Cycloaddition of carbonyl compounds and alkynes to (di)silenes and (di)germenes: reactivity and mechanism

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The chemistry of silenes, germenes, disilenes and digermenes has been extensively studied over the last 35 years; however, not much is known about the mechanisms of many of the fundamental reactions of this class of compounds, including cycloadditions. This review describes the current understanding of the reaction pathways for the cycloaddition of carbonyl compounds and alkynes to (di)tetrelenes. The question of whether or not the cycloaddition reactions of (di)tetrelenes follow the Woodward-Hoffman rules, established for alkenes and alkynes, is addressed.

1. Introduction

One of the most important advances in inorganic chemistry over the last 35 years was the discovery of stable (at room temperature under an inert atmosphere) multiply-bonded species of the heavy main group elements. The spectroscopic and structural characterization of these unsaturated species and computational studies of their electronic structure has profoundly influenced our understanding of structure, bonding and reactivity.[1] Furthermore, multiply-bonded compounds of the heavy main group elements have proven to be powerful building blocks in organometallic/inorganic synthesis just as alkenes and alkynes have proven to be in organic synthesis. An impressive array of previously inaccessible compounds, particularly ring systems, has been made from (di)tetrelenes (referring to the heavy Group 14 derivatives: tetrelenes $(R_2M=CR_2)$[2] and ditetrelenes $(R_2M=M'R_2)$). To achieve the full potential of these low valent, main group compounds, it is critical to have a broad understanding of their reactivity and a firm grasp of the reaction mechanisms.[3] However, despite the years of research into the synthesis and reactivity of (di)silenes and (di)germenes (which we will collectively refer to as (di)tetrelenes although we will discuss only the silicon and germanium derivatives herein),[4,5,6,7]

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detailed mechanistic studies are still relatively scarce. What does exist focuses primarily on the reactions of alcohols or water with (di)silenes.[8] Various factors contribute to the difficulties associated with studying the reaction mechanisms of (di)tetrelenes using traditional methods. For example, (di)tetrelenes are reactive toward air and moisture as well as many common functional groups, such as alcohols, amines, nitriles, and carbonyls, which drastically limits the scope of substituent and solvent effect studies that can be performed. The derivatives of (di)tetrelenes are not readily amenable to isotope studies. Few *E/Z* isomers of (di)tetrelenes are known and heteroleptic isomers have only become readily available in the last few years,[6] and thus, examination of the stereo- and regiochemistry of the addition reactions of these species is limited. Finally, the rates of many reactions are quite fast requiring specialty equipment to monitor them. In the last two decades, however, the power of density functional theory (DFT) has been utilized to great effect in the elucidation of reaction mechanisms, including those of (di)tetrelenes. Furthermore, the use of mechanistic probes, particularly suited to the chemistry of (di)tetrelenes, has been extensively employed in this area.

In this review, we focus on progress made over the last 15 years towards understanding the mechanisms of two of the most important reactions of doubly-bonded silicon and germanium compounds: the cycloaddition of carbonyl compounds (aldehydes and ketones) and alkynes. These two reactions have figured,[9,10,11] and continue to figure,[12] prominently in the chemistry of (di)tetrelenes. With an understanding of these two fundamental reaction pathways, we hope these reactions, which have been of primary importance in the development of this chemistry, will play a role in future applications in areas such as organic synthesis, polymer chemistry and materials science. For example, the highly regioselective addition reactions of terminal alkynes to silenes may be of utility in organic synthesis,[13] the reaction between an alkyne and a disilene

has recently been utilized in the formation of organosilicon hybrid polymers,[12b] and both the addition of alkynes and carbonyl compounds have been examined as a means of functionalizing Si- and Ge(100) reconstructed surfaces which are composed of surface disilenes and digermenes, respectively.[14]

We begin the review with a brief discussion of the principle of cyclopropyl-based mechanistic probes and the common substrates used for the mechanistic studies. Then, for each reaction (i.e. the addition of carbonyl compounds and the addition of alkynes), we present some of the key early mechanistic findings as well as the results of computational studies. We then detail the experimental work in the area, which has been largely carried out using cyclopropyl-based aldehyde and alkyne probes in our laboratories. Finally, we will summarize the results and compare them to the chemistry of the lightest congener of doubly-bonded Group 14 compounds, alkenes.

2. Cyclopropyl-based mechanistic probes

An aldehyde and an alkyne mechanistic probe, based on the 2-alkoxy-3-phenylcyclopropylcarbinyl hypersensitive probes pioneered by Newcomb,[15] have been developed for and used extensively in the elucidation of the reaction mechanisms of the addition of carbonyl compounds and alkynes to (di)tetrelenes. The probe function of these molecules stems from the regiochemically distinct rearrangements that occur upon the formation of a reactive intermediate at the cyclopropylcarbinyl position: structural isomers are formed depending on the nature of the intermediate adjacent to the cyclopropyl ring (radical/cation/anion). The magnitude of the rate constants for the rearrangements is integral to the ability of these compounds to behave as mechanistic probes. The rate constants must be

large enough such that the rearrangement can effectively compete with other processes that may occur along the reaction pathway (such as ring closure or disproportionation).[15] The phenyl-substituted cyclopropyl carbinyl probes are termed "hypersensitive" or "ultrafast" since they can reveal transformations that occur on the nano- to picosecond time scale.[15] Furthermore, although many mechanistic probes have been designed to reveal the involvement of free radical intermediates, it is equally important to note that the absence of a characteristic free radical rearrangement can be construed as strong evidence against a radical mechanism.[16]

The oxy-substituted cyclopropylcarbinyl radical, **1**, formed from cyclopropyl aldehyde **2** undergoes ring-opening rearrangement selectively toward the phenyl substituent.[17,18] The absolute rate constant for the ring-opening rearrangement of oxy-substituted cyclopropylcarbinyl radical **1a** is unknown; however, there are several estimates available that indicate the lower limit of the rate constant is likely 10^{10} s^{-1}.[17,18,19,20] In contrast, the oxy-substituted α-cyclopropylcarbinyl cation **3a** derived from aldehyde **2a** is not expected to undergo ring-opening (Scheme 1) since the acid-catalyzed removal of an acetal protecting group from the parent phenyl cyclopropyl aldehyde is known to occur without the formation of any ring-opened products.[21] Thus, aldehyde **2a** can be used to discriminate between the formation of oxy-substituted cyclopropylcarbinyl radicals and cations (Scheme 1).
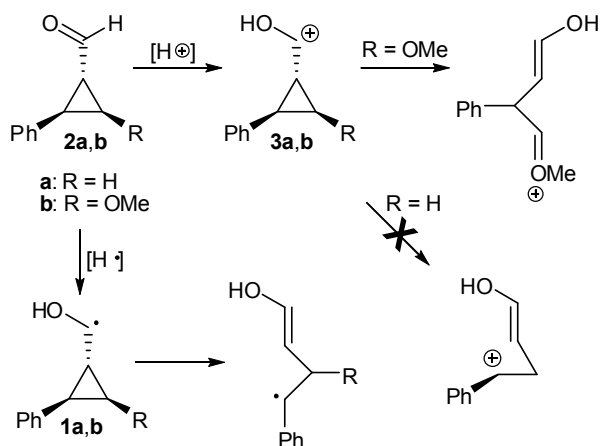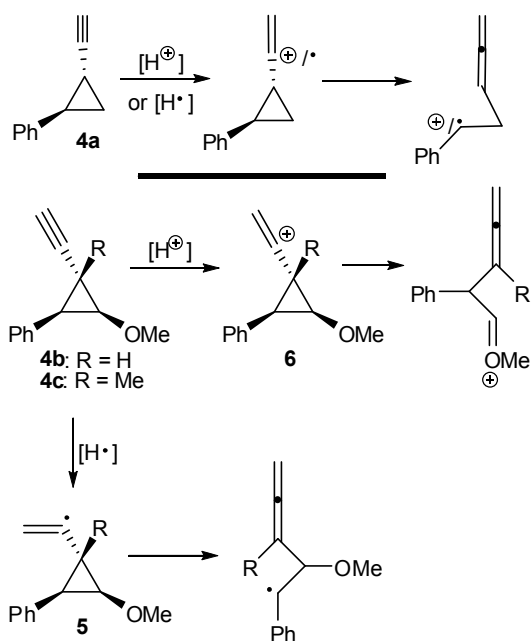
Scheme 1 Reactivity of cyclopropyl aldehydes

The reactivity of aldehyde **2b**, under both radical and cationic conditions, provides further evidence for the discrimination between radicals and cations formed at the cyclopropylcarbinyl position.[22] As with aldehyde **2a**, the formation of cyclopropylcarbinyl radical **1b** leads to ring-opening rearrangement toward the phenyl substituent; whereas formation of the cyclopropylcarbinyl cation **3b** causes ring-opening rearrangement to occur toward the methoxy substituent (which is not present in **2a**). The rate constant for this cationic ring opening rearrangement will likely be less than that observed for the corresponding radical[15b] since cyclopropylcarbinyl cation **3b** is stabilized by the α oxy-substituent.

A series of cyclopropyl alkynes, **4a-c,** has also been developed for use as mechanistic probes (Scheme 2).[23,24] The α-cyclopropylvinyl radical **5**, derived from alkyne **4b** or **c**, opens rapidly and regioselectively towards the phenyl substituent yielding a benzyl radical. In contrast, the α-cyclopropylvinyl cation **6**, derived from alkyne **4b** or **c**, rearranges selectively towards the methoxy substituent (Scheme 2). Cyclopropyl alkyne **4a** does not contain a methoxy substituent and, as such, ring-opening rearrangement toward the phenyl substituent is observed when either a radical or a cation is generated at the α-cyclopropylvinyl position (Scheme 2).[23] Thus, alkyne

4a is able to detect the formation of a radical/cationic intermediate; however, there will be no structural differentiation observed in the products. The analogous anion (as modeled by the vinyllithium derivative of **4a**) is stable towards ring opening.[23] The rate constants for rearrangement of the α-cyclopropylvinyl cations derived from alkynes **4a-c** are estimated to be 10^{10}-10^{12} s^{-1},[23] and the rate constant for rearrangement of the α-cyclopropyl vinyl radical derived from **4a** is (1.6 ± 0.2) x 10^{10} s^{-1}.[24] Thus, alkynes **4a-c** can be used to discriminate between the formation of vinyl-substituted cyclopropylcarbinyl radicals and cations (Scheme 2).

Scheme 2 Reactivity of cyclopropyl alkynes

3. Substrates

Much of the experimental studies on the mechanism of the addition of carbonyl compounds and alkynes have utilized the following prototypical substrates: $Mes_2Si=SiMes_2$

(7),[25] (Me$_2$t-BuSi)$_2$Si=Si(SiMe$_2$t-Bu)$_2$ (**8**),[26] Mes$_2$Ge=SiMes$_2$ (**9**),[27] Mes$_2$Ge=GeMes$_2$ (**10**),[28]

Mes$_2$M=CHCH$_2$t-Bu, where M = Si (**11**)[29] and M = Ge (**12**),[30] (Me$_3$Si)$_2$Si=C(OSiMe$_3$)R, where

R = t-Bu (**13a**)[31a] or R = 1-Ad (**13b**),[31b] and Mes$_2$Ge=CR$_2$, **14**, where CR$_2$ = fluorenylidene.[32]

Although compounds **7-12** and **14** can be considered to be naturally polarized and representative

examples of each species, the Si=C bond of the Brook silenes **13a,b** is relatively non-polar due

to the electronic nature of the substituents.[33] The siloxy group on carbon and the two silyl

groups on silicon render Brook silenes the least polar of a series of silenes with hydrogen, silyl,

alkyl, chloro and alkynyl substituents in various substitution patterns. The most polar silenes

have silyl substituents on carbon and the least polar silenes have silyl substituents on silicon as

evaluated using total Natural Bond Order polarity (i.e. difference between the total charge on

silicon minus the total charge on carbon).[33a]

With substrates **7-14**, a number of useful comparisons can be made. For example, a

comparison can be made between the reactivity of different ditetrelenes with the same

substituents by examining the chemistry of the tetramesityl-substituted disilene **7**, germasilene **9**

and digermene **10**. On the other hand, the influence of substituents (aryl versus silyl) on the

chemistry of a given ditetrelene (a disilene) can be made by comparing the chemistry of **7** versus

8. Likewise, a comparison can be made between the reactivity of different tetrelenes with the

same substituents by examining the chemistry of silene **11** and germene **12** and the influence of

substituents on the reactivity of a tetrelene can be made by comparing the reactivity of the

Brook silenes **13a,b** to the naturally polarized silene **11**.

4. Mechanism of carbonyl addition to (di)tetrelenes

4.1 Early mechanistic work and computational studies

One of the most extensively studied reactions of ditetrelenes is the addition of carbonyl compounds to yield ditetreloxetanes (Scheme 3).[10,11,34] The addition of formaldehyde to the parent disilene, germasilene and digermene ($H_2Si=SiH_2$, $H_2Ge=SiH_2$, and $H_2Ge=GeH_2$, respectively) was examined using density functional and multiconfigurational perturbation theory in an effort to elucidate the energetically most favourable reaction pathway.[35] In the addition of formaldehyde to disilene and germasilene, several pathways to the ditetreloxetane were located, involving either a zwitterionic or biradical intermediate; the biradical pathway was the most energetically favourable in each case. Conversely, only one pathway, stepwise via a zwitterionic intermediate, was located for the addition of formaldehyde to digermene.[35]
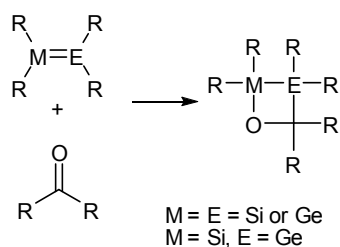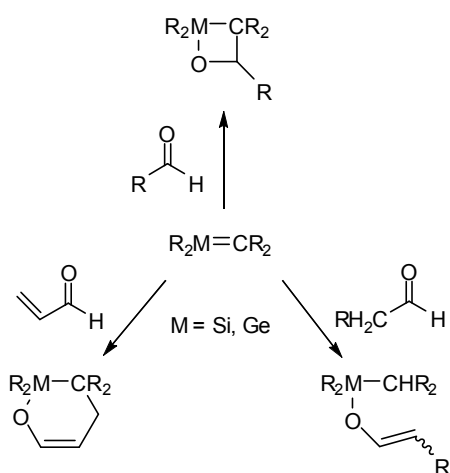

Scheme 3 Generalized scheme for the addition of carbonyl compounds to ditetrelenes. The label, R, reflects the variety of substituents which have been utilized, which may be the same or different.

As with ditetrelenes, the addition of carbonyl compounds to silenes and germenes is one of the most well-studied reactions of these species.[9,11,36,37] In silene chemistry, the initially formed siloxetane typically converts to an equivalent of an alkene and a silanone; the silanone then oligomerizes to a cyclosiloxane (Scheme 4).[38] This type of addition reaction is known for both naturally polarized and non-polar silenes. The formation of an ene-addition product from the addition of an enolizable carbonyl compound and the formation of [4+2]-type adducts from the addition of an unsaturated carbonyl compound are also possible (Scheme 5). Similar behaviour

has been reported for germenes although cleavage of an initially formed germoxetane is not common[7,37] and, in one case, the opposite regiochemistry for the addition was noted.[37a]
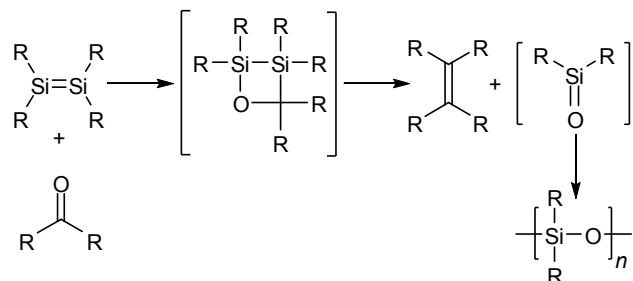
Scheme 4 Generalized scheme for the addition of carbonyl compounds to silenes. The label, R, reflects the variety of substituents which have been utilized, which may be the same or different.

Scheme 5 Generalized scheme depicting reaction types for the addition of carbonyl compounds to silenes and germenes. The label, R, reflects the variety of substituents which have been utilized, which may be the same or different.

The mechanism of siloxetane formation has been proposed to be a concerted process or stepwise via either a zwitterionic or biradical intermediate; however, in some of these cases, little or no evidence was provided in support of the proposals. A few early reports, however, did provide some indirect evidence for the intermediacy of zwitterions (donor-acceptor complexes)

during the addition of carbonyl compounds to silenes. For example, Wiberg proposed the initial

formation of adducts **15** during the cycloaddition between benzophenone and the silenes

$R_2Si=C(SiMe_3)(SiMeR^1_2)$, where R = Me and R^1 = t-Bu or R = Ph and R^1 = Me.[39] In support of

this hypothesis, the molecular structures of two related species were characterized by X-ray

crystallography: the THF complex of silene, **16**,[40] and the benzophenone adduct of a silanimine,
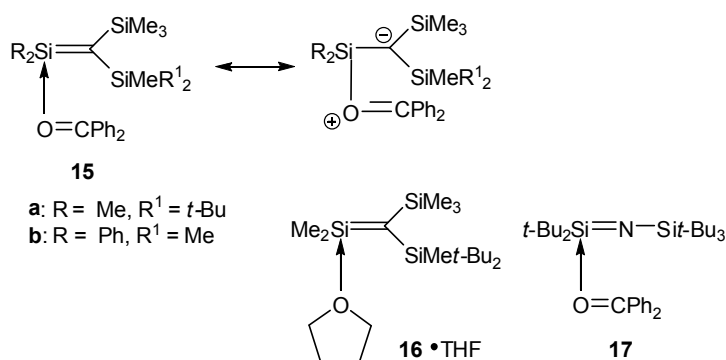
17.[41]

Chart 1

Additional evidence for the formation of a zwitterionic intermediate was provided by Leigh

and co-workers by examination of the kinetics of the addition of enolizable ketones to

substituted diarylsilenes.[42] The rate constant for the addition reaction was observed to increase

when electron-withdrawing aryl substituents were present on the silenic silicon centre and when

electron-donating substituents were on the carbonyl carbon. The proposed mechanism involved

the initial and reversible formation of a zwitterionic intermediate followed by rate-limiting

proton transfer (Scheme 6). Similar results were observed during the addition of acetone to the

related neopentyl silene, $Ph_2Si=CH(CH_2t$-Bu).[43]
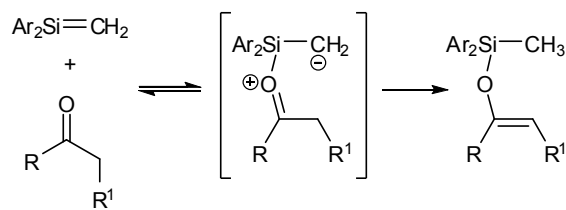
Scheme 6 Addition of enolizable ketones to diarylsilenes

Several computational studies of the mechanism of aldehyde/ketone addition to both silenes and germenes have been reported. Mosey *et al.* examined the addition of formaldehyde to silene ($H_2Si=CH_2$) and germene ($H_2Ge=CH_2$), using density functional and multiconfigurational perturbation theory.[35] Three reaction pathways were located for the silene: concerted, zwitterionic and biradical; however, the concerted pathway was considered to be too high in energy to be feasible ($\Delta G = 115$ kJ/mol). Comparison of the relative energies of the reactions passing through either a zwitterionic or biradical intermediate indicated that the zwitterionic pathway was slightly energetically more favourable; however, the authors concluded that the exact pathway followed will be significantly influenced by the nature of the substituents on the silene and/or the polarity of the reaction solvent. Accordingly, in a computational study by Su and co-workers of the addition of acetone to a 1,1-bis(silyl)silene, (adamantylidene)C=Si(SiMe$_3$)(SiMe$_2$*t*-Bu), the reaction follows what appears to be a bimolecular, concerted, [$2\pi_s + 2\pi_s$] pericyclic pathway.[44] The authors noted that the considerable polarity of the C=Si double bond in the (adamantylidene)C=Si(SiMe$_3$)(SiMe$_2$*t*-Bu) derivative relieves the symmetry restriction of the Woodward-Hoffman rules.

In contrast to the chemistry of silene, only concerted [2+2] cycloaddition pathways were located for the addition of formaldehyde to the parent germene[35] and the addition of acetone to the substituted germene, (adamantylidene)C=Ge(SiMe$_3$)(SiMe$_2$*t*-Bu).[44] The addition of 1,4-

benzoquinone to $H_2Ge=CH_2$[37b] and the addition of crotonaldehyde or methyl vinyl ketone to

$HP=C=GeH_2$[37c] have also been examined using density functional theory. In each case, the one-

step cycloaddition reaction of the carbonyl functionality to the Ge=C bond was described as

being asynchronous, with Ge-O bond formation preceding C-C bond formation. The [4+2] and

ene reaction pathways for the reaction between unsaturated carbonyl compounds and the

phosphagermaallene were also examined and shown to proceed by one-step reactions. The [4+2]

cycloaddition followed the standard suprafacial-suprafacial pericyclic approach. The exact

pathway followed ([2+2], [4+2] or ene; Scheme 5) depends on the α,β-unsaturated carbonyl

compound and the steric demands of the unsaturated main group substrate.[37c] Interestingly, the

cycloaddition of methyl vinyl ketone or acrolein to the Brook-type germenes

$((Me_3Si)_2Ge=C(OSiMe_3)R$, R=1-Ad or t-Bu) produced the opposite [4+2] regioisomer where

the oxygen of the carbonyl compound becomes bonded to the germenic carbon rather than to the

germanium.[37a] A detailed computational study of the addition of acrolein to

$(Me_3Si)_2Ge=C(OSiMe_3)t$-Bu (and a simplified model) was carried out: the energetics and

geometries of the transition states and local minima along both biradical and concerted reaction

pathways were examined for both regiochemistries of the addition. The authors concluded that

the most likely (lowest energy) reaction pathway takes place between the germene and the s-

trans conformer of acrolein and involves a biradical intermediate with a Ge-C bond between the

two π-bonded substrates. The observed regioselectivity is a consequence of the relative barriers

from the biradical intermediates to the next species along the reaction pathway: with initial Ge-

C bond formation, the barrier to formation of the product is approximately 58 kJ/mol whereas,

with initial Ge-O bond formation, the barrier (to another conformation of the biradical) is

approximately 74 kJ/mol.

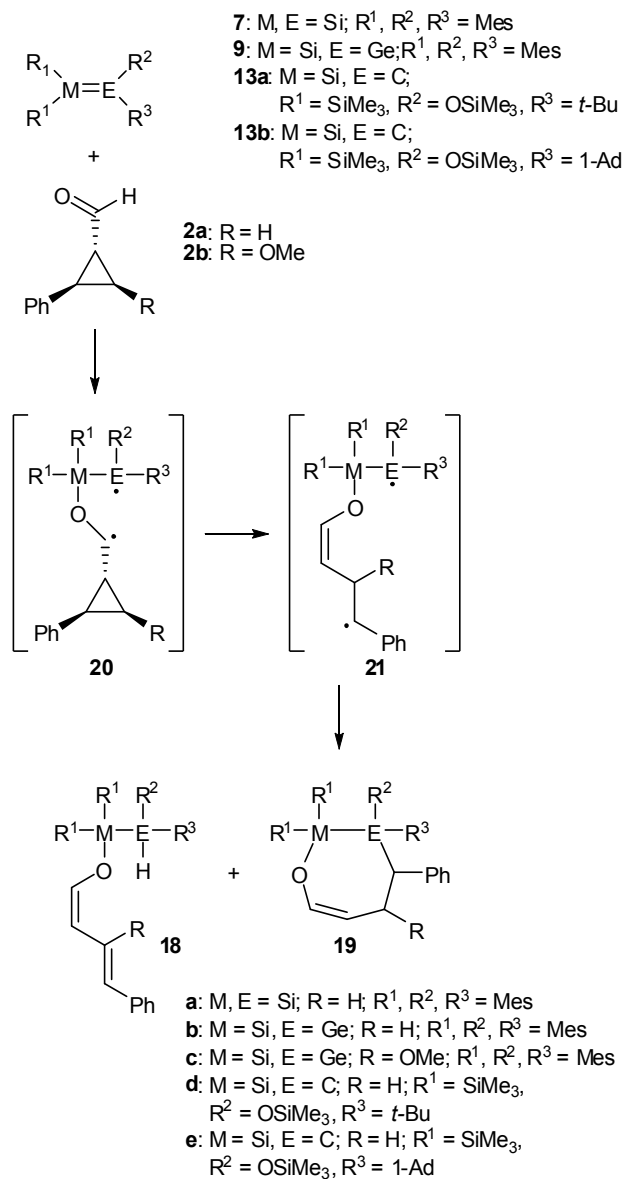## 4.2 Experimental studies utilizing mechanistic probes

The addition of carbonyl compounds to tetramesityldisilene (**7**),[45] -germasilene (**9**),[46] and -digermene (**10**)[28c] have all been reported; in each case a ditetreloxetane is formed (Scheme 7). Similarly, the addition of carbonyl compounds to Brook silenes[47] and the naturally polarized silene, $Mes_2Si=CH(CH_2t\text{-}Bu)$ (**11**),[29b] have been examined and, typically, siloxetanes are the major products, although in some cases ene-type addition products are also formed. The addition of a number of aldehydes and ketones, including diketones and quinones, to germene **14** has been reported and is more varied with all modes of reactivity ([2+2], [4+2] and ene; Scheme 5) being observed depending on the structure of the carbonyl compound.[37,48]

$Mes_2M=EMes_2$

7: M, E = Si
8: M = Si, E = Ge
9: M, E = Ge
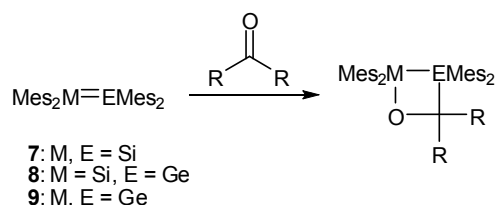
Scheme 7 Generalized scheme for the addition of carbonyl compounds to ditetrelenes. The label, R, reflects the variety of substituents which have been utilized, which may be the same or different.

The mechanism of aldehyde addition to several (di)tetrelenes has been examined, including $Mes_2Si=SiMes_2$ (**7**),[19,22] $Mes_2Ge=SiMes_2$ (**9**),[19,22] $Mes_2Ge=GeMes_2$ (**10**),[49] silenes $Mes_2Si=CH(CH_2t\text{-}Bu)$ (**11**)[50] and $(Me_3Si)_2Si=C(R)(OSiMe_3)$ (**13a**: R = t-Bu; **13b**: R = 1-Ad),[50] and germene $Mes_2Ge=CR_2$ (**14**),[51] using probe methodology. The addition of aldehydes **2a,b** to $Mes_2Si=SiMes_2$ (**7**), $Mes_2Ge=SiMes_2$ (**9**) and $(Me_3Si)_2Si=C(R)(OSiMe_3)$ (**13a**: R = t-Bu; **13b**: R = 1-Ad) led to the formation of structurally similar products: a *cis,trans*-diene **18** and/or an oxacycloheptene **19**, as generalized in Scheme 8. As is evident from the structure of the products, the cyclopropyl group has undergone ring-opening. The exact location of the phenyl

group in the products, adjacent to the former carbon of the doubly-bonded species or at the terminus of the diene, reveals the nature of the intermediate formed during the reaction, a biradical. In all cases, the observed products can be rationalized as follows: addition of aldehyde **2a,b** to the (di)tetrelene to form a 1,4-biradical intermediate **20**, which undergoes a cyclopropyl ring-opening rearrangement toward the phenyl substituent to yield the 1,7-biradical **21**. Disproportionation or cyclization of the 1,7-biradical intermediate **21** leads to the observed products **18** and **19**, respectively.

7: M, E = Si; R^1, R^2, R^3 = Mes
9: M = Si, E = Ge;R^1, R^2, R^3 = Mes
13a: M = Si, E = C;
       R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = *t*-Bu
13b: M = Si, E = C;
       R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = 1-Ad

2a: R = H
2b: R = OMe

20

21

18

19

a: M, E = Si; R = H; R^1, R^2, R^3 = Mes
b: M = Si, E = Ge; R = H; R^1, R^2, R^3 = Mes
c: M = Si, E = Ge; R = OMe; R^1, R^2, R^3 = Mes
d: M = Si, E = C; R = H; R^1 = SiMe$_3$,
     R^2 = OSiMe$_3$, R^3 = *t*-Bu
e: M = Si, E = C; R = H; R^1 = SiMe$_3$,
     R^2 = OSiMe$_3$, R^3 = 1-Ad

Scheme 8 Addition of cyclopropyl aldehydes to (di)tetrelenes

In the reactions of the Brook silenes **13a,b**, additional products were also formed: siloxetanes **22** and acylsilanes **23**. It is most reasonable to propose that siloxetanes **22** are formed by the competitive cyclization of the same 1,4-biradical intermediate **20**, while

acylsilanes **23** likely arise from the initial addition of the carbonyl carbon (rather than oxygen) to the silenic silicon to form a biradical intermediate followed by a [1,3]-hydrogen shift.
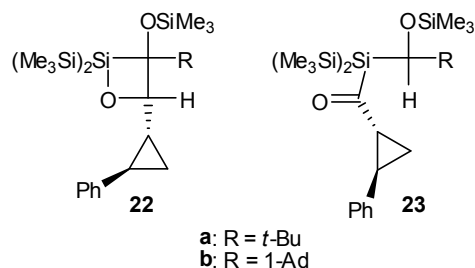

a: R = *t*-Bu
b: R = 1-Ad

Chart 2

The above results demonstrate that the mechanism of aldehyde addition to $Mes_2Si=SiMes_2$ (**7**) and $Mes_2Ge=SiMes_2$ (**9**) involves the formation of a biradical intermediate, and are consistent with the previously reported computational study,[35] which identified a biradical mechanism as the lowest energy pathway for the addition of formaldehyde to $H_2Si=SiH_2$ and $H_2Si=GeH_2$.

On the other hand, the computational investigation into the addition of formaldehyde to $H_2Si=CH_2$ revealed that the biradical and zwitterionic pathways were close in energies,[35] and thus, the nature of the silene/solvent will likely have a significant influence experimentally. In the case of the Brook silenes **13a,b**, which were found to follow a biradical pathway, the substituents render the Si=C far less polarized than in a prototypical silene, and thus, a biradical pathway seems reasonable. Interestingly, the addition of acrolein to a Brook germene was also found to follow a biradical pathway, consistent with the reactivity of the Brook silene.[37a]

In contrast to the addition of cyclopropyl aldehydes **2** to disilene **7**, germasilene **9** and the Brook silenes **13a,b**, the reactivity of $Mes_2Ge=GeMes_2$ (**10**),[49] $Mes_2Si=CHCH_2t$-Bu (**11**),[50] and $Mes_2Ge=CR_2$ (**14**)[51] toward aldehydes **2a,b** was markedly different. In these cases, a

17

(di)tetreloxetane **24** was formed as generalized in Scheme 9. No products where the cyclopropyl ring had opened were observed. Given the anticipated large rate constant for rearrangement of the oxygen substituted cyclopropylcarbinyl radical,[17-20] which is expected to be of sufficient magnitude to compete effectively with ring closure, the reactions do not proceed via a biradical intermediate since no ring-opened products were formed. Thus, the possibilities of concerted reactions or pathways involving zwitterionic intermediates were considered for digermene **10**, germene **14** and silene **11**.
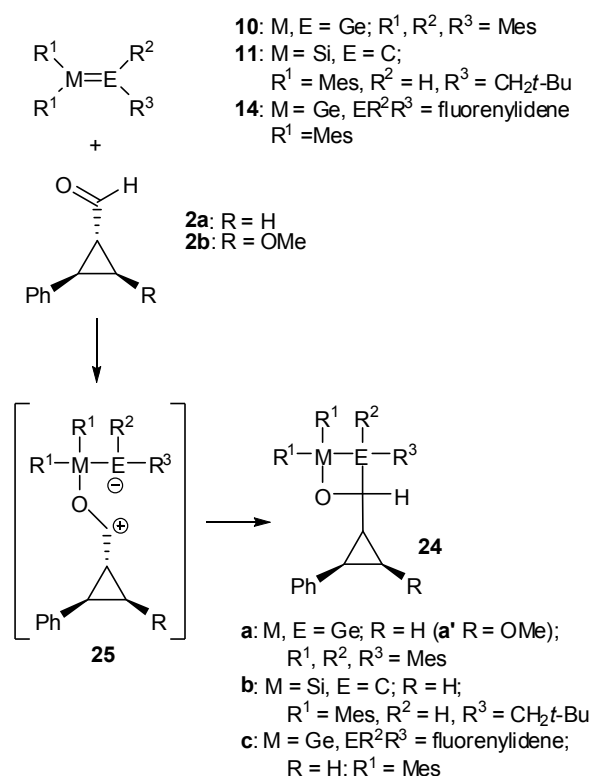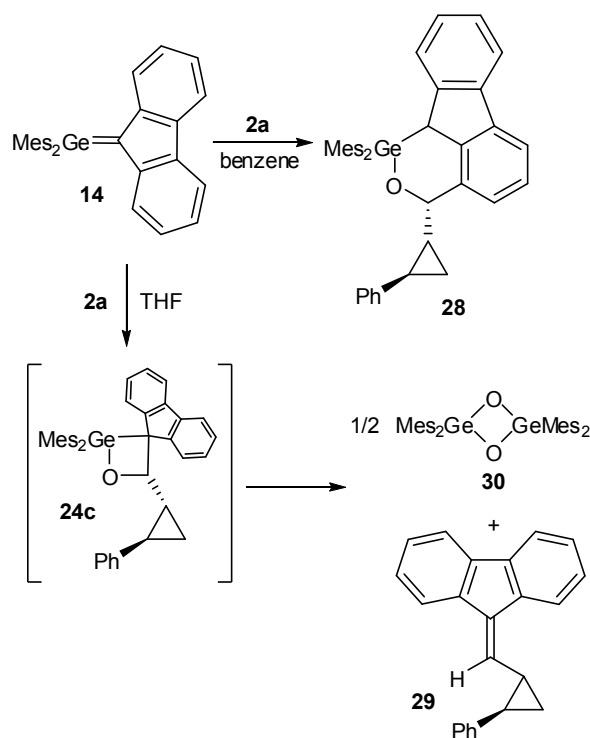

Scheme 9 Addition of cyclopropyl aldehydes to (di)tetrelenes

The experimental results using the aldehyde probe for both digermene **10** and germene **14** are consistent with the computational studies of the parent systems where no reaction pathways involving a radical intermediate were located.[35] Given that a pathway involving zwitterionic

intermediates was the *only* reaction pathway found in the addition of formaldehyde to the parent

digermene, it is most reasonable to propose a stepwise mechanism through a zwitterionic

intermediate for the addition of **2a,b** to digermene **10**.[49]

In the reaction of germene **14** (Scheme 9), germoxetane **24c** was not actually isolated as it

apparently undergoes a facile cycloreversion in the opposite manner, behaviour reminiscent of

the chemistry of siloxetanes (Schemes 4 and 10).[51] The lack of products from cyclopropyl ring-

opening, along with the results of the computational studies, which indicate the absence of any

intermediates,[35,37b,c,] suggest a concerted [2+2] reaction between germene **14** and aldehyde **2a** to

give germoxetane **24c** (Schemes 9 and 10). Notably, a dramatic solvent effect was observed on

the product distribution in this reaction.[51] In THF, the predominant products were **29** and **30**,

derived from **24c**, whereas in benzene, the addition of **2a** to germene **14** gave **28** almost

exclusively (Scheme 10). In the original publication, the two different types of products (those

derived from **24c** or **28**) were initially proposed to be formed from two different pathways.[51]

Given that the cyclopropyl ring remains intact in oxygermin **28**, oxygermin **28** was proposed to

be formed via a concerted [4+2] cycloaddition between germene **14** and aldehyde **2a** followed

by a H-transfer. On the other hand, nucleophilic addition of an initially formed zwitterionic

complex between germene **14** and a donor (where the most likely donors were THF or fluoride

ion) to **2a** was proposed to lead to germoxetane **24c**.[51] However, in a subsequent study, Hall and

Zhou examined the addition of cyclopropyl aldehyde **2a** to germene **14** using density functional

theory with the polarizable continuum model.[12c] They demonstrated that THF *does not* form a

complex with germene **14** and concluded that the change in reactivity observed experimentally

is a consequence of the differential lowering of the energies of key transition states and

intermediates with large dipole moments along the reaction pathway leading to **24c** compared to

that leading to **28** in THF. The cycloaddition step itself was found to be concerted. In light of

these results, it appears that the mechanisms for both the formation of the [2+2] and the [4+2]

cycloaddition of carbonyl compounds with germenes follow concerted reaction pathways.

Scheme 10 Addition of cyclopropyl aldehyde **2a** to germene **14**

As mentioned previously, the computational investigation into the addition of formaldehyde

to $H_2Si=CH_2$ revealed that a concerted pathway was unlikely and that the biradical and

zwitterionic pathways were close in energies, and thus, the nature of the silene/solvent will have

a significant influence on the operational mechanism.[35] Changing the silene from the Brook

silenes **13a,b** to the naturally polarized silene **11** evidently alters the cycloaddition pathway

from biradical to zwitterionic. The formation of a zwitterionic intermediate during the addition

of aldehyde **2a** to silene **11** is also consistent with previous experimental work where the initial

formation of a donor-acceptor adduct between a silene and a carbonyl compound was proposed.[39-42] Ester **26** and vinylsilane **27** were also produced in reaction of aldehyde **2a** with **11**. Ester **26** is a dimer of aldehyde **2a**, whose formation can be explained by the addition of a second equivalent of the aldehyde to an intermediate zwitterion (**25**; which acts as a Lewis acid) in a Tishchenko-type reaction.[52] This reactivity is also consistent with the formation of a zwitterionic intermediate, rather than a concerted mechanism, during the course of the addition of aldehyde **2a** to silene **11**. The formation of vinylsilane **27** does not give much insight into its mechanism of formation other than a radical is not formed at the cyclopropyl carbinyl position along the reaction pathway.
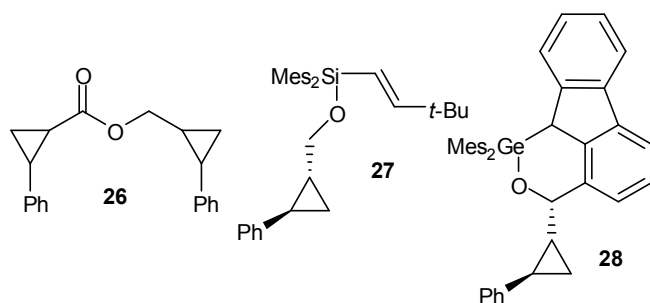
Chart 3

4.3 Summary: Mechanism of the addition of carbonyl compounds to (di)tetrelenes

Table 1 summarizes the nature of the most likely reaction pathways for the addition of carbonyl compounds to (di)tetrelenes on the basis of the currently available experimental and computational evidence.

Table 1: Summary of the mechanistic pathways determined for the addition of carbonyl compounds to (di)tetrelenes

Entry	(Di)tetrelene (R = H,	Mechanistic pathway

	alkyl or aryl)	
1	$R_2Si=SiR_2$	[2+2]: biradical
2	$R_2Si=GeR_2$	[2+2]: biradical
3	$R_2Ge=GeR_2$	[2+2]: zwitterionic
4	$(R_3Si)_2Si=C(OSiR_3)R$	[2+2]: biradical
5	$R_2Si=CR_2$	[2+2]: zwitterionic
6	$(R_3Si)_2Ge=C(OSiR_3)R$	[2+2]: biradical
7	$R_2Ge=CR_2$	[2+2]: concerted [4+2]: concerted

A number of interesting comparisons can be made. The reactivity of two types of silenes, one in which the Si=C is naturally polarized (Entry 5, i.e. **11**) and the other where the Si=C is relatively non-polar (Entry 4, i.e. **13a,b**), towards carbonyl compounds has been examined and a significant difference was observed. The more polar silene was found to react with an aldehyde by way of a zwitterionic intermediate (Entry 5) whereas the non-polar silene reacted with an aldehyde forming an intermediate biradical (Entry 4). Consequently and not surprisingly, it is evident that the polarity of the Si=C of the silene, as influenced by its substituents, is a significant factor in pathway selectivity. When the silene is polarized, the dipoles of the Si=C and the O=C bonds align with the π systems perpendicular allowing the non-bonding electrons of the carbonyl group to interact with the π^* orbital at the silicon of the silene.[35] In the absence of a significant dipole on the silene, the two molecules approach one another with a much larger dihedral angle (C-O-Si-C of ~90º) leading to the diradical intermediate.[35] Similarly, the substituents play a significant role when comparing the reactivity of a Brook-type germene (Entry 6, $(Me_3Si)_2Ge=C(OSiMe_3)t$-Bu) and a naturally polarized germene (Entry 7, i.e. **14**);

however, in this case, the reaction mechanism changes from biradical to concerted. The difference in pathway selectivity between naturally polarized silenes (Entry 5) and germenes (Entry 7) with carbonyl compounds (zwitterionic versus concerted, respectively) is also notable. On the basis of the relative electronegativities of silicon versus germanium, silenes are more polar than the analogous germenes. The relative polarities of two tetrelenes has also been confirmed using total polarity calculations on two comparable derivatives.[44] Evidently, although the alignment of the dipoles may also occur between the naturally polarized germene and the carbonyl compound, the decreased thermodynamic stability of the Ge-O bond does not favour the formation of an intermediate and a pericyclic reaction occurs which may be synchronous or asynchronous depending on the exact species involved.[35,37b,44]

The variation in the reactivity of disilenes (Entry 1) and germasilenes (Entry 2), which both involve a biradical intermediate, and digermenes (Entry 3) which involves the intermediacy of a zwitterion is also striking. The change in mechanism can also be explained on the basis of the relative strengths of the Si-O (492 kJ/mol) and Ge-O (410 kJ/mol) bonds.[35] A careful examination of the structures of the intermediates reveals that the M-O bond is fully formed in the biradical intermediate but not in the zwitterion. As a consequence, the energy of the biradical intermediate is differentially lowered when a Si-O bond is formed because of the greater strength of that bond in comparison to the Ge-O bond, and thus, the pathway involving the biradical intermediate becomes energetically more favourable.

5. Mechanism of Alkyne Addition to (Di)tetrelenes

5.1 Early mechanistic work and computational studies

The addition of alkynes to ditetrelenes to produce ditetrelacyclobutenes is a well-studied reaction (Scheme 11).[10,11,53] Two early mechanistic studies of the addition of alkynes to disilenes have been reported; however, the findings are contradictory. The first study, by Sakurai and co-workers, examined the addition of diphenylacetylene to *trans*- or *cis*-1,2-dimethyl-1,2-diphenyldisilene to produce a mixture of diastereomeric disilacyclobutenes, which upon stereoselective oxidation using oxygen yielded 1-oxa-2,5-disilacyclopentenes (Scheme 12).[54] Scrambling of the stereochemistry about the Si-Si bond was observed providing evidence for the formation of an intermediate. The authors proposed the formation of a biradical; however, no evidence for the nature of the intermediate was provided.
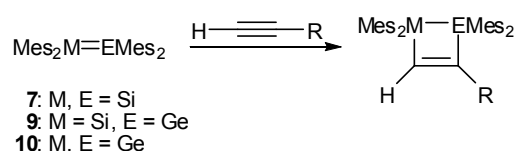
Scheme 11 Addition of alkynes to ditetrelenes
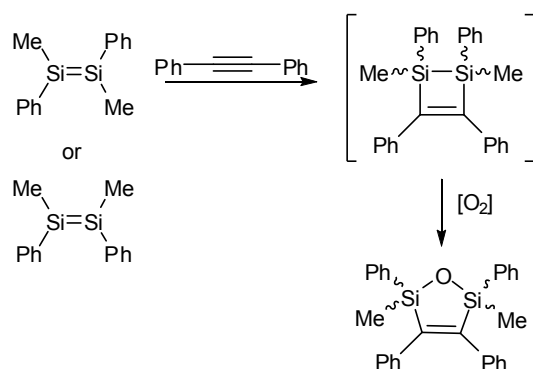
Scheme 12 Addition of diphenylacetylene to cis/trans isomers of a disilene

In the second study a variety of alkynes were added to tetramesityldisilene (**7**) producing the corresponding disilacyclobutenes.[55] Only terminal alkynes with functional groups such as

carbomethoxy-, phenyl-, trimethylsilyl- or ethoxyacetylene added to the disilene; no reaction

was observed with terminal alkynes with hydrocarbon substituents such as 1-hexyne and

propyne, or symmetrically-substituted alkynes such as acetylene, diphenylacetylene, and

dimethyl acetylenedicarboxylate as well as with phenyl(trimethylsilyl)acetylene.[55a] A

scrambling of the stereochemistry of the cycloadduct derived from the addition of

phenylacetylene and ethoxyacetylene to *trans*-1,2-di-*t*-butyl-1,2-dimesityldisilene was observed,

as in Sakurai's example; however, West *et al.* concluded that the intermediate formed was a

zwitterion.[55b] This conclusion was reached on the basis of the observation that

tetramesityldisilene only reacted with terminal alkynes that may behave as a nucleophile. Both

Sakurai and West's studies establish that the cycloaddition of an alkyne to a disilene is stepwise;

however, no evidence for the nature of the intermediate was presented in either case.

Neumann *et al.* examined the reactivity of $Me_2Ge=GeMe_2$, via the thermolysis of either a

germanorbornadiene or a digermabicyclooctadiene, towards alkynes.[56] The digermene

($Me_2Ge=GeMe_2$) was only observed to react with an electron poor alkyne, hexafluoro-2-butyne,

and thus, a zwitterionic intermediate was proposed, although no evidence to support this claim

was provided.

Many examples of the cycloaddition between alkynes and silenes to give silacyclobutenes

have been reported.[9,53] The addition of alkynes to Brook silenes has been extensively studied by

both Brook *et al.*[31,57] and Ishikawa *et al.*;[58] however, only a few studies aimed at understanding

the mechanism of the reaction were reported. The stereoselectivity of the cycloaddition of

phenylacetylene and trimethylsilylacetylene to *E/Z* mixtures of the Brook silenes

$(Me_3Si)(R)Si=C(1-Ad)(OSiMe_3)$,   R   =   Mes   (2,4,6-trimethylphenyl)   or   Tip   (2,4,6-

triisopropylphenyl), was examined.[57] In each case, a mixture of isomeric silacyclobutenes was

produced in a ratio consistent with the *E/Z* ratio of the starting silene mixture. It was assumed that if an intermediate biradical or zwitterion were formed, bond rotation about the former silenic Si-C bond would lead to a variance in the ratio of the isolated products; thus, a concerted pathway for the addition of the alkynes to the silenes was proposed.

Ishikawa and co-workers extensively studied the addition of alkynes to Brook silenes and the formation of biradical intermediates was often implicated.[58] They examined the addition of propyne to the parent Brook silene, $(H_3Si)_2Si=C(CH_3)(OSiH_3)$[58e] and the addition of silyl-substituted alkynes to $(Me_3Si)_2Si=C(t\text{-}Bu)(OSiMe_3)$[58m] computationally using density functional theory at the B3LYP/6-31G* level. In the earlier study,[58e] the authors concluded that a biradical intermediate is formed, although the intermediate itself was not located on the potential energy surface; however, in the latter study,[58m] the authors indeed located a biradical intermediate along the lowest energy reaction pathway.

In contrast, the addition of alkynes to naturally polarized silenes has received much less attention in comparison with the relatively non-polar Brook silenes. Although several examples of alkyne addition to naturally polarized silenes have been reported, there are few studies examining the mechanism of the reaction. There is very little reported on the addition of alkynes to germenes.

The addition of acetylene to the parent silene $(H_2Si=CH_2)$ and germene $(H_2Ge=CH_2)$ to give tetrelacyclobutenes has been examined computationally.[59] In both cases, the potential energy surfaces for the addition of the alkyne are relatively flat suggesting that the effect of the substituents on the alkyne and the tetrelene and the nature of the solvent will influence the exact reaction pathway followed. For both silene and germene, in addition to a concerted reaction

pathway, two pathways involving the formation of biradical intermediates were located in the gas-phase (either from initial M-C or C-C bond formation) as well as a pathway involving the formation of a zwitterionic intermediate (with initial C-C bond formation and a positive charge located on the silicon/germanium) (Scheme 13). The one-step process did not follow a standard pericyclic cyclization pathway rather acetylene was found to initially coordinate to the metalloid and then move slowly toward the tetrelenic carbon to facilitate ring formation. For both silene and germene, the biradical pathways were the lowest energy pathways. For silene, the pathway involving a biradical intermediate with initial Si-C bond formation was slightly favoured whereas the pathway with initial C-C bond formation was favoured in the germanium case (Scheme 13). Similarly, Apeloig and co-workers located a biradical intermediate in the cycloaddition of acetylene to 1,1-dichlorosilene although no details were given.[60]
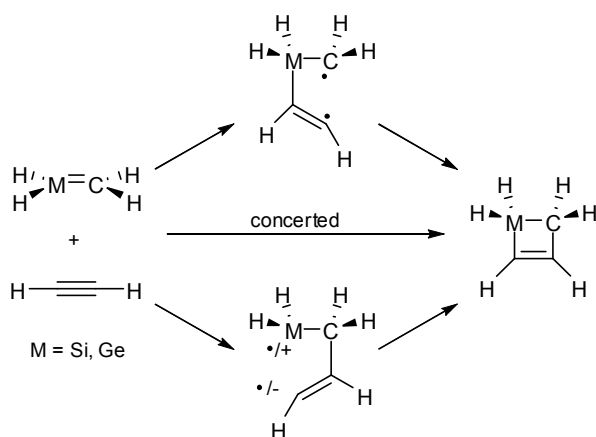
Scheme 13 Possible mechanisms for the addition of alkynes to tetrelenes to form tetrelacyclobutenes

5.2 Experimental studies using mechanistic probes

Cyclopropyl alkynes **4** have been employed as mechanistic probes with two disilenes, $R_2Si=SiR_2$ where R = Mes (**7**)[61] or R= $SiMe_2t$-Bu (**8**),[62] digermene $Mes_2Ge=GeMes_2$ (**10**),[63] silene $Mes_2Si=CHCH_2t$-Bu (**11**),[64] two germenes, $Mes_2Ge=CHCH_2t$-Bu (**12**)[65] and

dimesitylfluorenylidenegermane (**14**),[66] and two Brook silenes $(Me_3Si)_2Si=C(R)(OSiMe_3)$ (**13a,b**).[67,68] The addition of alkyne **4c** to the (di)tetrelenes **7**, **8**, **10**, and **13a,b** led to the formation of structurally related products as generalized in Scheme 14. Two types of products were formed: (di)tetrelacyclobutene **31** and (di)tetrelahepta-1,2-diene **32**. On the basis of the structure of the 7-membered ring allene **32**, it is evident that the cyclopropyl ring has undergone ring-opening rearrangement toward the phenyl substituent, which is consistent with the formation of a biradical intermediate. Thus, addition of alkyne **4c** to the (di)tetrelene initially forms the 1,4-biradical intermediate **33**, which upon ring-opening rearrangement yields the 1,7-biradical **34**. Cyclization of intermediates **33** and **34** leads to the products **31** and **32**, respectively.

7: M, E = Si; R^1, R^2, R^3 = Mes
8: M, E = Si; R^1, R^2, R^3 = SiMe$_2$t-Bu
10: M, E = Ge; R^1, R^2, R^3 = Mes
13a: M = Si, E = C;
      R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = t-Bu
13b: M = Si, E = C;
      R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = 1-Ad

a: M, E = Si; R^1, R^2, R^3 = Mes
b: M, E = Si; R^1, R^2, R^3 = SiMe$_2$t-Bu
c M, E = Ge; R^1, R^2, R^3 = Mes
d: M = Si, E = C;
    R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = t-Bu
e: M = Si, E = C;
    R^1 = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = 1-Ad
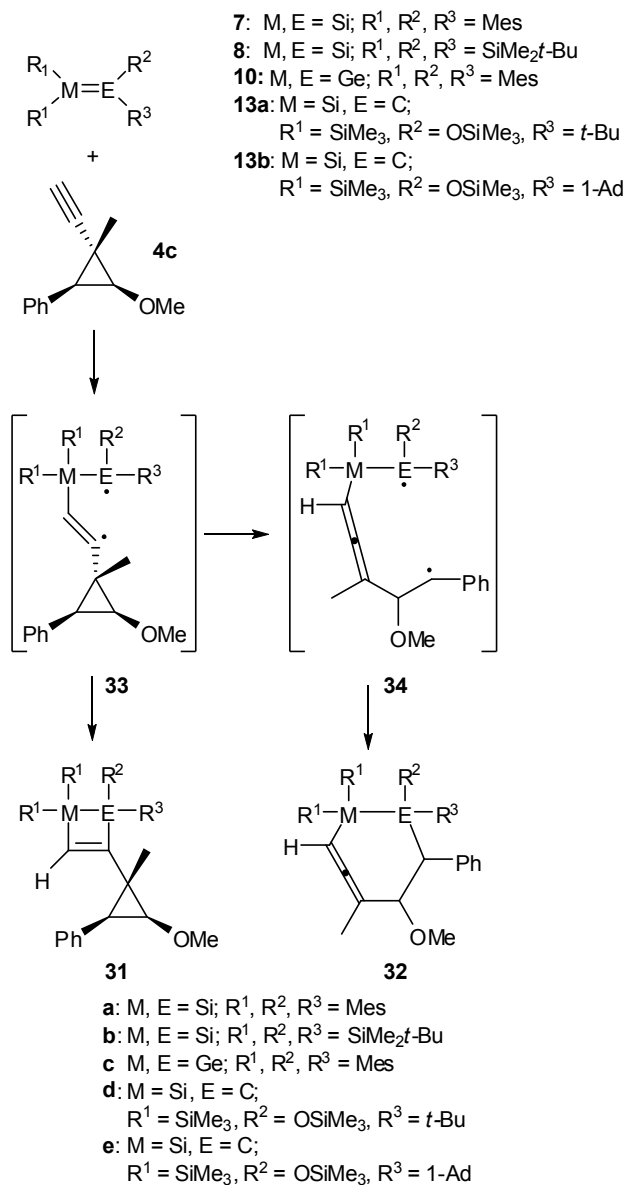
Scheme 14 Addition of cyclopropyl alkyne **4c** to (di)tetrelenes

In addition to digermacyclobutene **31c** and digermacyclohepta-1,2-diene **32c**, 1,1,2,2-tetramesitylmethoxydigermane (**35**) and digermacyclopenta-1,3-diene **36** were observed upon treatment of alkyne **4c** with digermene **10**. The production of digermacyclopenta-1,3-diene **36** was unexpected; however, given that the reaction between **4c** and **10** was performed at high

temperature (100 versus 25 °C) for a prolonged period of time (5 days versus overnight) in comparison to the reaction between **4c** and **7**,[61] it is not surprising that additional products were formed. 5-Endo-trig cyclization has been observed with internal, unactivated allenes that have nucleophiles in the homoallylic position under strong heating conditions,[69] and thus, ring-closure of biradical **34** to form a cyclopentene in not unreasonable (Scheme 15). The abstraction of hydrogen from the solvent, subsequent elimination of methanol, and oxidation of the Ge-H to a Ge-OH, would then lead to the production of **36**. The elimination of methanol provides a plausible explanation for the production of digermane **35**, which is the known methanol addition product of digermene **10**.[70]

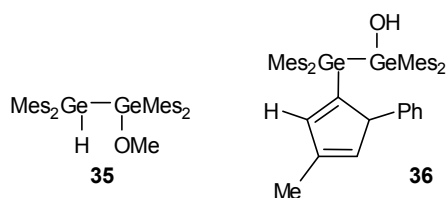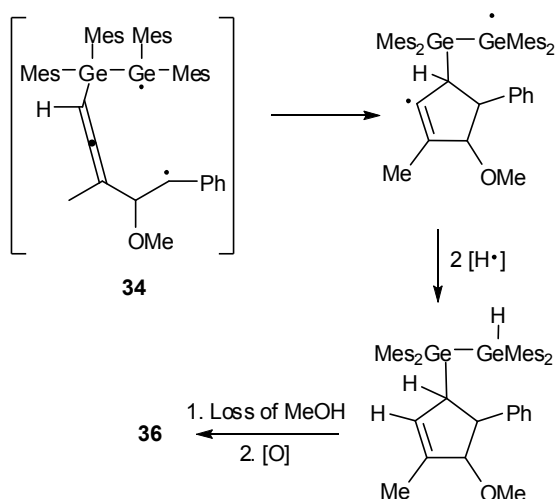Chart 4

Scheme 15 Formation of digermacyclopenta-1,3-diene **36**

The silacyclohepta-1,2-diene **32d** derived from the addition of alkyne **4c** to the Brook silene

13a is not isolated or observed since under the reaction conditions a second equivalent of silene

adds across the allene moiety to yield silacycloheptenes **37** and **38** (Scheme 16).[67] Similar

reactivity is also observed for the addition of alkyne **4c** to silene **13b**.[68] The second equivalent of

silene adds across the allene moiety with the same regiochemistry (i.e. initial formation of a Si-

C bond), the silenic silicon adds to the central allenic carbon likely because of the formation of a

stabilized allylic radical intermediate.
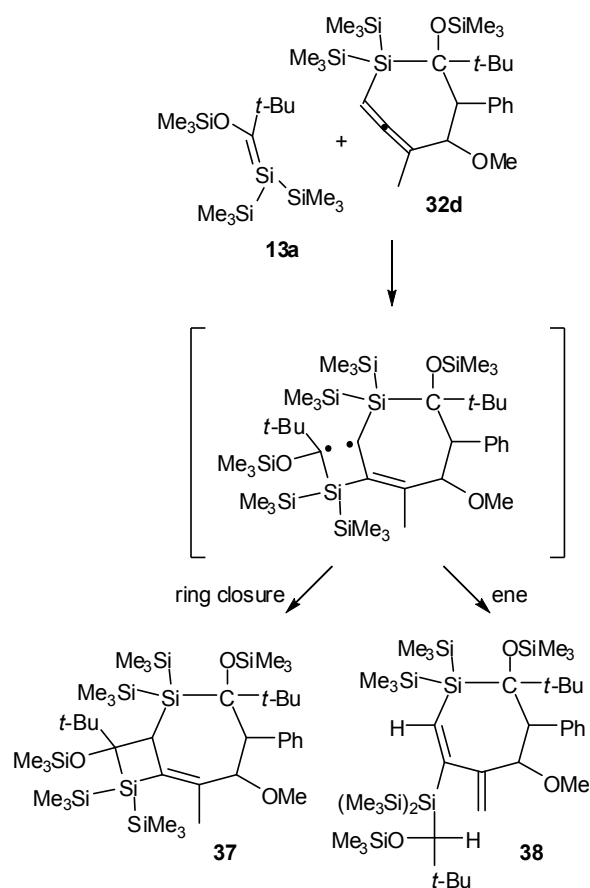
Scheme 16 Formation of silacycloheptenes **37** and **38**

When alkynes **4a** and/or **b** are employed in this chemistry, the formal ene-addition products **39** are often observed due to the presence of the α-hydrogen on the alkyne;[62,67,68] the use of alkyne **4c** inhibits this reaction pathway. It is likely that these types of products are formed via a concerted mechanism since in two cases (the addition of alkyne **4b** to disilene **8**[62] and the addition of alkyne **4a** to silene **13a**[68]; Scheme 17) the ene-adduct was the sole product formed and no ring opening was observed.

$R_1 \diagdown M{=}E \diagup R^2$
$R^1 \diagup \qquad \diagdown R^3$

8: M, E = Si; R^1, R^2, R^3 = SiMe$_2$t-Bu
13a: M = Si, E = C;
$\quad R^1$ = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = t-Bu

+

4a: R = H
4b: R = OMe

$R^1 \; R^2$
$R^1{-}M{-}E{-}R^3$
$H{-} \qquad H$

R = H, OMe

R
Ph **39**

a: M, E = Si; R^1, R^2, R^3 = SiMe$_2$t-Bu, R = OMe
b: M = Si, E = C;
$\quad R^1$ = SiMe$_3$, R^2 = OSiMe$_3$, R^3 = t-Bu, R = H
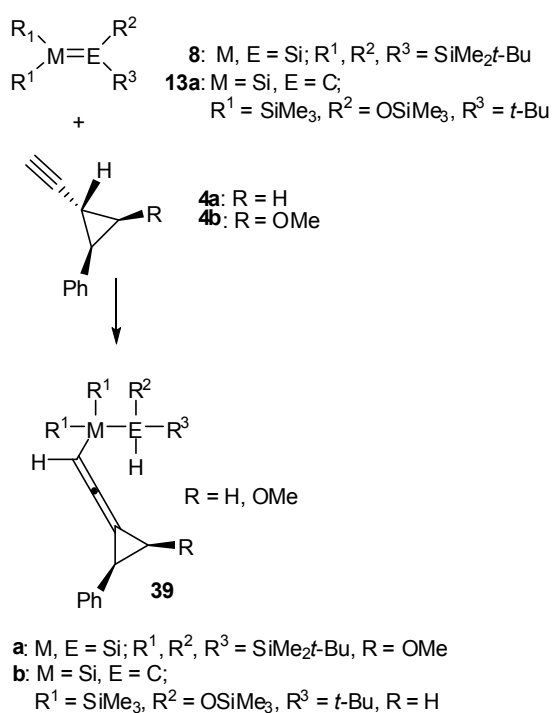
Scheme 17 Formation of silylallenes **39**

The addition of alkynes to disilenes **7/8**, digermene **10**,[63] and Brook silenes **13a,b** proceeds through a biradical intermediate. The results from the addition of **4c** to disilenes **7/8** are consistent with the previously reported mechanistic study by Sakurai and co-workers, where a biradical intermediate was proposed due to scrambling about the Si-Si bond of *trans*- or *cis*-1,2-dimethyl-1,2-diphenyldisilene upon the addition of diphenylacetylene (Scheme 12).[54] Although

the results using mechanistic probes are not consistent with the *conclusions* of the study by West

and co-workers,[55] where a zwitterionic intermediate was proposed, they are consistent with the

results since the terminal alkynes examined (carbomethoxy-, phenyl-, trimethylsilyl- or

ethoxyacetylene) are also capable of stabilizing a vinyl radical. The results from the addition of

4c to digermene **10** are not inconsistent with the conclusions of the previous reactivity study by

Neumann *et al.*, who proposed a zwitterionic intermediate; however, the preference for

$Me_2Ge=GeMe_2$ to react with an electrophilic alkyne, hexafluoro-2-butyne, can also be explained

through the intermediacy of a biradical.

Both biradical and concerted mechanisms have been previously proposed for the addition of

alkynes to Brook silenes.[57,58e,m] The results from the addition of **4c** to Brook silenes **13a,b** are

consistent with the experimental and computational studies performed by Ishikawa where

biradical intermediates were observed;[58e,m] however, the results are not consistent with the

conclusions of Brook and co-workers, who proposed a concerted mechanism on the basis that no

change was observed between the *E/Z* ratio of the silene, $(Me_3Si)(R)Si=C(1-Ad)(OSiMe_3)$, and

the isomer ratio in the silacyclobutenes produced. Brook assumed that the formation of a

reactive intermediate upon alkyne addition would allow for rotation about the silenic Si-C bond

and vary the isomer ratio in the product; however, the rate constants for both the cyclization and

the bond rotation in a putative intermediate are unknown. Although the results of the study do

not appear to be consistent with our work on the addition of **4c** to silenes **13a,b**, the lifetime of

the biradical intermediate formed may likely be just too short to allow for bond rotation with

such bulky substituents.

In contrast to the addition of the cyclopropyl alkynes to disilenes **7/8**, digermene **10**, and

Brook silenes **13a,b**, the reactivity of a naturally polarized silene $Mes_2Si=CHCH_2t$-Bu (**11**)[64]

was drastically different. No cycloaddition products or ring-opened products were observed. Instead, the addition of **4a-c** to silene **11** led exclusively to silylacetylenes **40** (Scheme 18), which are the products from insertion of the acetylenic CH across the Si=C bond. In an attempt to promote cycloaddition, a methylated cyclopropyl alkyne probe was utilized; however, silene **11** failed to react with the methylated alkyne. Thus, no information could be extracted from this study as to the mechanism of alkyne cycloaddition to silene **11**.


a: R = H, R^1 = H
b: R = H, R^1 = OMe
c: R = Me, R^1 = OMe
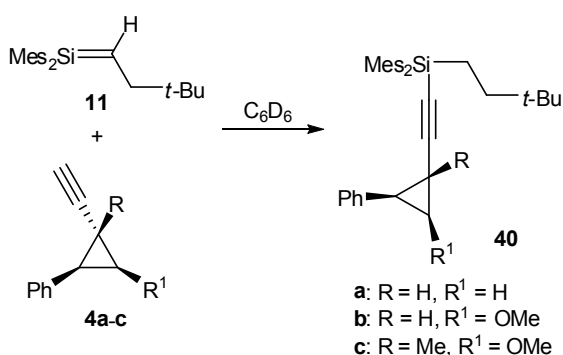
Scheme 18 Reaction of a naturally polarized silene with terminal alkynes

The reactivity of the related germene, Mes$_2$Ge=CH(CH$_2$t-Bu) **12** with alkynes was more varied (Scheme 19).[65] C–H insertion products **41** were observed for many types of alkynes, including aryl-, silyl- and alkyl-substituted alkynes. The formation of the C-H insertion adducts was attributed to a chain reaction initiated by trace amounts of base present as a consequence of the method used to synthesize the germene (i.e. LiF or residual Mes$_2$GeFCH(Li)CH$_2$t-Bu; Scheme 20). [2 + 2]-Type cycloadducts were also formed with both aromatic alkynes and ethoxyacetylene; although the opposite regiochemistry was observed with the two types of alkynes (**42** and **43**, respectively; Schemes 19 and 21). On the basis of the computational results[59] and the regiochemistry of the isolated germacyclobutenes **42**, the formation of 1-germa-

3-aryl-cyclobut-3-enes **42** is believed to proceed via a biradical intermediate with initial Ge-C

bond formation. On the other hand, ethoxyacetylene, due to its enhanced nucleophilicity, is

believed to form via a hypercoordinated transition state **44** similar to that located along the

concerted reaction pathway.[59] Finally, insufficient evidence was available to deduce the

mechanism for the formation of the ene-type products **45**; however, it is reasonable to suggest

that the ene-product and the [2+2] cycloadducts arise from a common intermediate (i.e. a

biradical). The formation of various types of alkyne cycloadducts with germenes is consistent

with the flat potential energy surface observed in the computational study of the addition of

acetylene to the parent germene.[59]
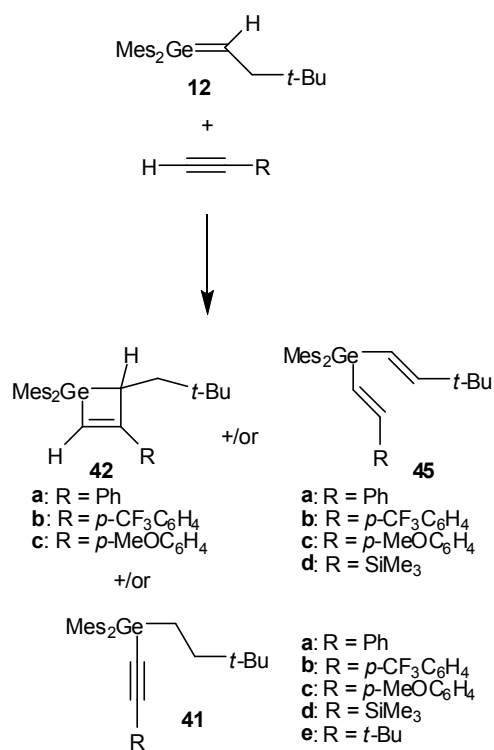
Scheme 19 Reaction of a germene with various alkynes

R————GeMes₂(CH=CH₂)

Mes₂(CH₂=CH)GeF

R
‖‖ ——Base⊖——→ R————⊖ ——12——→ Mes₂Ge—┤
H
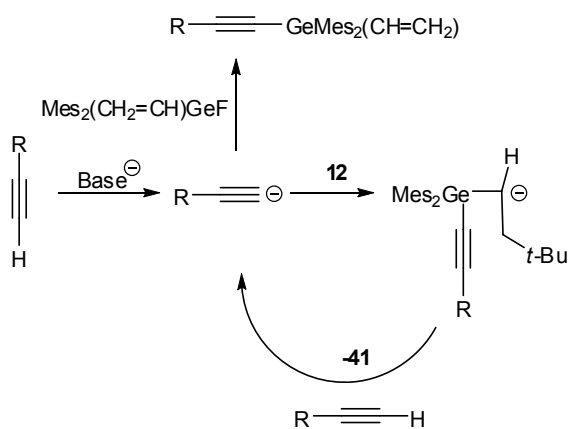
Scheme 20 Chain mechanism for the formation of **41**
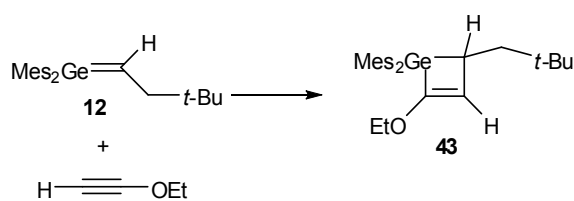
Scheme 21 Reaction of a germene with ethoxyacetylene

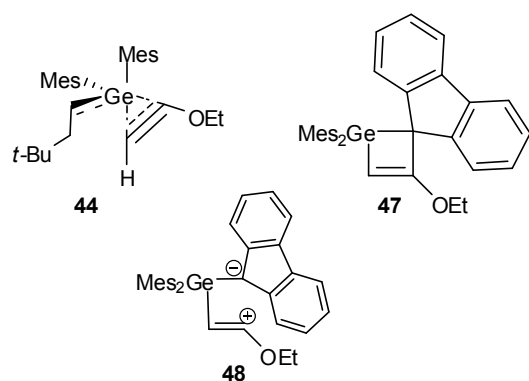Chart 5

In contrast, the reaction of dimesitylfluorenylidenegermane with terminal alkynes, including the alkynyl mechanistic probe **4a**, resulted in the formation of [4 + 2] cycloadducts **46** where the germene acts as the 4π component and the alkyne as the 2π component (Scheme 22).[66] Upon the addition of alkyne **4a**, ring opening of the cyclopropyl moiety was not observed. On this evidence and on the basis of the energy match between the HOMOs and LUMOs of the germene and alkynes, the benzogermacyclohexenes (**46**) are believed to be formed through a concerted, inverse-demand Diels-Alder reaction (Scheme 22). Again, the addition of ethoxyacetylene to germene **14** showed anomalous results.[66] Not only was the [4+2] cycloadduct **46** formed, a [2+2] cycloadduct **47** was also observed and, interestingly, the regiochemistry of the adduct was opposite to what was observed in the addition of ethoxyacetylene to germene **12** (**43** versus **47**). The change in regiochemistry was attributed to the difference in the ability of the germenic carbon to accommodate a negative charge and as a consequence, rather than the reaction progressing through a hypercoordinated transition state (**44**), the formation of the open-chain zwitterionic intermediate **48** was proposed.
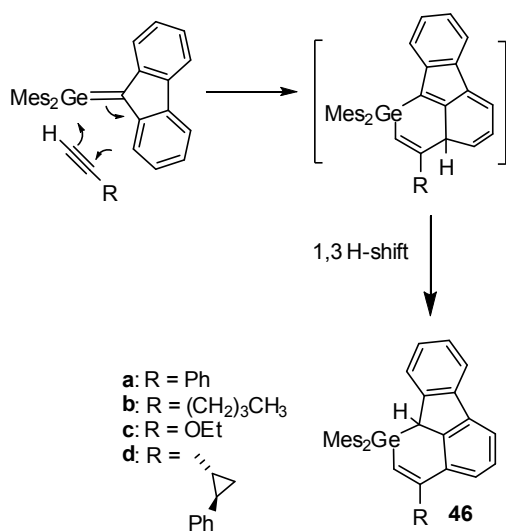
Scheme 22 Reaction of alkynes with a conjugated germene

5.3 Summary: Mechanism of the addition of alkynes to (di)tetrelenes

All [2+2] cycloaddition reactions observed between alkynes and (di)tetrelenes, either experimentally or computationally, proceeded through stepwise mechanisms with one exception. The results are summarized in Table 2. Most often, a biradical intermediate is formed along the reaction pathway except in the reaction of a germene with the electron-rich ethoxyacetylene which appears to react through a zwitterionic intermediate or a asynchronous, one-step reaction pathway. The change in mechanism is undoubtedly a consequence of the different electronic structure of the alkyne. The one example of a [4+2] cycloaddition with an alkyne (with germene **14**), does indeed appear to take place through a concerted reaction pathway (Entry 7).

Table 2: Summary of the mechanistic pathways determined for the addition of alkynes to (di)tetrelenes

Entry	(Di)tetrelene (R=H, alkyl or aryl)[*]	Mechanistic pathway
1	$R_2Si=SiR_2$ R=aryl or silyl	[2+2]: biradical
2	$R_2Si=GeR_2$	[2+2]: biradical
3	$R_2Ge=GeR_2$	[2+2]: biradical
4	$(R_3Si)_2Si=C(OSiR_3)R$	[2+2]: biradical
5	$R_2Si=CR_2$	Potential energy surface relatively flat; biradical pathway in [2+2] cycloaddition has the lowest energy in the parent system

| 6 | $R_2Ge=CR_2$ | Potential energy surface relatively flat; biradical pathway in [2+2] cycloaddition has the lowest energy in the parent system; variable reactivity reported; dependent on the nature of the substituents on the alkyne |
| 7 | Conjugated $R_2Ge=CR_2$ | [4+2]: one step (germene acts as the 4π component) |

*unless otherwise indicated

In the addition of alkynes, the reaction mechanism for the formation of a [2+2] adduct is remarkably consistent despite the varied nature of the doubly-bonded group 14 substrate (Entries 1-7). However, it is difficult to make a definitive statement about the reactivity of naturally polarized silenes and germenes with alkynes because there are relatively few studies on these derivatives and silenes or germenes derived from α-elimination reactions may actually involve (chain) reactions of the acetylide anions rather than the neutral alkyne (Scheme 20).[60,64,65] Nonetheless, the evidence suggests that the polarity of the double bond of the (di)tetrelene is less important as a determining factor in the addition of alkynes in comparison to the addition of carbonyl compounds to (di)tetrelenes.

In the absence of additional evidence, both computational and experimental, it is difficult to rationalize the apparent preference for reaction pathways involving biradicals in the addition of an alkyne to a given (di)tetrelene except to note the lack of dipoles in most of the interacting species and the similarity in the strengths of the bonds being formed. Additional studies on the addition of alkynes to heteroleptic ditetrelenes as well as naturally polarized tetrelenes, which can be made cleanly without the presence of traces of base, are needed to determine if the intermediacy of biradicals is generally observed in this chemistry.

6. Comparison to the reactivity of alkenes and final remarks

Cycloaddition reactions of alkenes, as understood in terms of the Woodward-Hoffmann (W-H) selection rules, play a very important role in the regio- and stereoselective preparation of organic ring systems and a key question in the chemistry of the heavy congeners of alkenes is whether or not they, too, follow W-H rules. Beginning with the first definitive report of a silene,[71] the ease with which silenes dimerize in the dark in the absence of steric protection was noted. Dimerization is a formal [2+2] cycloaddition reaction and, according to the W-H rules, should not be symmetry allowed under thermal conditions. Many more examples of thermal, formally [2+2] cycloaddition reactions were observed with (di)tetrelenes as the reactivity of these species was studied over the years, which led to questioning whether or not the W-H rules can be applied to the cycloaddition reactions of (di)tetrelenes. There are three options to consider: (1) the cycloaddition reactions of (di)tetrelenes do follow the W-H rules and the observed [2+2] cycloadditions proceed through stepwise or non-pericyclic, one-step mechanisms, (2) the cycloaddition reactions of (di)tetrelenes do follow W-H rules but require careful analysis due to altered shapes and lower energy separation between the frontier orbitals. Indeed, Woodward and Hoffman cautioned that the involvement of heteroatoms requires special consideration.[72] 3) The W-H rules are simply not applicable to (di)tetrelenes.

For the most part, reactive intermediates, either zwitterionic or biradical, were formed along the reaction pathway in the cycloaddition of carbonyl compounds or alkynes to (di)tetrelenes. These reactions, which occur under thermal conditions, are, therefore, *not* violating the W-H rules: the mechanisms are not symmetry-forbidden pericyclic additions, rather the reactions occur through thermally-accessible, stepwise reaction pathways. For the limited number of mechanistic studies of [4+2] cycloadditions of carbonyl compounds and alkynes to (di)tetrelenes reported, the reactions appear to take place in one step, again, following the established rules in

carbon chemistry. Only two apparent exceptions were noted to date: the concerted addition of carbonyl compounds to germenes and the addition of selected alkynes to silenes and germenes. In the first case, the cycloaddition involves an apparent $[2\pi_s + 2\pi_s]$ synchronous or asynchronous pericyclic reaction involving oxygen and, in the second case, the formation of the cycloadduct appears to take place by initial coordination of the alkyne to just the silicon (or germanium) of the tetrelene followed by migration of a carbon to give the apparent [2+2] adduct. Both cases require further analysis to firmly establish the concertedness of the reactions and to understand the influence of the dipoles of the reacting partners on the symmetry of the reaction. *Thus, on the basis of research on the addition of carbonyl compounds and alkynes to disilenes, digermenes, germasilenes, silenes and germenes to date, we believe that the cycloaddition of unsaturated derivatives of silicon and germanium do indeed follow Woodward-Hoffman rules.*

The understanding of the mechanisms of the reactions of unsaturated main group compounds is still very much in its infancy. The work described herein focusses on symmetrically substituted ditetrelenes, the mechanism of the addition of carbonyl compounds and alkynes to heteroleptic derivatives will reveal how general the reactivity is. The influence of solvents on the reaction mechanism is also an area for exploration, particularly to determine if solvents can change the pathway followed.[12c,35,73] Furthermore, there are many other cycloaddition reactions for which the mechanism is unknown, for example, the cycloaddition addition of alkenes or nitriles. In addition to doubly-bonded derivatives of silicon and germanium, the chemistry of triply-bonded derivatives is under active investigation.[1d,74] The addition of alkynes to such compounds as digermynes[75] and transition metal tetrelyne complexes[76] figures prominently in reactivity studies. In some cases, remarkable selectivity is

observed and the mechanism of the reaction will be critical to understanding the selectivity and applying the chemistry. There is much work to be done!

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