

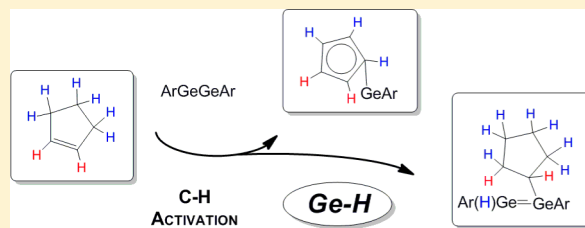
The Role of Group 14 Element Hydrides in the Activation of C–H Bonds in Cyclic Olefins

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S Supporting Information

ABSTRACT: Formally, triple-bonded dimetallynes ArEEAr [$\text{E} = \text{Ge}$ (**1**), Sn (**2**); $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$] have been previously shown to activate aliphatic, allylic C–H bonds in cyclic olefins, cyclopentadiene (CpH), cyclopentene ($\text{c-C}_5\text{H}_8$) and 1,4-cyclohexadiene, with intriguing selectivity. In the case of the five-membered carbocycles, cyclopentadienyl species ArECp [$\text{E} = \text{Ge}$ (**3**), Sn (**4**)] are formed. In this study, we examine the mechanisms for activation of CpH and $\text{c-C}_5\text{H}_8$ using experimental methods and describe a new product found from the reaction between **1** and $\text{c-C}_5\text{H}_8$, an asymmetrically substituted digermene $\text{ArGe(H)Ge(c-C}_5\text{H}_9)\text{Ar}$ (**5**), crystallized in 46% yield. This compound contains a hydrogenated cyclopentyl moiety and is found to be produced in a 3:2 ratio with **3**, explaining the fate of the liberated H atoms following triple C–H activation. We show that when these C–H activation reactions are carried out in the presence of *tert*-butyl ethylene (excess), compounds $\{\text{ArE}(\text{CH}_2\text{CH}_2\text{tBu})_2\}$ [$\text{E} = \text{Ge}$ (**8**), Sn (**9**)] are obtained in addition to ArECp ; in the case of CpH , the neoheptyl complexes replace the production of H_2 gas, and for $\text{c-C}_5\text{H}_8$ they displace cyclopentyl product **5** and account for all the hydrogen removed in the dehydroaromatization reactions. To confirm the source of **8** and **9**, it was demonstrated that these molecules are formed cleanly between the reaction of $(\text{ArEH})_2$ [$\text{E} = \text{Ge}$ (**6**), Sn (**7**)] and *tert*-butyl ethylene, new examples of noncatalyzed hydro-germylation and -stannylation. Therefore, the presence of transient hydrides of the type **6** and **7** can be surmised to be reactive intermediates in the production of **3** and **4**, along with H_2 , from **1** and **2** and CpH (respectively), or the formation of **3** and **5** from **1**. The reaction of **6** or **7** with CpH gave **3** or **4**, respectively, with concomitant H_2 evolution, demonstrating the basic nature of these low-valent group 14 element hydrides and their key role in the ‘cascade’ of C–H activation steps. Additionally, during the course of these studies a new polycyclic compound $(\text{ArGe})_2(\text{C}_7\text{H}_{12})$ (**10**) was obtained in 60% yield from the reaction of 1,6-heptadiene and **1** via double $[2 + 2]$ cycloaddition and gives evidence for a nonradical mechanism for these types of reactions.



INTRODUCTION

C–H activation of inert hydrocarbons is a challenging and important chemical transformation, having potential application in both fuel production and organic synthesis.¹ In typical metal-mediated processes, activation is achieved via inner- or outer-sphere mechanisms, indicating either oxidative addition directly at a metal center or homolytic reaction at an activated ligand, such as an oxo group.^{2,3} A variation of inner-sphere-type reactivity is heterolytic 1,2-oxidative addition across a polar multiple metal–nonmetal bond, e.g., metal–imido double bond.⁴ Activations using inorganic main group species meanwhile are usually understood to operate via homolytic radical-initiated reactions;^{5–8} inner-sphere 1,2-addition pathways in which a transition metal is absent have yet to be delineated for these types of compounds, although outer-sphere reactivity has been recently described for tin and aluminum oxides.⁹ Kempe and co-workers reported an intramolecular C–H cleavage of Cp^- induced by polar Lu–Re metal–metal single bonds in the presence of alkyl ligand as base, and a complex series of intramolecular C–H and C–N activations at a $\text{W}\equiv\text{W}$ bond has been described.¹⁰ Additionally, Wayland and Del

Rossi have demonstrated 1,2-addition of a variety of allylic C–H bonds across a Rh–Rh single bond in a porphyrin dimer, resulting in cleavage of the metal–metal bond, although it is thought that this bond dissociates to give a pair of metalloradicals prior to C–H activation.¹¹ Heterolytic cleavage of an allylic C–H bond has also been recently found to occur in a pair of polar frustrated Lewis pair systems based on group 13 and 15 element centers.¹²

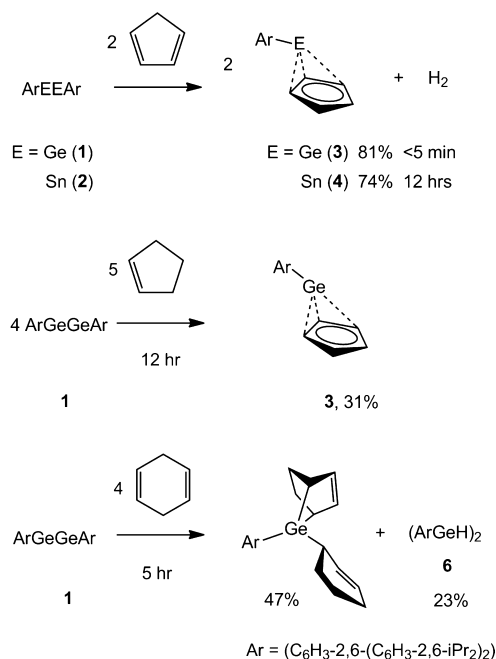
We recently reported that the formally triple-bonded dimetallynes ArEEAr [$\text{E} = \text{Ge}$ (**1**), Sn (**2**); $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$] react with the cyclic olefins cyclopentadiene (CpH), cyclopentene, and 1,4-cyclohexadiene (CHD) to afford C–H activation products at room temperature.¹⁴ The reaction of **1** and **2** with CpH gave ArECp [$\text{E} = \text{Ge}$ (**3**), Sn (**4**)], containing an aromatized cyclopentadienyl anion, along with evolution of hydrogen gas. **1** reacted with cyclopentene to give the same dehydroaromatization product in lower yield, formed from triple C–H activation and was also found to react with

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CHD to give a mixture of $(\text{ArGeH})_2$, trace amounts of benzene, and a 7-germanorbornadiene species bound to a cyclohex-2-enyl fragment (Scheme 1). These transformations are unique to

Scheme 1. Summary of Previously Reported C–H Activation Reactions between Dimetallynes and Olefins¹⁴



the field of C–H activation in that they constitute 1,2-additions across a multiple metal–metal bond.¹⁵ Furthermore, both the products obtained and the nonpolarity of the multiple bonds are consistent with homolytic cleavage, providing a striking counterpoint to the known reactivity at polar metal–element multiple bonds. As a new motif in the field of C–H activation, these reactions demand further study.

In this paper we use experimental methods to examine these reactions in more detail in order to gain mechanistic insight and discover both the implicit and explicit role of hydrides as intermediary species and products in these C–H activation reactions. We delineate the mechanism of activation of CpH and continue by describing similar efforts to find a likely pathway for the oxidation of $\text{c-C}_5\text{H}_8$. In particular we have isolated a new side product from the reaction between **1** and cyclopentene, a multiple-bonded asymmetric digermene featuring hydride and hydrogenated cyclopentyl substituents $\text{ArGe}(\text{H})\text{Ge}(\text{c-C}_5\text{H}_9)\text{Ar}$ (**5**) which explains the fate of the liberated hydrogen atoms in the transformation of $\text{c-C}_5\text{H}_8$ to C_5H_5^- . Finally we describe reactions with other olefins, including the reaction of **1** with 1,6-heptadiene to give a tricyclo species $(\text{ArGe})_2(\text{C}_7\text{H}_{12})$ (**10**), the result of cycloaddition rather than C–H activation and which gives compelling evidence for a nonradical pathway for these competing reactions between olefins and dimetallynes.

EXPERIMENTAL

General Procedures. All operations were carried out by using modified Schlenk techniques under an atmosphere of dry argon or nitrogen. Solvents were dried over an alumina column and degassed prior to use. The ¹H and ¹³C NMR spectroscopic data were recorded on Varian INOVA 300 or 400 MHz spectrometers. The ¹H and ¹³C NMR spectra were referenced to the deuterated solvent. The starting

materials $(\text{ArGe})_2$,^{13b} $(\text{ArSn})_2$,^{13c} $(\text{ArGeH})_2$, and $(\text{ArSnH})_2$ were prepared according to previously published procedures.^{16,17} Cyclopentene, 1,6-heptadiene, and *tert*-butyl ethylene were purchased from Aldrich and distilled over sodium prior to use. Cyclopentadiene was freshly cracked immediately before use.

Synthesis of $\text{ArGe}(\text{Cp})$ (3**) and $\text{ArGe}(\text{H})\text{Ge}(\text{c-C}_5\text{H}_9)\text{Ar}$ (**5**).** To a solution of $(\text{ArGe})_2$ (**1**) (0.400 g, 0.42 mmol) in 50 mL pentane, cyclopentene (50 μL , 0.54 mmol) was added via syringe, resulting in a color change from dark red to emerald green over a period of 12 h. Recrystallization at -20°C overnight gave green crystals of **5** (0.195 g, 0.19 mmol, 46% yield), mp 120°C (dec). ¹H NMR (C_6D_6 , 298 K): δ = 1.00 (d, 12H, *o*-CH(CH₃)₂, *J* = 6.9 Hz), 1.03 (d, 12H, *o*-CH(CH₃)₂, *J* = 6.9 Hz), 1.05 (d, 12H, *o*-CH(CH₃)₂, *J* = 6.9 Hz), 1.12 (d, 12H, *o*-CH(CH₃)₂, *J* = 6.9 Hz), 1.14–1.37 (m, 5H, *c*-C₅H₉), 1.52 (br, 2H, *c*-C₅H₉), 1.69 (br, 2H, *c*-C₅H₉), 2.92 (sept, 4H, CH(CH₃)₂, *J* = 6.9 Hz), 3.00 (sept, 4H, CH(CH₃)₂, *J* = 6.9 Hz), 5.87 (s, 1H, Ge–H) 6.96–7.30 (m, 18H, *m*-C₆H₃, *p*-C₆H₃, *m*-Dipp and *p*-Dipp; Dipp = 2,6-*i*Pr₂-C₆H₃). ¹³C{¹H} NMR (150 MHz, C_6D_6 , 298 K): δ = 0.4, 21.8, 22.8, 25.6, 26.5, 29.8, 44.3, 45.9, 47.3, 121.9, 123.1, 124.7, 126.8, 131.6, 134.7, 141.3, 142.7, 145.1, 146.3, 148.6; λ_{max} (ϵ in mol^{−1} L cm^{−1}) = 406 nm (1500). IR (NaCl, Nujol; selected): Ge–H 2010 cm^{−1}. Cooling of the mother-liquor to -80°C for 4 days gave colorless crystals of **3** (0.142 g, 0.26 mmol, 31% yield), mp 155°C ; characterizing data reported previously.¹⁴

Synthesis of $\{\text{ArGe}(\text{CH}_2\text{CH}_2^t\text{Bu})\}_2$ (8**) from $(\text{ArGeH})_2$ and *tert*-Butyl Ethylene.** To a green solution of $(\text{ArGeH})_2$ (0.020 g, 0.021 mmol) in C_6D_6 (0.6 mL), *tert*-butyl ethylene was added via syringe. After 48 h, ¹H NMR spectroscopy gave a spectrum consistent with $\{\text{ArGe}(\text{CH}_2\text{CH}_2^t\text{Bu})\}_2$ (major) and ArGeH_3 (minor).¹⁴ ¹H NMR (300 MHz, C_6D_6 , 298 K): δ = 0.62 (d, *J* = 6.8 Hz, 12H), 0.77 (d, *J* = 6.7 Hz, 12H), 0.83 (s, 18H), 0.87 (m, 4H), overlapping doublets 1.11 (d, *J* = 6.7 Hz, 12H), 1.13 (d, *J* = 6.7 Hz, 12H) 1.21 (m, 4H), 2.57 (sept, *J* = 6.7 Hz, 4H, CH(CH₃)₂), 2.90 (sept, *J* = 6.7 Hz, 4H, CH(CH₃)₂), 6.82–7.35 (m, 18H, *m*-C₆H₃, *p*-C₆H₃, *m*-Dipp, and *p*-Dipp).

Synthesis of $\{\text{ArSn}(\text{CH}_2\text{CH}_2^t\text{Bu})\}_2$ (9**) from $(\text{ArSnH})_2$ and *tert*-Butyl Ethylene.** To a red solution of $(\text{ArSnH})_2$ (0.019 g, 0.019 mmol) in C_6D_6 (0.6 mL), *tert*-butyl ethylene was added via syringe. After 48 h, ¹H NMR spectroscopy gave a spectrum consistent with the clean synthesis of $\{\text{ArSn}(\text{CH}_2\text{CH}_2^t\text{Bu})\}_2$ in essentially quantitative yield. ¹H NMR (600 MHz, C_6D_6 , 298 K): δ = 0.54 (br, 4H, ³*J* = 4.8 Hz, CH₂CH₂C(CH₃)₃), 0.82 (s, 18H, CH₂CH₂C(CH₃)₃), 1.07 (d, 24H, ³*J* = 24 Hz, CH(CH₃)₂), 1.31 (d, 24H, ³*J* = 6.8 Hz, CH(CH₃)₂), 1.51 (m, 4H, CH₂CH₂C(CH₃)₃), 3.23 (sept, 8H, ³*J* = 6.8 Hz, CH(CH₃)₂), 7.12 (d, 6H, ³*J* = 7.8 Hz, Ar), 7.16–7.18 (m, 6H, Ar), 7.29 (t, 6H, ³*J* = 7.8 Hz, Ar).

Synthesis of $\{\text{ArGe}\}_2(\text{C}_7\text{H}_{12})$ (10**).** To a solution of $(\text{ArGe})_2$ (**1**) (0.400 g, 0.42 mmol) in 40 mL pentane, 1,6-heptadiene (62 μL , 0.46 mmol) was added via microliter syringe giving a pale-yellow solution after six hours. Recrystallization at -20°C overnight gave colorless crystals of **10** (0.262 g, 0.25 mmol, 60% yield), mp 195 – 198°C (dec.). ¹H NMR (600 MHz, C_6D_6 , 298 K): δ = 1.13 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.7 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.40–1.47 (m, 2H), 1.49–1.56 (m, 2H), 1.63–1.33 (m, 2H), 1.89 (pq, 2H), 3.04 (br, 8H), 4.41 (m, 4H), 7.00–7.04 (m, 6H), 7.22 (d, 8H), 7.32 (pt, 4H). ¹³C{¹H} NMR (150 MHz, C_6D_6 , 298 K): δ = 10.7, 13.9, 18.5, 22.0, 22.3, 22.4, 22.6, 22.9, 23.0, 23.7, 23.9, 24.1, 25.2, 25.3, 25.4, 25.6, 25.8, 25.9, 28.9, 30.3, 30.4, 30.5, 30.30.6, 30.7, 30.9, 33.3, 33.7, 35.4, 38.8, 67.6, 122.4, 122.6, 122.7, 122.8, 123.2 (2 C), 128.1, 128.2, 128.7, 130.4, 131.0, 131.0, 140.7, 140.8, 141.2, 141.6, 145.4, 146.3.

X-ray Crystallographic Studies of 5-Hexane and 10-Pentane. The crystal structures were solved by direct methods using the SHELX version 6.1 program package, corrected for Lorentz and polarization effects with SAINT¹⁸ and absorption using Blessing's method as incorporated into the program SADABS.^{19,20} The SHELXTL²¹ program package was implemented to determine the probable space groups and set up the initial files. The structures were determined by direct methods with the successful location of a majority of the nonhydrogen atoms using the program XS.²¹ The structure was refined with XL.²² Noteworthy parameters are summarized in Table 1. In 5-hexane, **5** was found to possess two different central cores, one a

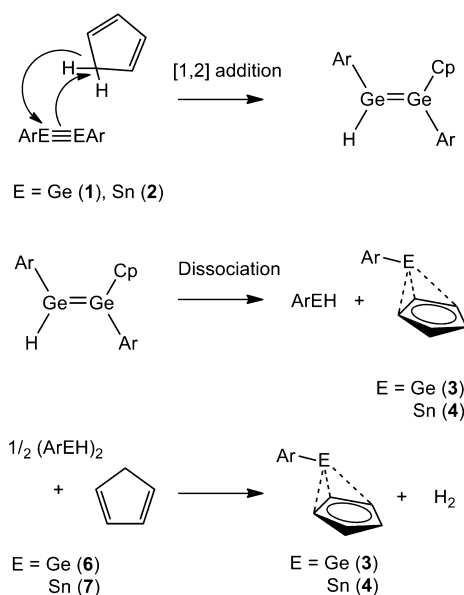
Table 1. Selected X-ray Crystallographic Data for 5-hexane and 10-pentane

compound	5-hexane	10-pentane
empirical formula	C ₇₁ H _{98.12} Ge ₂	C _{69.50} H ₉₂ Ge ₂
formula weight, g mol ⁻¹	1096.79	1072.61
T/λ	90(2) K/1.54178 Å	90(2) K/1.54178 Å
crystal system	monoclinic	monoclinic
space group/Z	C2/c/8	P21/c/4
a, Å	21.587(1)	20.5795(16)
b, Å	14.923(1)	13.4167(10)
c, Å	39.688(2)	22.7242(17)
β, °	90.48(1)	109.826(2)
V, Å ³	12784.7(6)	5902.5(8)
ρ, mg/m ³	1.140	1.207
abs. coeff, mm ⁻¹	1.428	1.538
F(000)	4705	2292
crystal size, mm	0.23 × 0.14 × 0.11	0.37 × 0.30 × 0.22
θ range, °	4.10–68.50	7.72–67.75
reflns collected	18113	27667
ind. reflns	10 458	10 462
	R(int) = 0.0305	R(int) = 0.0246
obs. reflns (I > 2σ(I))	9593	10 390
completeness to 2θ	89.00%	97.90%
max, min trans.	0.8552, 0.7375	0.7236, 0.6030
goodness-of-fit F2	1.054	1.071
final R [I > 2σ(I)]	R1 = 0.0486, wR2 = 0.1342	R1 = 0.0282 wR2 = 0.0737
R (all data)	R1 = 0.0521 wR2 = 0.1368	R1 = 0.0283 wR2 = 0.0738

short Ge(1)=Ge(2) bond 2.3098(5) Å with a lone hydride 94% of the time and also a 6% core composed of Ge(1b)–Ge(2b) = 2.614 Å and three hydrides requiring partial rotations of three methyl groups, namely, C(26), C(44), and C(76) to accommodate the various disorders. Three orientations of a full occupancy hexane molecule were also optimized. Hydrogen atoms were idealized, except for H(61) which was allowed to refine freely throughout the final refinement stages. For 10-pentane, the solvent molecule was found to lie on a special position and therefore C(71) was found to be half occupied such that C(72) is also half the time of a terminal methyl group. The final difference Fourier maps were featureless indicating that the structures are both correct and complete.

RESULTS AND DISCUSSION

First we consider the simplest of the reactions, the formation of Cp products 3 and 4 from CpH and 1 and 2, respectively, along with hydrogen gas (Scheme 1). This type of reactivity is known for highly reducing species, e.g., alkali metals, for which electron transfer is found to initiate the formation of C₅H₆[−] and proceeds to rapidly form an aromatized Cp[−] and a H• radical.²³ We propose an alternate mechanism for the dimetallene reaction, based on oxidative addition followed by a simple acid–base reaction. First, there is an oxidative addition of the C–H bond across the triple E≡E bond to give an unsymmetric digermene Ar(H)Ge=Ge(C₅H₅)Ar intermediate, which then dissociates the two different metallanediyl fragments due to the weak E=E bond (Scheme 2). This results in the formation of a divalent group 14 element hydride of the type (ArEH)_x¹⁶ and the metallanediyl product ArGeCp, which can be considered to be, in effect, an overall σ bond metathesis. Hydride species of this type have been isolated and reported previously, cf., (ArGeH)₂ (6) and (ArSnH)₂ (7), synthesized from the direct reaction of H₂ and ArEEAr or reduction of (ArECl)₂

Scheme 2. Proposed Pathway for C–H Activation of CpH by ArEEAr (E = Ge, Sn)

species.^{16,17,24a,25} Subsequently, the production of hydrogen results from deprotonation of another equivalent of CpH (pK_a = 18) by (ArEH)_x.

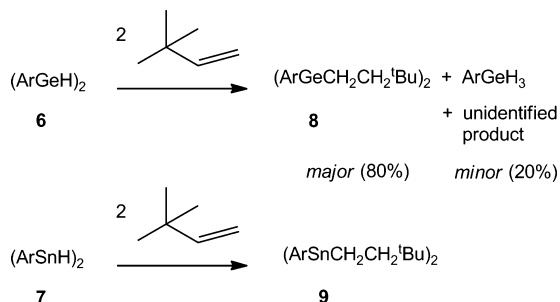
To test this proposed route, a number of reactions with various olefins were undertaken in order to verify the presence of transient group 14 element hydrides (ArEH)_x as intermediary products. By running the C–H activation reactions in the presence of an olefin that can insert into these main group hydride bonds, we can form an alkyl species which should not participate in further chemistry and can be easily detected by ¹H NMR. Insertion of olefins into E–H bonds usually requires a transition-metal catalyst (e.g., in hydrosilylation),²⁶ however for subvalent group 14 element species, it has been recently found that insertion is a facile process in the absence of external catalysts or elevated temperatures.²⁷ Presumably, this occurs via cooperative interaction of the olefin σ and π bonds with a vacant p-orbital and occupied s-orbital present in the low-coordinate species.²⁸ It was supposed that if a subvalent hydride was present in the reaction of dimetallene with CpH, it could be detected by the addition of an excess of olefin, as a competitive substrate versus CpH toward the hydride. This hypothesis assumes that the insertion reaction is faster than deprotonation, a factor which can be managed by using an excess of the insertion substrate. A possible complication is that the dimetallene species 1 and 2 undergo both reversible and irreversible cycloaddition reactions with various olefins.^{13,29} However, although these reactions are comparatively fast, they are highly selective, and using the Ar ligand, they typically only occur with small or activated olefins, e.g., ethylene and norbornadiene, but not with substituted olefins, such as propene or butenes (see later for a greater discussion of this phenomenon).^{29a}

Screening 1 and 2 with a variety of linear and branched olefins using NMR techniques showed that *tert*-butyl ethylene is unreactive with these dimetallenes, even in excess with heating to 100 °C for several days. Furthermore, this substrate has been previously shown to function as an effective acceptor for incipient H• radicals, giving neohexane as the hydrogenated

product³⁰ and so may function as an indicator of two different mechanisms.

The reactions with (ArEH)₂ E = Ge (6) and Sn (7) were undertaken and demonstrate successful insertion into the E–H bonds to give {ArE(CH₂CH₂^tBu)}₂ E = Ge (8) or Sn (9), respectively (Scheme 3). These transformations were identified

Scheme 3. Reactions between Hydrides and *tert*-Butyl Ethylene

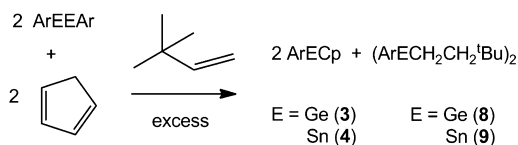


by ¹H NMR and by the disappearance of the distinctive E–H stretch in the IR spectra; unfortunately, despite many attempts, single crystals of these compounds could not be obtained. This type of reaction has precedent in our laboratory for the closely related species {Ar*Sn(CH₂CH₂^tBu)}₂ (Ar* = C₆H₃-2,6-(C₆H₃-2,4,6-^tPr₃)₂), obtained in good yield from (Ar*SnH)₂ and *tert*-butyl ethylene, and which has been fully characterized, including an X-ray crystallographic study. The use of *tert*-butyl ethylene therefore ought to be a reliable substrate for insertion into intermediary hydrides generated in C–H activation reactions.

In the case of the germanium reaction, the additional side product, ArGeH₃, was observed in low yield (ca. 10%), along with a similar quantity of an unidentified terphenyl-bound species. Further experimentation revealed that (ArGeH)₂ reacts with H₂ to give a mixture of ArGeH₃ (15%) and Ar(H)₂GeGe(H)₂Ar (85%), whereas (ArSnH)₂ is inert to further reaction; recent calculations indicate that these reactions proceed via ArGeGeH₂Ar.^{24c} These new observations reveal a higher reactivity for germanium and demonstrate that the apparently straightforward insertion reactions between low-valent group 14 element hydrides and olefins likely operate in a complex manner, perhaps yielding free H₂ as a side product. The reaction of this olefin with E–H bonds meanwhile contrasts with Ir hydride systems in which reductive elimination occurs as part of a catalytic cycle to yield neohexane and a reactive Ir species which is capable of C–H activation.³⁰

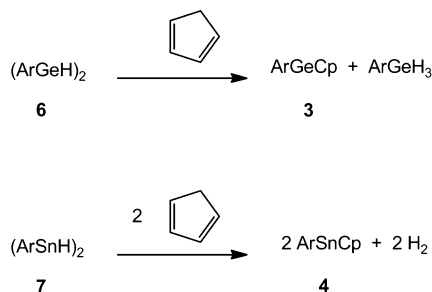
We found that reaction of 1 or 2 with CpH in the presence of excess *tert*-butyl ethylene yields a mixture of Cp compounds 3 or 4 and insertion products 8 or 9, respectively, in a 2:1 molar ratio, as shown by ¹H NMR spectroscopy (Scheme 4). No hydrogen was detected in these reactions, although H₂ is evolved in the original reaction of 1 or 2 with CpH. This

Scheme 4. Reaction of CpH with Dimetallynes Carried out in the Presence of Excess *tert*-Butyl Ethylene



demonstrates that the insertion reaction, with excess olefin (respective to CpH), is preferential to CpH deprotonation under these conditions, which would produce H₂. Indeed, NMR experiments revealed that (ArSnH)₂ reacts with CpH to give 4 and H₂, whereas (ArGeH)₂ reacts with CpH to give 3 and ArGeH₃ (Scheme 5). In the Ge reaction, (ArGeH)₂ is

Scheme 5. Reactions between Hydrides and CpH



assumed to act as an acceptor for the H₂ produced in situ (see above). Together, these reactions verify the two steps of the C–H activation process: First, (ArEH)₂ (or monomeric form thereof) is formed as an intermediate, and second, the species 6 or 7 can function as a base to deprotonate the acidic proton in CpH. If the electron-transfer route was taken, as proven for alkali metals, then it would be expected that either H₂ or neohexane should be detected when the reaction was carried out with dimetallene in the presence of *tert*-butyl ethylene.

One inconsistent feature of these studies is our observation of ArGeH₃ with the (ArGeH)₂ reactions, whereas for the original reactions with digermene 1 we do not find significant quantities of this side product. We believe that this is the case because when H₂ is produced in the dimetallene C–H activation reaction, 1 is in excess with respect to the intermediary amounts of (ArGeH)_x, and therefore any H₂ produced is much more likely to react with 1 and form a monohydrogenated (divalent) species. In the case of the hydride reactions, 6 is in excess therefore H₂ is likely to react with divalent 6 and form tetravalent ArGeH₃, which is not active as a base or insertion substrate.

The triple C–H activation of cyclopentene by 1 to give aromatized Cp product 3 (31% recrystallized yield) is clearly a more demanding reaction than that discussed for CpH, and the less reactive distannylene 2 is not capable of this transformation.¹⁴ In our initial report we could not characterize any side products, despite the low yield of 3 implying their presence, however we are happy to now report the full outcome of this reaction and therefore deduce a likely pathway for the reaction. It was found, after optimization, that the addition of 1.25 equiv of cyclopentene to red digermene 1 over 12 h gave a dark-green solution. ¹H NMR spectroscopy (C₆D₆) revealed the presence of Cp compound 3 and a new product 5 which could be separated from 3 by fractional crystallization allowing full structural characterization of this species.

Compound 5, Ar(H)Ge=Ge(c-C₅H₉)Ar, was isolated as a green solid in 46% recrystallized yield. The X-ray structural data were consistent with a trans-pyramidal digermene core arrangement with new bonds to terminally bound hydride and cyclopentyl moieties (Figure 1). A small impurity (6%) of digermene ArGe(H)₂Ge(H)(c-C₅H₉)Ar was found to cocrystallize in the crystal selected for X-ray studies, which may result from the addition of H₂ to 5 or its unsymmetric isomer ArGe=

an intermediate by partial oxidative dehydrogenation of $c\text{-C}_5\text{H}_8$ and is favorable because the diene would consequently be expected to be reduced by the mechanism described earlier (Scheme 2), i.e., the Ge–C bond is formed by a [1, 2]-addition to the Ge–Ge triple bond of **1**. This route could be prefigured by a $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-H,H}$ coordination mode followed by a sigmatropic rearrangement in which both an allylic and an unactivated secondary C–H bond are broken. Alternatively addition could occur at a single center to form the asymmetric isomer of **6**, $\text{ArGeGe(H)}_2\text{Ar}$, which has been described previously.²⁴ Although we do not detect free hydrogen in the cyclopentene reaction (unlike the CpH reaction), this would be expected; **1** is known to react quickly (within one minute at room temperature) with H_2 to form **6**,^{16a} which in turn participates in insertion chemistry with the excess cyclopentene to yield **5**. One notable feature of this proposed route is the stepwise nature of the transformations, i.e., that the initial reaction is simply an abstraction of two H atoms leaving a conjugated diene as a free organic product, which then in turn participates in a series of further reactions. Attempts to trap the CpH intermediate have failed due to the incompatibility of these trapping agents with **1** (e.g., alkali metals, strong bases, transition-metal carbonyls).

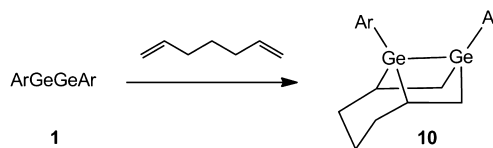
Another possibility to consider is that allylic activation may proceed by oxidative addition of the C–H bond, in a manner similar to that proposed for the CpH reaction, giving a Ge(II) cyclopentenyl species, similar to the Banaszak-Holl compounds,⁷ as intermediate. This seems less likely given the necessity of further C–H activation of a Ge-bound cyclopentenyl group. If this transformation occurred in an intramolecular manner, the products obtained would be in higher oxidation states, i.e., +3 and +4, inconsistent with the major products that have been characterized. Intermolecular H abstraction cannot be ruled out, however it seems unlikely given the previously noted steric effect of the large terphenyl groups.

Further experiments with dimetallynes **1** and **2** showed no reactivity with either cyclohexene, norbornene, cycloheptatriene, fluorene, 1,5-cyclooctadiene, or triphenyl methane at temperatures up to 80 °C. This is in contrast with reported disilynes (stabilized by large silyl substituents) which undergo [2 + 2] cycloadditions with cyclohexene, although larger substrates have yet to be reported.^{37,38} This may be due to the different steric environment at the dimetalynes cores; this question will remain until a synthetic route to $(\text{ArSi})_2$ can be discovered. Given the negligible olefin strain energies of $c\text{-C}_5\text{H}_8$ and $c\text{-C}_6\text{H}_{10}$, it is likely that the reaction between **1** and cyclopentene is enabled by reduced steric hindrance (tightening of C=C angles from 123.6° to 111.3°) and therefore must be near the limit tolerated by the ArGeGeAr complex. Norbornene has similar bond angles (108.6°) and some olefin strain energy (ca. 2 kcal/mol), but presumably this reaction is impeded by the bulk imposed by the additional CH_2CH_2 atoms. Norbornadiene has been found to undergo a [2 + 2] cycloaddition with **1** and **2** under ambient conditions;^{29a} the energy required to overcome the kinetic barrier imposed by the bulky ligands may in this case be attributed to a higher olefin strain energy of norbornadiene versus norbornene (15.5 kcal/mol higher).³⁹

Although we have yet to find either C–H or cycloaddition reactions with many of these larger cyclic olefins, during the process of screening we discovered that, although smaller olefins such as propene are unreactive to these dimetallynes,

1,6-heptadiene reacts with **1** in a double set of [2 + 2] cyclizations to yield a new tricyclic compound $(\text{ArGe})_2(\text{C}_7\text{H}_{12})$ (**10**) (Scheme 10).

Scheme 10. Synthesis of **10** from **1** and 1,6-heptadiene



The structure, as determined by X-ray methods, shows a Ge–Ge single bond at 2.4691(3) Å incorporated into a tricyclic organogermane architecture with two 1,2-digermacyclobutane rings and a 1-germacyclohexane moiety in chair conformation (Figure 3). This central core is a 3,9-digerma analogue of the

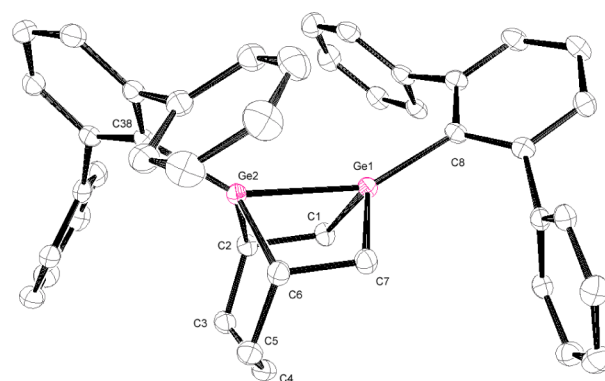


Figure 3. Thermal ellipsoid (50%) plot of **10**. H atoms and isopropyl groups not shown. Selected bond lengths [Å]: Ge(1)–Ge(2) 2.4691(3), Ge(1)–C(8) 1.9763(14), Ge(1)–C(1) 1.9829(15), Ge(1)–C(7) 1.9953(15), Ge(2)–C(38) 1.9672(15), Ge(2)–C(6) 1.9988(15), Ge(2)–C(2) 2.0052(15).

hypothetical all-carbon molecule tricyclo[3.3.1.0^{3,9}]nonane. Germacyclohexane moieties are known and display similar geometry to that found in **10**.⁴⁰ The Ge–Ge bond distance is normal for a single bond (c f., 2.44 Å in elemental germanium), indicating less strain than in the digermahypostrophene cage compound $(\text{ArGe})_2(\text{C}_8\text{H}_8)$ in which the Ge–Ge distance is found at 2.566(1) Å and is susceptible to thermolysis under mild heating.^{29c} Otherwise, bond distances and angles within the molecule are unexceptional.

This is an insightful result as 1,6-hexadiene has been used as a means of detecting radical pathways for cycloaddition chemistry, e.g., through a 1,4-diradical intermediate of the type shown in Scheme 7, for which the unpaired electron that develops on the β -carbon is found to undergo rapid ($k = 1 \times 10^5 \text{ s}^{-1}$) internal cyclization with the remaining double bond giving a cyclopentane moiety which is easily characterized.⁴¹ This radical cycloaddition pathway must be considered as the nonradical [2 + 2] cyclization is symmetry forbidden by the Woodward–Hoffmann rules. We find here that cycloaddition has proceeded unimpeded, therefore supporting a mechanism that proceeds through a [1 + 2] addition followed by rearrangement, as proposed and calculated by Sekiguchi, Nagase, and co-workers for a disilyne.³⁸ This is in contrast to the disilene $\{(\text{tBuMe}_2\text{Si})_2\text{Si}\}_2$ which reacts with the same substrate to give an ene addition product with allylic C–H abstraction, i.e., a 1,5 hydrogen shift.⁴¹

Although the unsaturated bonds in the cycloalkenes described provide weakened allylic C–H bonds that drive the regioselectivity observed in these reactions, it is still unclear why these reactions occur in preference to cycloaddition chemistry, which have also been observed for dimetallynes and would be expected to be particularly favorable with CpH, a classic Diels–Alder diene.^{13,29} In the case of transition-metal systems in which a terminal M=X moiety can C–H activate aliphatic substrates, cycloaddition is found to occur in preference in the case of olefinic compounds.⁴ In our case, an answer to this dichotomous behavior may lie in the partial diradical character of the EE multiple bonds, which are intermediate between double and triple bonds and difficult to model. The distannyne core of **2** is more spatially accessible than the lighter digermene analogue **1**, evidenced by the longer E=E distance (Ge–Ge 2.2850(6) Å in **1**,^{13b} Sn–Sn 2.6675(4) Å in **2**),^{13a} yet we observe a lower reactivity for **2** compared to **1**. This has been reported previously for the activation of other small molecules^{13,30c} and can be explained by a lower diradical character in **2** compared to **1**, previously indicated by calculations.⁴² This is consistent with the C–H activation reactions being initiated by a radical-type abstraction mechanism.

CONCLUSION

Use of *tert*-butyl ethylene as a competitive substrate for intermediary products in a series of C–H activations has provided strong evidence for the role of low-valent group 14 element hydrides in producing the observed aromatized hydrocarbon products. Furthermore, a unique asymmetric digermene **5** was isolated from the reaction between digermene **1** and cyclopentene, in which, unexpectedly, a cyclopentyl group is found. It was shown that this hydrogenated moiety arises from insertion of the olefin into a terminal Ge–H bond and demonstrates the potential for these types of compounds for olefin hydrogenation reactions. The pathways deduced from experimental evidence indicate that the true C–H activation steps occur across the triple bond of the dimetallene species. In the case of cyclopentadiene, we propose a [1, 2]-addition of the doubly allylic C–H bond across a Ge≡Ge bond, whereas for cyclopentene an oxidative dehydrogenation is thought to occur. The consequent hydride “side products” are not inert and continue to play a role in the reactions, as a base with CpH and as an acceptor for olefin insertion with *c*-C₅H₈. With this insight into the reactivity of the enigmatic E≡E bond and the high reactivity of hydride derivatives, we hope to expand these C–H activation reactions to new substrates and with the aim of achieving catalytic turnover by using an acceptor olefin which undergoes reductive elimination after insertion, in the manner demonstrated by the successful iridium systems.^{1d,e,31}

Furthermore, during the course of these investigations we discovered a novel double [2 + 2] cycloaddition with 1,6-heptadiene to give an unusual digermene cage structure **10**, lending support to a nonradical mechanism for the olefin cyclization reactions. It still remains to be determined what factors dictate the preference for allylic C–H activation versus cycloaddition, although it appears at this point that the former involves a radical pathway, whereas the latter is initiated by a concerted [1 + 2] addition. Further studies will continue to explore the multifaceted nature of these reactive molecules.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data, in CIF format for **5** and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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