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

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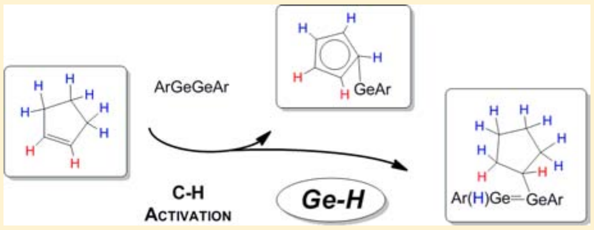
Supporting Information



ABSTRACT: Formally, triple-bonded dimetallynes ArEEAr [E = Ge (**1**), Sn (**2**); Ar = C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$] have been previously shown to activate aliphatic, allylic C−H bonds in cyclic olefins, cyclopentadiene (CpH), cyclopentene (c-C_5H_8) and 1,4-cyclohexadiene, with intriguing selectivity. In the case of the five-membered carbocycles, cyclopentadienyl species ArECp [E = Ge (**3**), Sn (**4**)] are formed. In this study, we examine the mechanisms for activation of CpH and c-C_5H_8 using experimental methods and describe a new product found from the reaction between **1** and c-C_5H_8, an asymmetrically substituted digermene ArGe(H)Ge(c-C_5H_9)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 {ArE(CH_2CH_2tBu)}$_2$ [E = Ge(**8**), Sn(**9**)] are obtained in addition to ArECp; in the case of CpH, the neohexyl complexes replace the production of H_2 gas, and for c-C_5H_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 (ArEH)$_2$ [E = 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 (ArGe)$_2$(C_7H_{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 $W\equiv W$ 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 [E = Ge (**1**), Sn (**2**); Ar = C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$][13] 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 [E = 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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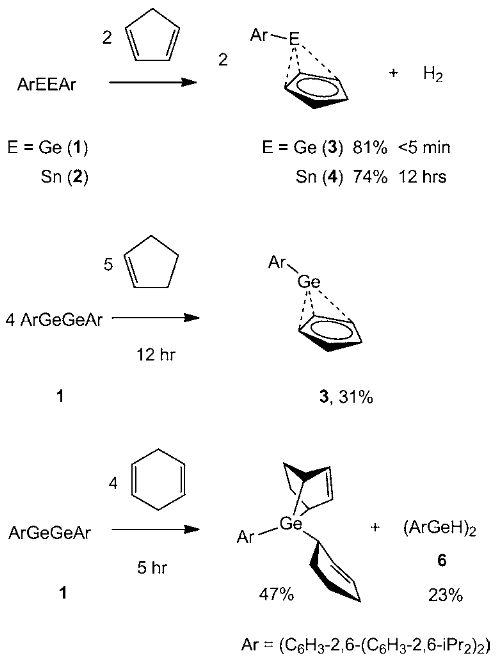
CHD to give a mixture of $(ArGeH)_2$, trace amounts of benzene, and a 7-germanorbornadiene species bound to a cyclohex-2-enyl fragment (Scheme 1). These transformations are unique to the field of C−H activation in that they constitute 1,2-additions across a multiple metal−metal bond.[15] Furthermore, 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.

Scheme 1. Summary of Previously Reported C−H Activation Reactions between Dimetallynes and Olefins[14]



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 c-C_5H_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 ArGe(H)Ge(c-C_5H_9)Ar (**5**) which explains the fate of the liberated hydrogen atoms in the transformation of c-C_5H_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 $(ArGe)_2(C_7H_{12})$ (**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 ^{13}C NMR spectroscopic data were recorded on Varian INOVA 300 or 400 MHz spectrometers. The ^1H and ^{13}C NMR spectra were referenced to the deuterated solvent. The starting materials $(ArGe)_2$,[13b] $(ArSn)_2$,[13c] $(ArGeH)_2$, and $(ArSnH)_2$ 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 ArGe(Cp) (**3**) and ArGe(H)Ge(c-C_5H_9)Ar (**5**).* To a solution of $(ArGe)_2$ (**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*-$CH(CH_3)_2$, J = 6.9 Hz), 1.03 (d, 12H, *o*-$CH(CH_3)_2$, J = 6.9 Hz), 1.05 (d, 12H, *o*-$CH(CH_3)_2$, J = 6.9 Hz), 1.12 (d, 12H, *o*-$CH(CH_3)_2$, J = 6.9 Hz), 1.14−1.37 (m, 5H, c-C_5H_9), 1.52 (br, 2H, c-C_5H_9), 1.69 (br, 2H, c-C_5H_9), 2.92 (sept, 4H, $CH(CH_3)_2$, J = 6.9 Hz), 3.00 (sept, 4H, $CH(CH_3)_2$, J = 6.9 Hz), 5.87 (s, 1H, Ge-*H*) 6.96−7.30 (m, 18H, *m*-C_6H_3, *p*-C_6H_3, *m*-Dipp and *p*-Dipp; Dipp = 2,6-$^iPr_2$-C_6H_3). $^{13}C\{^1H\}$ 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 $\{ArGe(CH_2CH_2{}^tBu)\}_2$ (**8**) from $(ArGeH)_2$ and tert-Butyl Ethylene.* To a green solution of $(ArGeH)_2$ (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 $\{ArGe(CH_2CH_2{}^tBu)\}_2$ (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, $CH(CH_3)_2$), 2.90 (sept, J = 6.7 Hz, 4H, $CH(CH_3)_2$), 6.82−7.35 (m, 18H, *m*-C_6H_3, *p*-C_6H_3, *m*-Dipp, and *p*-Dipp).

*Synthesis of $\{ArSn(CH_2CH_2{}^tBu)\}_2$ (**9**) from $(ArSnH)_2$ and tert-Butyl Ethylene.* To a red solution of $(ArSnH)_2$ (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 $\{ArSn(CH_2CH_2{}^tBu)\}_2$ in essentially quantitative yield. ^1H NMR (600 MHz, C_6D_6, 298 K): δ = 0.54 (br, 4H, ^3J = 4.8 Hz, $CH_2CH_2C(CH_3)_3$, 0.82 (s, 18H, $CH_2CH_2C(CH_3)_3$, 1.07, (d, 24H, ^3J = 24 Hz, $CH(CH_3)_2$), 1.31 (d, 24H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.51 (m, 4H, $CH_2CH_2C(CH_3)_3$), 3.23 (sept, 8H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 7.12 (d, 6H, ^3J = 7.8 Hz, Ar), 7.16−7.18 (m, 6H, Ar), 7.29 (t, 6H, ^3J = 7.8 Hz, Ar).

*Synthesis of $\{ArGe\}_2(C_7H_{12})$ (**10**).* To a solution of $(ArGe)_2$ (**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). $^{13}C\{^1H\}$ 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 SAINT[18] and absorption using Blessing's method as incorporated into the program SADABS.[19,20] The SHELXTL[21] 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

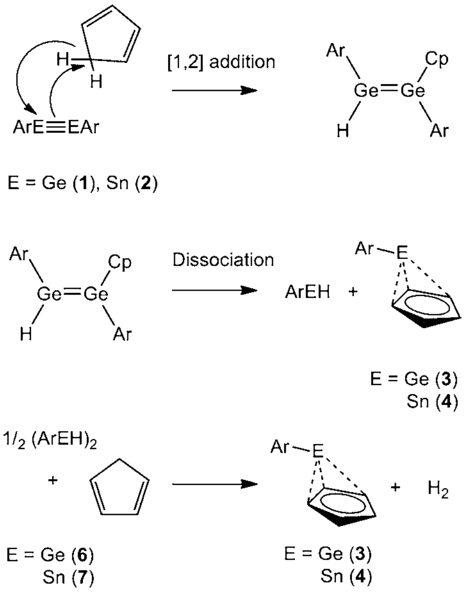
compound	5·hexane	10·pentane
empirical formula	$C_{71}H_{98.12}Ge_2$	$C_{69.50}H_{92}Ge_2$
formula weight, gmol^{-1}	1096.79	1072.61
T/λ	90(2) K/1.54178 Å	90(2) K/1.54178 Å
crystal system	monoclinic	monoclinic
space group/Z	$C2/c/8$	$P21/c/4$
a, Å	21.587(1)	20.5795(16)
b, Å	14.923(1)	13.4167(10)
c, Å	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 ($I > 2\sigma(I)$)	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 [$I > 2\sigma(I)$]	$R1$ = 0.0486,	$R1$ = 0.0282
	w$R2$ = 0.1342	w$R2$ = 0.0737
R (all data)	$R1$ = 0.0521	$R1$ = 0.0283
	w$R2$ = 0.1368	w$R2$ = 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 $C_5H_6^-$ and proceeds to rapidly form an aromatized Cp^- and a $H^\bullet$ radical.[23] We propose an alternate mechanism for the dimetallyne 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 digermyne Ar(H)Ge=Ge(C_5H_5)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 $(ArEH)_x$[16] 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 H_2 and ArEEAr or reduction of $(ArECl)_2$ species.[16,17,24a,25] Subsequently, the production of hydrogen results from deprotonation of another equivalent of CpH (pK_a = 18) by $(ArEH)_x$.

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

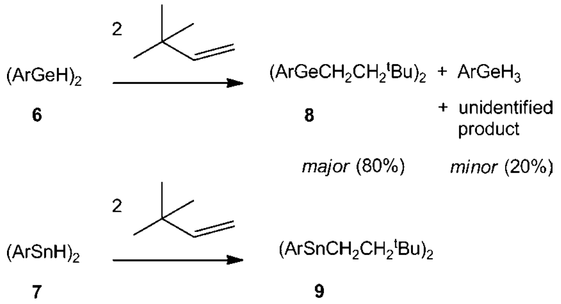


To test this proposed route, a number of reactions with various olefins were undertaken in order to verify the presence of transient group 14 element hydrides $(ArEH)_x$ as intermediary products. By running the C−H activation reactions in the presence of an olefin that can insert into these main group 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 dimetallyne 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 dimetallyne 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 dimetallynes, 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 $H^\bullet$ radicals, giving neohexane as the hydrogenated product[30] 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 $\{ArE(CH_2CH_2{}^tBu)\}_2$ E = Ge (**8**) or Sn (**9**), respectively (Scheme 3). These transformations were identified 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 $\{Ar^*Sn(CH_2CH_2{}^tBu)\}_2$ ($Ar^* = C_6H_3$-2,6-$(C_6H_3$-2,4,6-$^iPr_3)_2$), 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.

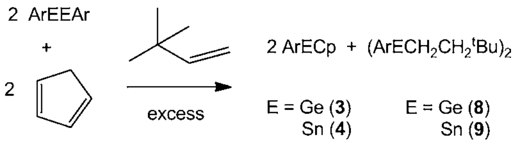
Scheme 3. Reactions between Hydrides and *tert*-Butyl Ethylene



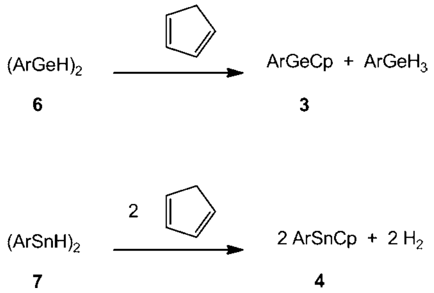
In the case of the germanium reaction, the additional side product, $ArGeH_3$, was observed in low yield (ca. 10%), along with a similar quantity of an unidentified terphenyl-bound species. Further experimentation revealed that $(ArGeH)_2$ reacts with H_2 to give a mixture of $ArGeH_3$ (15%) and $Ar(H)_2GeGe(H)_2Ar$ (85%), whereas $(ArSnH)_2$ is inert to further reaction; recent calculations indicate that these reactions proceed via $ArGeGeH_2Ar$.[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 H_2 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 H_2 is evolved in the original reaction of **1** or **2** with CpH. This demonstrates that the insertion reaction, with excess olefin (respective to CpH), is preferential to CpH deprotonation under these conditions, which would produce H_2. Indeed, NMR experiments revealed that $(ArSnH)_2$ reacts with CpH to give **4** and H_2, whereas $(ArGeH)_2$ reacts with CpH to give **3** and $ArGeH_3$ (Scheme 5). In the Ge reaction, $(ArGeH)_2$ is assumed to act as an acceptor for the H_2 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 H_2 or neohexane should be detected when the reaction was carried out with dimetallyne in the presence of *tert*-butyl ethylene.

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



Scheme 5. Reactions between Hydrides and CpH



One inconsistent feature of these studies is our observation of $ArGeH_3$ with the $(ArGeH)_2$ reactions, whereas for the original reactions with digermyne **1** we do not find significant quantities of this side product. We believe that this is the case because when H_2 is produced in the dimetallyne C−H activation reaction, **1** is in excess with respect to the intermediary amounts of $(ArGeH)_x$, and therefore any H_2 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 H_2 is likely to react with divalent **6** and form tetravalent $ArGeH_3$, 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 distannyne **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 digermyne **1** over 12 h gave a dark-green solution. ^1H NMR spectroscopy (C_6D_6) 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**, $Ar(H)Ge{=}Ge(c\text{-}C_5H_9)Ar$, 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 digermane $ArGe(H)_2Ge(H)(c\text{-}C_5H_9)Ar$ was found to cocrystallize in the crystal selected for X-ray studies, which may result from the addition of H_2 to **5** or its unsymmetric isomer ArGe=

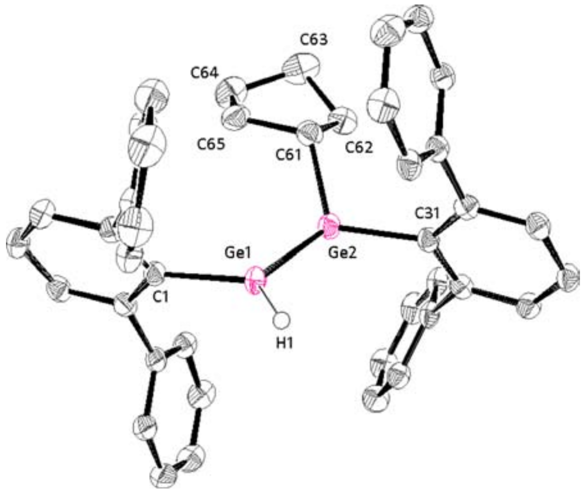


Figure 1. Thermal ellipsoid (50%) plot of **5**. H atoms except H(1) and isopropyl groups are not shown. Selected bond lengths [Å] and bond angles [°]: Ge(1)−C(1) 1.976(3), Ge(1)−Ge(2) 2.3098(5), Ge(2)−C(61) 1.988(3), Ge(2)−C(31) 1.988(3), Ge(1)−H(1) 1.460(0), C(61)−C(62) 1.529(4), C(61)−C(65) 1.541(4), C(62)−C(63) 1.535(5), C(63)−C(64) 1.575(6), C(64)−C(65) 1.498(5); C(1)−Ge(1)−Ge(2) 117.4(1), C(61)−Ge(2)−C(31) 112.2(1), C(61)−Ge(2)−Ge(1) 119.1(1), C(31)−Ge(2)−Ge(1) 114.0(1), C(62)−C(61)−C(65) 105.5(2), C(61)−C(62)−C(63) 103.0(3), C(62)−C(63)−C(64) 101.6(3), C(65)−C(64)−C(63) 103.1(3), C(64)−C(65)−C(61) 107.9(3).

Ge(H)(c-C_5H_9)Ar. This is discussed in greater detail in the Experimental section. Analysis of the ^{1}H NMR spectrum of the recrystallized product does not show any signals attributable to this species that are observable above the baseline noise, therefore it is not a significant side product in the bulk solid. The C_5 ring is bound through one carbon with a Ge−C bond length of 1.988(3) Å, a normal distance for Ge(II)-alkyl single bonds and was found to be fully saturated, with average C−C−C angles (104.2(3)°) and distances (1.536(5) Å) consistent with sp^3 carbon hybridization. The hydrocarbon hydrogen atoms could be located crystallographically in the structure which shows a saturated c-C_5H_9 group. Additionally, the structural data were best refined with a single terminal germanium hydride on Ge(1) set at a distance of 1.46(0) Å. Spectroscopic features for Ge−H were found as a band at 2010 cm^{-1} in the IR spectrum and as a signal in the ^{1}H NMR spectrum at 5.87 ppm. These values are similar to those found in Ar(H)Ge═Ge(H)Ar (2100 and 2060 cm^{-1} and 5.87 ppm).[16a] The Ge−Ge distance of 2.3098(5) Å is within the range found for Ge═Ge double bonds in digermenes.[16a] The multiple bonding is further evidenced by an $n_- \rightarrow n_+$ absorption at 406 nm (ε = 1500 mol^{-1} L cm^{-1}). Significant pyramidalization is observed at Ge(2), with an out-of-plane angle of 36.8° consistent with the presence of nonbonding electron density,[32] supporting a Ge(II)/Ge(II) structure, as opposed to Ge(I)/Ge(IV) with both the hydride and cyclopentyl substituent bound to Ge(2). The Ge(2)−Ge(1)−C(Ar) angle of 117.4(1)° also is consistent with this designation: two-coordinate Ge(II) centers typically bind at tighter angles of 90−100°.[31,32] There are no reported examples of structurally characterized unsymmetrically substituted digermenes for comparison with **5**.[31,33,34] This asymmetric substitution at the Ge═Ge moiety is not, however, reflected in Ge−C(Ar) distances, which are found to be within esd values [Ge(1)−C(1) 1.976(3) and Ge(2)−C(31) 1.988(3) Å], similar to that found in the asymmetric distannene compound (Ar)Sn(μ-Br)Sn($CH_2C_6H_4$-4-^{i}Pr)(Ar).[35]

One striking feature of this digermene is that the Ge−Ge bond does not dissociate to give $(ArGeH)_2$ and $\{ArGe(c\text{-}C_5H_9)\}_n$. This is in contrast with the proposed mechanism for the C−H activation of CpH (Scheme 2), in which we propose that the formation of a similar asymmetric digermene intermediate $\{Ar(H)Ge{=}Ge(\eta^5\text{-}Cp)Ar\}$ is followed by facile Ge−Ge bond cleavage. The increased coordination number of the π-bound Cp ligand would be expected to give a greater driving force toward dissociation than the σ-bonded c-C_5H_9 moiety, by virtue of a greater steric and electronic stabilization of the germanediyl form, and a high kinetic barrier for the latter prevents the formation of symmetrical products, such as $\{ArGe(R)\}_2$. Solid samples of **5** are stable indefinitely under anaerobic conditions, however in solution they decompose over a period of weeks. No evidence for reductive elimination of the cyclopentyl and hydride groups, i.e., the formation of cyclopentane, could be found.

The data described above show clearly that C−H activation of the methylene groups in two molecules of c-C_5H_8 has given dehydrogenated c-C_5H_5 coupled with the partial hydrogenation of three other molecules of c-C_5H_8 in **5**, i.e., a disproportionation of H atoms. This 3:2 molar ratio of **5** and **3** is observed accurately in the ^{1}H NMR spectrum of the reaction mixture without evidence for any other products (see Figure 2 and Scheme 6).

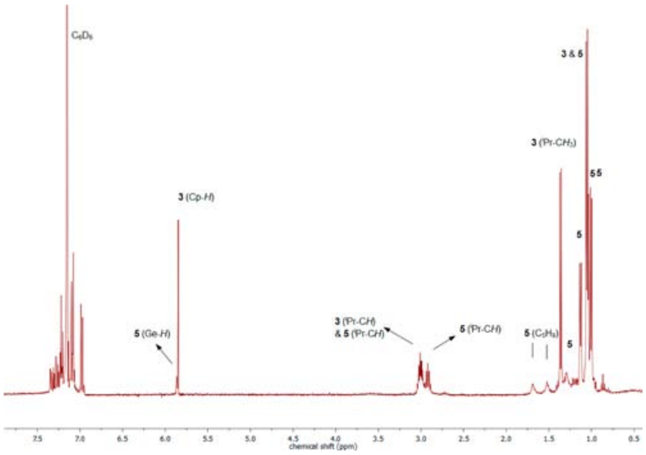
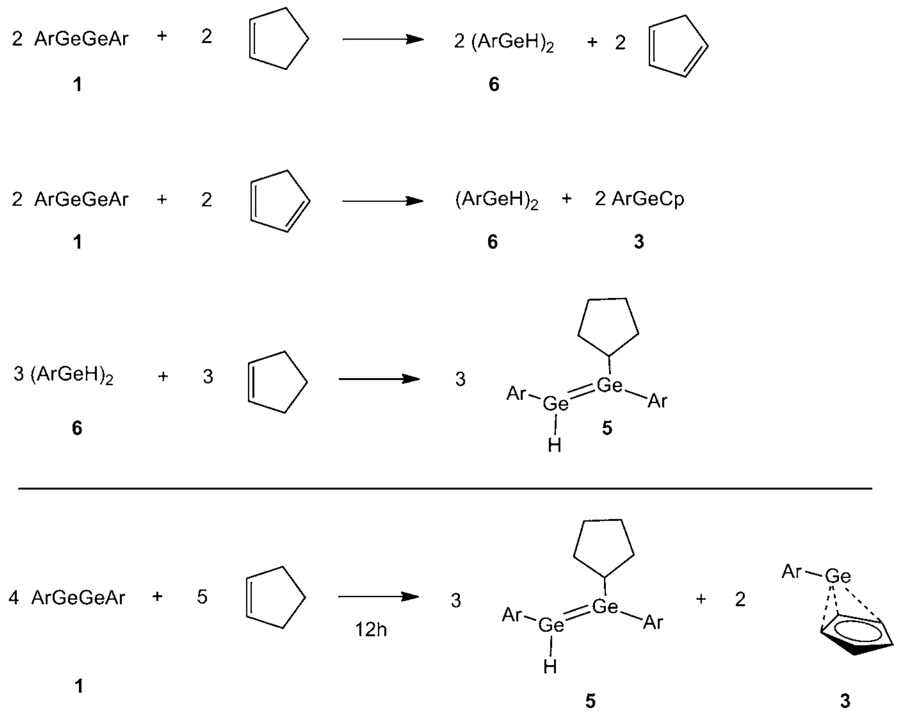


Figure 2. ^{1}H NMR spectrum (C_6D_6) of the crude reaction mixture of **1** with c-C_5H_8 showing clean conversion to **3** and **5** after 12 h. Overlapping signals at δ 1.05 and 3.00 ppm are noted; the complex aromatic region has not been delineated.

The presence of a Ge−H moiety in **5**, together with the isolation of $(ArGeH)_2$ from the related reaction of **1** and 1,4-cyclohexadiene, further implicates the likely role of germanium hydrides in these types of C−H activation processes. Insertion of 1 equiv of cyclopentene into a Ge−H bond would result in a cyclopentyl group of the type found in **5**. Indeed, Baceiredo and co-workers have recently reported this type of insertion reaction between a base-stabilized Si(II) hydride and cyclopentene.[27a] A further telling characteristic of product **5** is that it contains a cyclopentyl fragment rather than a cyclopentenyl group. The latter would be a logical product of C−H activation α to the unsaturated bond and has been reported by Banaszak-

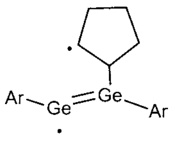
Scheme 6. A Balanced Reaction Scheme for the Formation of 5 and 3 from Digermyne 1



Holl in reactions using mixtures of a germylene or stannylene and aryl halide.[7]

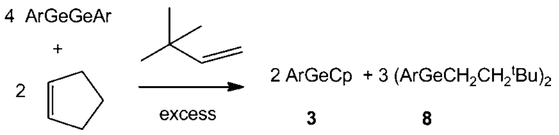
Finally, an unusual possibility to consider is that **5** results from a sterically frustrated [2 + 2] cycloaddition, which would give a β-digermenylalkyl diradical species shown in Scheme 7. C−H abstraction by these 1,4-diradical centers would furnish species **5**.

Scheme 7. A Putative 1,4-Diradical Intermediate in the [2 + 2] Cycloaddition of Cyclopentene with 1



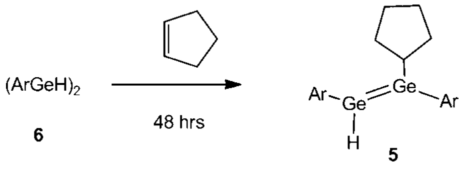
To probe this mechanism, the olefin, *tert*-butyl ethylene, was chosen for a competition experiment to determine the presence of transient hydrides. When **1** was reacted with cyclopentene in the presence of excess *tert*-butyl ethylene a similar color change from red to green was observed over 12 h. ^{1}H NMR spectroscopy revealed a clean mixture of C−H activated Cp product **3** and the insertion product **8** in 2:3 molar ratio with no other products (Scheme 8). No evidence was found for the cyclopentyl product **5** or hydrogenated alkanes (neohexane or cyclopentane). To test for diradical intermediates, the reaction with cyclopentene was found to be unaffected when carried out with an excess of dihydroanthracene.[36]

Scheme 8. Formation of Cp Derivative 3 and Insertion Product 8 from Digermyne and Cyclopentene in the Presence of Excess *tert*-Butyl Ethylene



These results are consistent with the formation of **3** as a primary C−H activation product and **5** as a secondary product formed by insertion of cyclopentene into a Ge−H bond. In the case of the competition experiment, insertion of *tert*-butyl ethylene is preferred exclusively, and no evidence for the formation of hydrogenated cyclopentyl species **5** could be found. In order to examine the identity of this germanium hydride intermediate, $(ArGeH)_2$ was reacted with both 1 equiv and excess cyclopentene and after 48 h gave a ^{1}H NMR spectrum identical to that obtained for **5** (Scheme 9). We observe a single insertion event despite the existence of two hydrides per dimer; presumably **5** is inert to further reaction for steric reasons. One curious observation is that the independent insertion experiment, although successful, occurred at a much slower rate than that observed for the C−H activation reaction: 2 days in contrast with 12 h for the latter. It is possible that a dissociated form of $(ArGeH)_2$ is formed, which effects this insertion more rapidly than the dimer.

Scheme 9. Reaction between Hydride 6 and c-C_5H_8



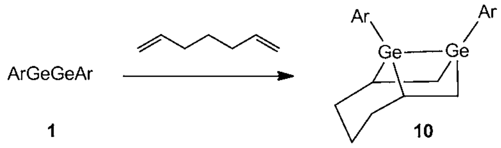
These data strongly indicate the presence of transient hydrides as the source of product **5** and contrast with the Crabtree iridium system which C−H activates cyclopentene in the presence of *tert*-butyl ethylene to make a cyclopentadienyl anion and neohexane, rather than insertion products.[1d,e,30] The question as to how the Ge−C bond is formed in **3** remains however. A likely route, shown in Scheme 6, forms free CpH as an intermediate by partial oxidative dehydrogenation of c-C_5H_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 μ_2-η^1:η^1-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**, ArGeGe$(H)_2$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 dimetallyne cores; this question will remain until a synthetic route to $(ArSi)_2$ can be discovered. Given the negligible olefin strain energies of c-C_5H_8 and c-C_6H_{10}, it is likely that the reaction between **1** and cyclopentene is enabled by reduced steric hindrance (tightening of C−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 $(ArGe)_2(C_7H_{12})$ (**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 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 $(ArGe)_2(C_8H_8)$ 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.

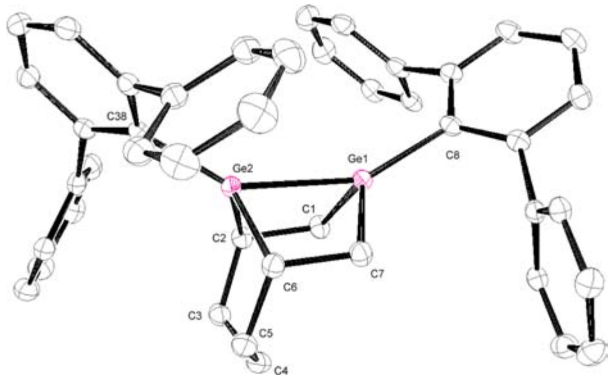


Figure 3. Thermal ellipsoid (50%) plot of **10**. H atoms and isopropyl groups not shown. Selected bond lengths [Å]: Ge(1)−Ge(2) 2.4691(3), Ge(1)−C(8) 1.9763(14), Ge(1)−C(1) 1.9829(15), Ge(1)−C(7) 1.9953(15), Ge(2)−C(38) 1.9672(15), Ge(2)−C(6) 1.9988(15), Ge(2)−C(2) 2.0052(15).

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 ($k = 1 \times 10^5$ 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 $\{(^tBuMe_2Si)_2Si\}_2$ 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 digermyne 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. Futhermore, a unique asymmetric digermene **5** was isolated from the reaction between digermyne **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 dimetallyne 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-C_5H_8. 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]

Futhermore, during the course of these investigations we discovered a novel double [2 + 2] cycloaddition with 1,6-heptadiene to give an unusual digermane 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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