reported by Sugamata and his co-workers (Scheme 4).²⁰ This 2-germapropadiene **5** was obtained in the form of pale-yellow crystals from the lithiation of dibromodisilylmethane followed

by the addition of GeCl₂. A crystallographic analysis of **5** revealed an almost linear C–Ge–C angle (176.16(1)°), and two almost equivalent C–Ge bonds (1.7764(2)/1.7740(2) Å), which indicates a double-bond character for the C–Ge moieties (Figure 9). The C–Ge bond length of **5** is one of the shortest C–Ge double bond lengths reported so far and significantly shorter than the C–Ge bond length (1.882(2) Å) for the base-stabilized 2-germapropadiene **1** described above.

The 2-germapropadiene **5** was also examined in solution, where its ¹³C NMR spectrum shows a singlet signal at δ 85.2 ppm for the terminal allene carbon atoms, indicating magnetically equivalent carbon atoms and thus an allene-type structure. Compared to the signal for the allene carbon atoms in tetra(trimethylsilyl)allene (δ 64.0 ppm),²¹ that of **5** is shifted to lower field due to the anisotropic effect of the C=Ge double bonds. The HOMO, HOMO-1, LUMO, and LUMO+1 of the 2-germapropadiene **5** thus revealed typical features of compounds with a linear allene structure (Figure 10).

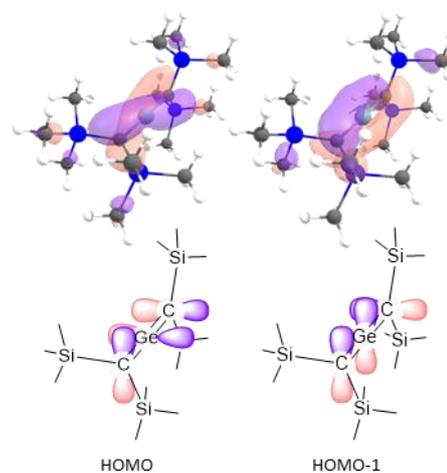
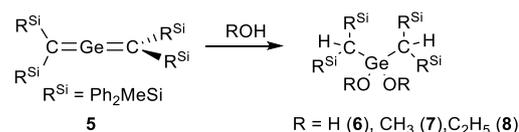


Figure 10. Kohn-Sham orbitals of the linear 2-germapropadiene, calculated at the B3PW91/6-311G(2d,p) level.



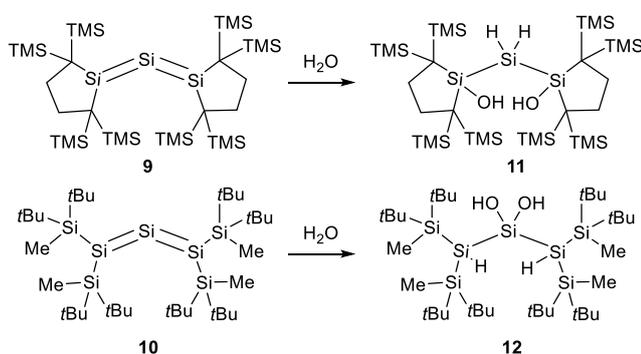
Scheme 5. Reactivity of the linear 2-germapropadiene **5**.

The reactivity of **5** was confirmed using electrophilic reagents such as water and alcohols. The corresponding germandiol **6** and dialkoxygermane **7** and **8** were obtained quantitatively, respectively (Scheme 5).

These results strongly reflect the electronic structure of a 2-germapropadiene **5**, with an effective electronic contribution from a localized negative charge on the germanium and positive charges on the carbon atoms. The electronic state of this 2-germapropadiene stands in contrast to that of tetrylones, in which the central high-period elements carry a positive charge.

The electron-donating nature of the substituents also affects the structure and properties of trisilaallenes. The synthesis of a cyclic alkyl trisilaallene **9** was reported by Kira, while that of a silyl-substituted trisilaallene **10** was reported by

Sekiguchi.²² The structure of **10** has not yet been determined crystallographically, and therefore, the following comparisons are based on theoretically optimized structures. The Si–Si–Si bond angle of the trisilaallene **9** (136.49(6)°) is significantly lower than that of the trisilaallene **10** (164.3°). The Si–Si bond lengths of the silicon-substituted and cyclic alkyl groups are 2.183 Å (average) for **10** and 2.177 Å (average) for **9**, respectively. Thus, it seems feasible to conclude that the silyl-substituted trisilaallene exhibits more of a bent-allene-type structure. The reactivity of these trisilaallenes is highly affected by these differences, i.e., in the reactions with alcohol or water, **10** is protonated at the terminal silicon atoms, whereas **9** is protonated on the central silicon atom (Scheme 6). Consequently, the trisilaallene **10** should be classified as an allene or vinylidene, while the **9** should be characterized as an ylidene.



Scheme 6. Hydrolysis of a cyclic alkyl-substituted trisilaallene **9** and a silyl-substituted trisilaallene **10**.

3. Group 15

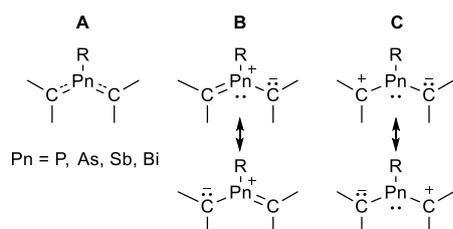
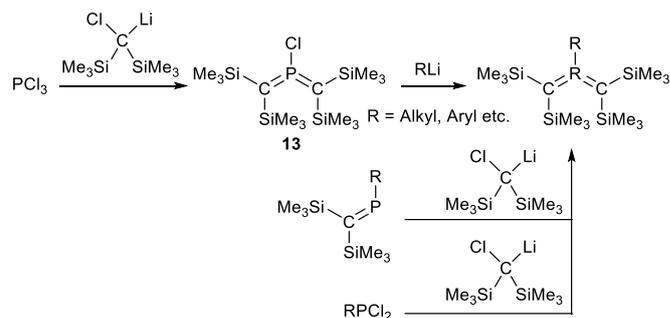


Figure 11. Canonical resonance structures A–C for pnictogen-centered heteroallene-type molecules.

Since the synthesis of 1-phosphaallene by Yoshifuji in 1984,⁴ a variety of heteroallenes containing at least one phosphorus atom have been reported.²³ Interestingly, phosphorus-centered allene-type molecules of the type bis(methylene)- λ^5 -phosphanes have been known longer for 2-phosphaallenes than for 1-phosphaallenes. Bis(methylene)- λ^5 -phosphanes are molecules that contain two methylene groups attached to a central phosphorus atom. The synthesis of bis(methylene)- λ^5 -phosphanes was first reported by Appel in 1982 and continued to be intensively studied after Nieke took over the work. Bis(methylene)- λ^5 -phosphanes are generally synthesized by the



Scheme 7. Synthesis of representative bis(methylene)- λ^5 -phosphanes.

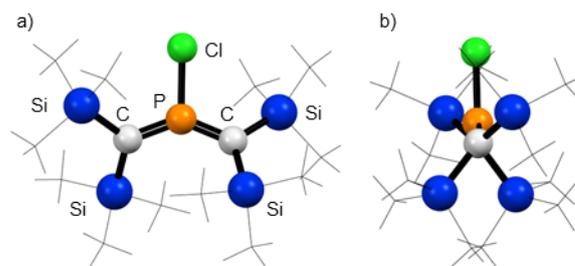


Figure 12. Molecular structure of *P*-chloro-bis(methylene)- λ^5 -phosphane **13**: (a) front view and (b) side view.

treatment of carbenes or carbenoids with phosphoalkenes (Scheme 7).

P-chloro derivatives can be easily functionalized on phosphorus via nucleophilic substitution reactions and many *P*-functionalized bis(methylene)- λ^5 -phosphanes have already been reported.²⁴

The molecular structure of *P*-chloro bis(methylene)- λ^5 -phosphane **13** exhibited C–P bonds (1.619(7)/1.639(7) Å) comparable to those of other reported phosphoalkenes (1.67 Å) and significantly shorter than those of typical C–P single bonds (1.85 Å) (Figure 12).^{25,26} The C–P–C bond angle (136.8°) of **13** is significantly larger than representative R–P=C angles in phosphoalkenes (103°). The terminal carbon atoms of the central moiety show an almost planar geometry (359.7°), which suggests that the terminal carbons are sp^2 -hybridized. An NBO analysis of the optimized structures of bis(methylene)- λ^5 -pnictanes revealed two C–Pn bonds and a 3-center-4-electron

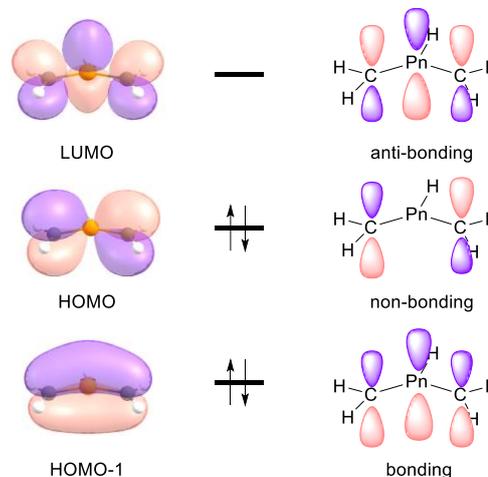


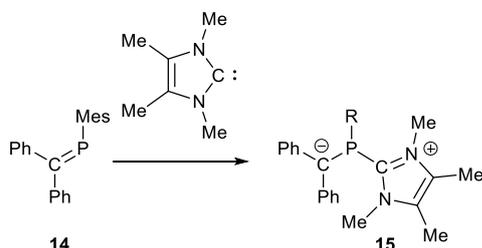
Figure 13. The 3-center 4-electron π -bond of the $>C-Pn-C<$ moiety in bis(methylene)- λ^4 -pnictanes.

π -bonds on the C–Pn–C moiety (HOMO, HOMO-1, and LUMO) (Figure 13).

The predominant contribution of the canonical resonance structure **A** in bis(methylene)- λ^5 -pnictanes was corroborated by the results of theoretical calculations.

Kennephol, Streubel, and Gates have reported the synthesis of a *N*-heterocyclic carbene(NHC)-phosphaalkene adduct **15**, via the reaction of MesP=CPh₂ (**14**) with a NHC (Scheme 8), which could be thought as a key intermediate in the anion-polymerization of phosphaalkenes. On the consideration of the resonance structures **B** and **C** in Figure 10, compound **15** can be considered as a ylide-type analogue of a 2-phosphaallene.²⁷ The molecular structure of the NHC-phosphaalkene adduct **15** features two different P–C bonds in the C–P(R)–C moiety (Figure 14). The short C1–P bond fall in the range of double bonds (MesP=CPh₂: 1.692(3) Å),²⁸ while the other P–C bond (1.851(2) Å) appears to be a single σ -bond. The C–P–C bond angle (112.73(9)°) is smaller than that of *P*-chloro bis(methylene)- λ^5 -phosphane **13** (136.8°). A ³¹P NMR spectroscopic analysis revealed that the signal for MesP=CPh₂ (δ = 234 ppm) was replaced by a broad signal at δ = 206.1 ppm, albeit that the chemical shift strongly depends on the solvent (THF: δ = 185 ppm; toluene: δ = 213 ppm). The similarity of this chemical shift to that of MesP=CPh₂ suggests that the NHC–phosphaalkene adduct **15** retains its C=P double-bond in solution.

A natural-resonance-theory (NRT) analysis of the NHC–phosphaalkene adduct **15** suggested that the major contributors to the canonical forms are the simple adduct and the asymmetric allylic form (Scheme 8).



Scheme 8. Synthesis of NHC-phosphaalkene adduct.

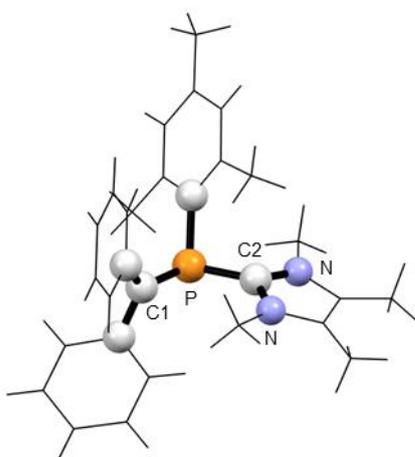


Figure 14. Molecular structure of NHC–phosphaalkene adduct **15**.

4. Group 16

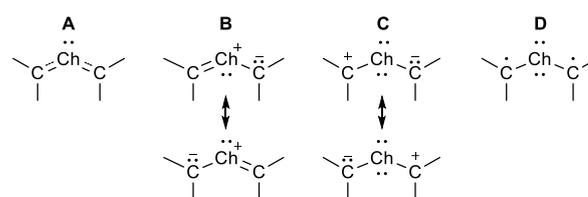
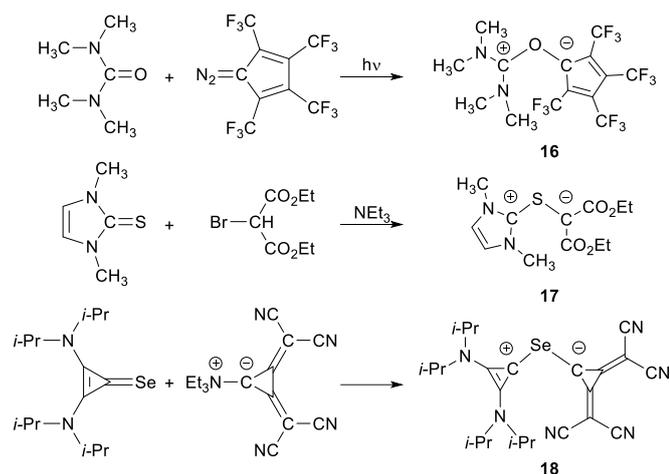


Figure 15. Canonical resonance structures **A–D** for chalcogen-centered heteroallene-type molecules.

The oxidation state of the central atom of group-16-element-centered heteroallenes should thus be extremely interesting, especially with respect to the duality between cumulative ($>C=Ch=C<$; Ch = group-16 element) and carbonyl ylide ($>C=Ch^+-C^-$) isomers, given that the latter may engage in [3 + 2] cycloaddition reactions as 1,3-dipolar reagents. The use of heavier analogues of carbonyl ylides, in which the central oxygen atom is replaced with a heavier group-16 element, as 1,3-dipolar agents has been reported for various organic reactions.²⁹ Although the reactivity of heavier analogues of carbonyl ylides has attracted substantial attention, especially with respect to their unique structural features, their instability under the applied reaction conditions usually requires their formation *in situ*. From a fundamental perspective, it would be of great interest to isolate group-16-element-based heteroallenes and investigate the intrinsic structural features of the C=Ch=C bonds. Some canonical structures for such heteroallenes are shown in Figure 15.



Scheme 9. Synthesis of stable carbonyl ylides and their heavier analogues.

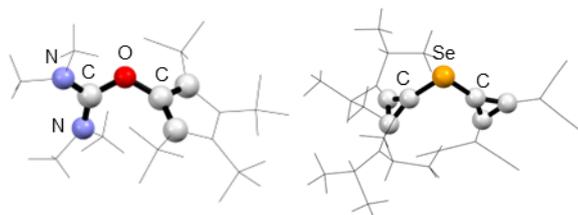
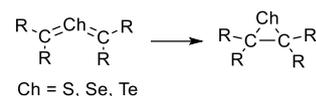


Figure 16. Molecular structures of a stable carbonyl ylide **16** and its selenium analogue **18**.

Ylide-type structures **B** and **C** are known as “carbonyl ylides”, which can be stabilized electronically by using “push-pull”-type substituents. Carbonyl ylides can be synthesized via the reaction of urea or its heavier congeners with the corresponding electron-deficient carbenoids (Scheme 9).

In 1976, the first stable thiocarbonyl ylides **17** were reported by Arduengo and Burgess.³⁰ The reaction of thiourea with alkyl bromide afforded the corresponding thiouronium salt. Subsequent treatment of the salt with NEt_3 led to the formation of thiocarbonyl ylides **17**. In 1983, a stable carbonyl ylide **16** was synthesized by Arduengo and co-workers via the photoreaction of diazotetrakis(trifluoromethyl)cyclopentadiene in the presence of tetramethylurea.³¹ The synthesis and structure of a selenocarbonyl ylide **18**, obtained from the reaction of diaminocyclopropaneselone with inner salts, has been reported by Seitz.³² The molecular structures of a carbonyl ylide **16** and a selenocarbonyl ylide **18** have been determined crystallographically (Figure 16). The structure of the carbonyl ylide **16** exhibits two different C–O bonds (1.348(8)/1.422(7) Å). The shorter C–O bond suggests a partial C–O π -bond between the carbonium center and the oxygen. In contrast, the other C–O bond appears to be a single σ -bond. The structure of the selenocarbonyl ylide **18** also shows slightly different C–Se bonds (1.88/1.90 Å), albeit that the difference is less pronounced. These carbonyl ylides and heavier analogues show the asymmetric nature due to the stabilization by suitable “push-pull” substituents.

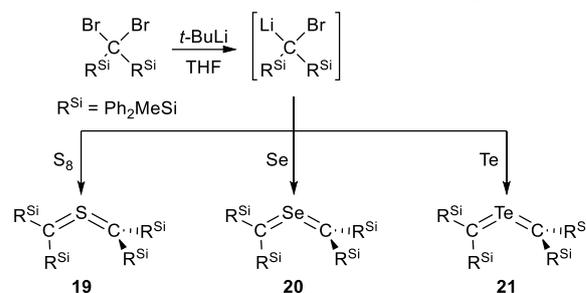
In contrast, the synthesis of allene-type molecules **A** remains elusive. This is most likely due to the easy isomerization of their allene-type forms to give the corresponding three-membered ring compounds, epichalcogenides (Scheme 10).



Scheme 10. Bis(methylene)- λ^4 -chalcogenanes and the corresponding epichalcogenides.

In 2018, the synthesis of a stable bis(methylene)- λ^4 -sulfane **19**, which represents the first example of a chalcogen-centered heteroallene-type molecule, was reported by one of the authors of this review via kinetic stabilization with efficient steric protection from a bulky silyl group.³³ This bis(methylene)- λ^4 -sulfane **19** can be obtained from the reaction between a bis(silyl)carbenoid, which is generated *in situ* from the reaction of $\text{R}^{\text{Si}}_2\text{CBr}_2$ with 2 equivalents of *t*-BuLi, and an equimolar amount of elemental sulfur. The corresponding bis(methylene)- λ^4 -selane (**20**)³⁴ and -tellane (**21**)³⁵ were synthesized in a similar fashion to that of the λ^4 -sulfane **19** (Scheme 11).

The molecular structure of the bis(methylene)- λ^4 -sulfane **19** exhibits a pseudo- C_2 symmetry with a bent C–S–C moiety (Figure 17). The C–S bonds (1.6591(3)/1.6561(3) Å) in this sulfane are almost identical, and fall in the range of typical C–S



Scheme 11. Synthesis of group-16-element-centered heteroallene-type molecules.

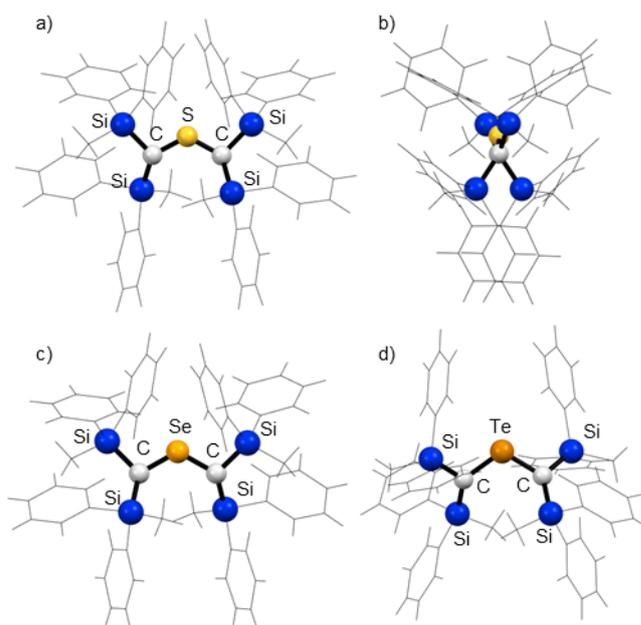


Figure 17. Molecular structures: (a) front view and (b) side view of a bis(methylene)- λ^4 -sulfane **19**; front view of a (c) bis(methylene)- λ^4 -selane **20** and (d) -tellane **21**.

double bonds. These C–S bond lengths are almost identical to those of a thiobenzophenone (1.66 Å).³⁶ Both the terminal carbon atoms of the C–S–C moiety are almost planar, which is indicative of considerable multiple-bond character for the C=S bonds in this bis(methylene)- λ^4 -sulfane **19**. The molecular structures of the bis(methylene)- λ^4 -selane **20** and - λ^4 -tellane **21** are similar to that of **19**. The short C–Se bonds in **20** (1.811(4)/1.808(3) Å) fall in the range of typical C=Se double bonds, albeit that they are slightly longer than that of 4,4'-dimethoxyselenobenzophenone (1.790(4) Å).³⁷ Furthermore, the almost identical carbon-tellurium bond lengths of 2.017(1) Å and 2.020(1) Å in **21** are significantly shorter than those of typical carbon–tellurium single bonds (2.16 Å).²⁶ These bonds are also slightly longer than that in a reported telluroketone tungsten complex and comparable to the C–Te(IV) unsaturated bond (2.003(7) Å) in a telluropyrylium salt.^{38,39} The C–Ch–C angles (Ch = S: 123.0(1)°, Se: 120.8(2)°, Te: 112.80(5)°) in the bis(methylene)- λ^4 -chalcogenanes narrow with progressively heavier elements.

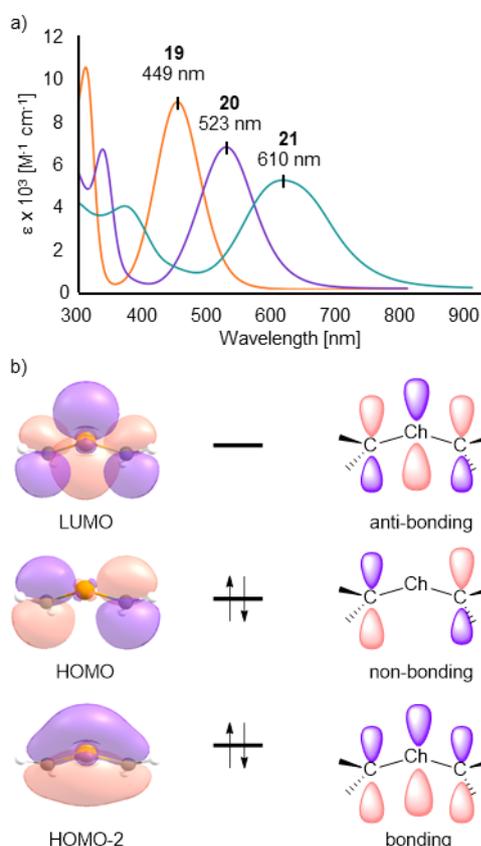
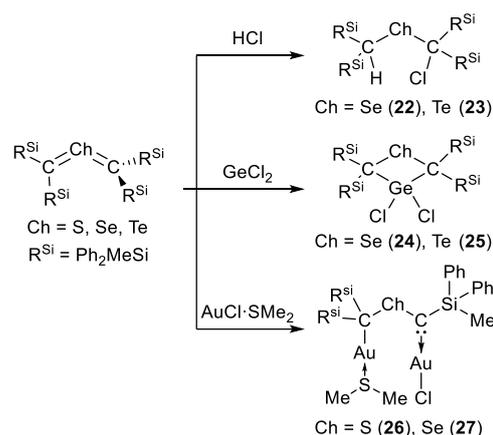


Figure 18. a) UV-vis spectrum of and b) the 3-center 4-electron π -bond of the $>C\text{-Ch-C}<$ moiety in bis(methylene)- λ^4 -chalcogenanes.

An NBO analysis of the optimized structures of these bis(methylene)- λ^4 -chalcogenanes showed two C–Ch bonds and 3-center-4-electron π -bonds on the C–Ch–C moieties (HOMO, HOMO-2; and LUMO) (Figure 18).

The predominant contribution of canonical resonance structure **A** in the bis(methylene)- λ^4 -chalcogenanes was corroborated by the results of the theoretical calculations.

The ⁷⁷Se NMR spectrum of bis(methylene)- λ^4 -selane **20** revealed a singlet signal at 1501 ppm, which is characteristic for unsaturated organoselenium compounds. Compared to the ⁷⁷Se NMR signatures of hitherto reported organoselenium compounds, such as di-*n*-butyl selenide (160 ppm),⁴⁰ this value is shifted to lower field, but still at higher field compared to that of di-adamantyl selenoketone (2134 ppm).⁴¹ The chemical shift thus falls within the range of tetravalent selenium species and selenium diimide (1651 ppm).⁴² The ¹²⁵Te NMR spectrum of bis(methylene)- λ^4 -tellane **21** exhibits a signal at 2230 ppm. This value is shifted to higher field compared to that of telluroketone (2858 ppm).⁴³ The UV-vis spectra of bis(methylene)- λ^4 -chalcogenanes **19–21** show characteristic absorptions at λ_{max} =



Scheme 12. Reaction of bis(methylene)- λ^4 -chalcogenanes with hydrogen chloride and dichlorogermylene dioxane complexes.

449 nm (**19**), 523 nm (**20**), and 610 nm (**21**), indicating the presence of strong interactions between each of the C–Ch multiple bonds due to their bent structures.

The reactivity of bis(methylene)- λ^4 -chalcogenanes toward alkynes and alkenes was examined, with the expectation that [3 + 2] cycloadducts would be formed. However, the bis(methylene)- λ^4 -chalcogenanes remained inert toward a variety of alkynes and alkenes, even under severe conditions. The reactions of bis(methylene)- λ^4 -selane **20** and -tellane **21** with hydrogen chloride quantitatively afforded the corresponding 1,3-adducts **22** and **23** (Scheme 12).

Furthermore, treatment of bis(methylene)- λ^4 -chalcogenanes with GeCl_2 -dioxane afforded unique four-membered ring compounds **24** and **25**, indicating that the formal [3 + 1] cycloaddition reaction is unique to these chalcogen-centered heteroallenes. The attempted reductions of the four-membered ring compounds were unsuccessful. The reactivity of bis(methylene)- λ^4 -sulfane **19** and -selene **20** with $\text{AuCl-Me}_2\text{S}$ was investigated.⁴⁴ Unexpected dinuclear

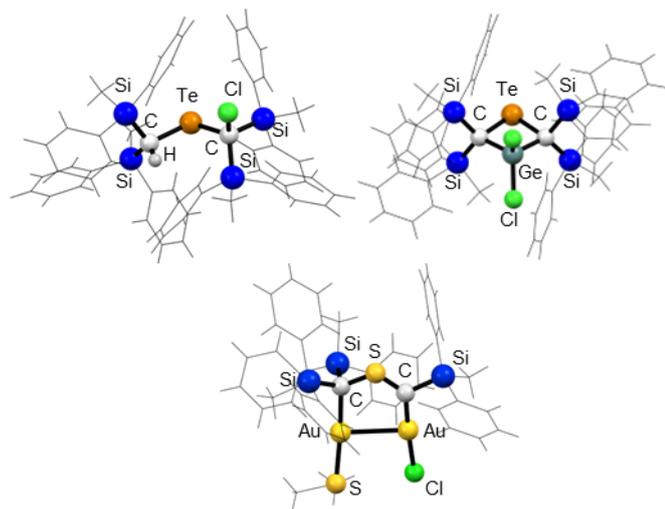


Figure 19. Molecular structures of bis(methylene)- λ^4 -tellane adducts.

(chalcogeno)(silyl)carbene gold(I) complexes **26** and **27** were obtained via the elimination of Ph_2MeSiCl .

Conclusions

Here, we have summarized recent progress in the area of 2-heteroallenes, which are heavier-main-group-element-centered heteroallenes. A characteristic feature of these species is that the electronic state of the central atom changes depending on the nature of the substituents on the terminal atoms. As the result, these species can exhibit allene-type or tetrylone-type molecular structures. This is one of the fascinating areas of research in main-group element chemistry. The unique properties of these intriguing compounds are still largely unexplored, and we look forward to further progress.

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