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# C−H Activation of Cycloalkenes by Dimetallynes (M = Ge, Sn) under Ambient Conditions

Owen T. Summerscales, James C. Fettinger, and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616, United States

S *Supporting Information*

ABSTRACT: Treatment of the dimetallynes Ar′EEAr′ [E = Ge, Sn; Ar′ = C_6H_3-2,6-$(C_6H_3$-2,6-i$Pr_2)_2$] with a cyclic olefin—cyclopentadiene (CpH), cyclopentene, 1,4-cyclohexadiene (CHD), or cyclohexene—showed that, with the exception of cyclohexene, they react readily, affording C−H activation at room temperature. Reaction of the digermyne and distannyne with CpH gave the cyclopentadienyl anion, which is bound in a π-fashion to a mononuclear group 14 element center, along with evolution of hydrogen gas. Unusually, the digermyne also reacted with cyclopentene to give the same dehydroaromatization product, formed from triple C−H activation/dehydrogenation. It also was found to react with CHD to give a mixture of $(Ar′GeH)_2$, benzene, and a new 7-germanorbornadiene species bound to a cyclohex-2-enyl fragment.

Scheme 1. Dehydroaromatization of Cycloalkenes Using Digermyne 1 or Distannyne 2
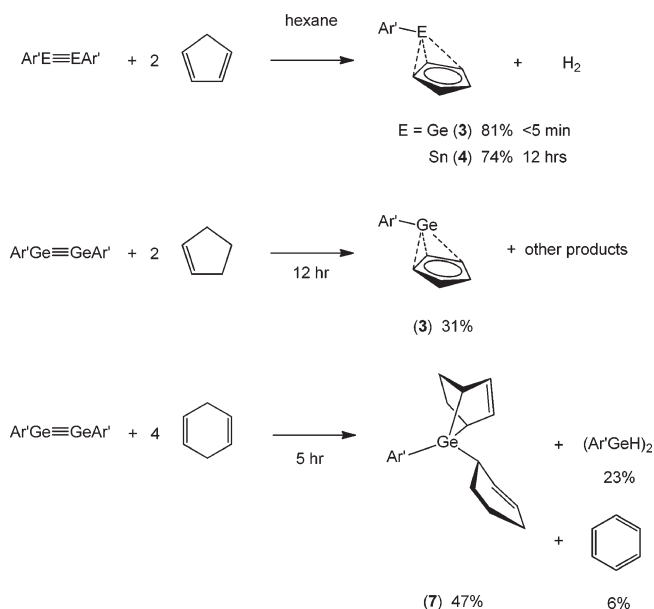
Aliphatic C−H bond activation is a formidable challenge which offers enormous possibilities for chemical synthesis and fuel production. Successful strategies that have been developed include activation using metal complexes, strong oxidizing agents, or main-group radicals.[1] The latter are usually transient molecules generated by in situ reduction of a high-valent precursor (e.g., SnBu$_3$H); however, it has been shown recently that multiple-bonded main-group elements can possess singlet diradical character that could, in principle, be harnessed for similar purposes without applying harsh reaction conditions.[2]

Recent work with the multiple-bonded heavier group 14 alkyne analogues Ar′EEAr′ [E = Ge (**1**), Sn (**2**); Ar′ = C_6H_3-2,6-$(C_6H_3$-2,6-i$Pr_2)_2$][3] has revealed unexpected reactivity toward unsaturated organic substrates that includes reversible coordination of ethylene,[4] reduction and C−C cleavage of 1,3,5,7-cyclooctatetraene (COT, E_0 = −1.99 V),[5] and oxidative addition of H$_2$ (bond dissociation energy (BDE) = 104 kcal mol^{-1}).[6]

In this paper we describe unexpected C−H activation reactions using digermyne **1** and distannyne **2** with three cyclic olefins: cyclopentadiene (CpH), cyclopentene (c-C$_5$H$_8$), and 1,4-cyclohexadiene (CHD). Instead of the expected [2n+2] alkene cyclization products, we observed multiple C−H activation and formation of dehydroaromatized species, namely the cyclopentadienyl anion and benzene, respectively (Scheme 1). Reaction of either red digermyne **1** or green distannyne **2** with 2 equiv of CpH over 30 min for **1** or 24 h (**2**) at room temperature gave, after workup, colorless crystals of **3** or **4** in high yield (81%

and 74%, respectively). These compounds could also be obtained independently and in good yield by a metathesis reaction between $(Ar′ECl)_2$ and NaCp.

X-ray diffraction of **3** (Figure 1) revealed a monomeric species with a planar, aromatic C$_5$H$_5$ moiety bound mainly through one carbon atom at Ge−C(31) 2.183(2) Å but also with close interactions to the adjacent atoms at Ge−C(32) 2.327(2) Å and Ge−C(35) 2.531(2) Å (Figure 2). Ring-slippage is well-known for main-group Cp derivatives, which display a wide range of bonding modes.[7] In **3**, the average internal carbon distances (1.410(2) Å) and angles (108.0(2)°) in the ring are consistent with a π-bound aromatic Cp anion, with a slight shortening of the C33−C34 bond (1.383(2) Å) at the part of the ring most distant from the Ge atom. This type of bond variation in ring-slipped molecules is known in the related half-sandwich (R)Ge(η^2-Cp*) [R = 2,4,6-$^tBu_3C_6H_2$, C(SiMe$_3$)$_3$][8] and inverse-sandwich $(Ar′E)_2(\mu_2$-η^2:η^2-COT) [E = Ge (**5**), Sn (**6**)] compounds.[5]

Unfortunately, definitive structural data for **4** could not be obtained due to the instability of the crystals in the oil used for mounting the sample; crystal disintegration is evident within
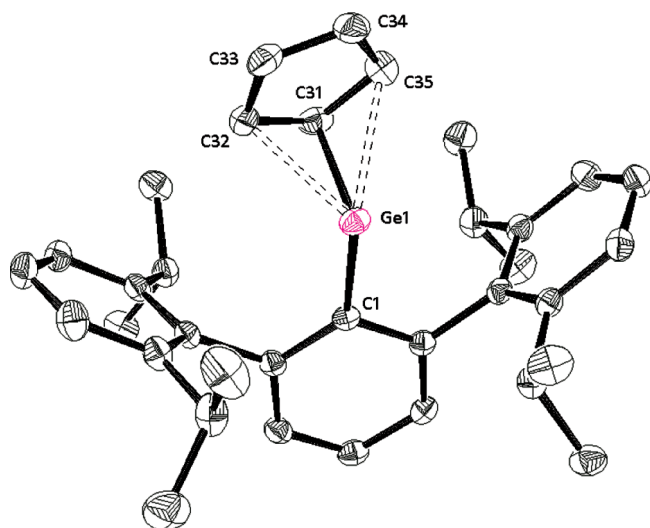
Figure 1. Thermal ellipsoid (50%) plot of **3**. H atoms are not shown. Selected bond lengths (Å) and bond angles (°): Ge(1)−C(1) 2.0350(13), Ge(1)−C(31) 2.1827(14), Ge(1)−C(32) 2.3272(14), Ge(1)−C(35) 2.531(2), C(31)−C(35) 1.419(2), C(31)−C(32) 1.423(2), C(32)−C(33) 1.419(2), C(33)−C(34) 1.383(2), C(34)−C-(35) 1.405(2); C(1)−Ge(1)−C(31) 95.87(5).
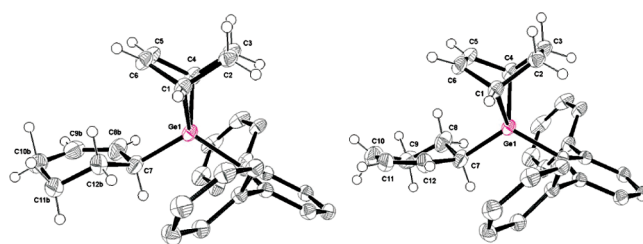

Figure 2. Thermal ellipsoid (50%) plots of the two co-crystallized rotamers of **7**. [i]Pr groups and H atoms are not shown for clarity, except for those on c-C_6H_9 and c-C_6H_8 moieties. Selected bond lengths (Å) and bond angles (°): Ge(1)−C(7) 1.975(2), Ge(1)−C(13) 1.9909(17), Ge(1)−C(4) 1.9937(19), Ge(1)−C(1) 1.9970(18), C(1)−C(2) 1.546(3), C(5)−C(6) 1.330(3), C(7)−C(8) 1.537(7), C(8)−C(9) 1.46(3), C(9)−C(10) 1.504(9), C(10)−C(11) 1.501(8), C(11)−C-(12) 1.33(2), C(7)−C(12) 1.522(7), C(7)−C(8b) 1.529(8), C-(8b)−C(9b) 1.39(3), C(9b)−C(10b) 1.504(9), C(10b)−C(11b) 1.503(9), C(11b)−C(12b) 1.53(3), C(7)−C(12b) 1.531(8); C-(4)−Ge(1)−C(1) 77.99(8), C(9b)−C(8b)−C(7) 114(2), C(11)−C-(12)−C(7) 119.5(16), C(12)−C(11)−C(10) 127.9(9), C(8b)−C(9b)−C(10b) 129.9(11).

seconds, presumably via a desolvation mechanism. Assignment of **4** as the Sn analogue of **3** was supported by nearly identical ^{1}H and $^{13}C\{^1H\}$ NMR (C_6D_6) and UV/vis spectra. A $^{119}Sn\{^1H\}$ resonance for **4** was found at 94 ppm, which is approximately midway between those of two-coordinate Sn(Ar′)$_2$ (2235 ppm)[9] and ten-coordinate Sn(Cp)$_2$ (−2199 ppm)[10] and in the same region as that of three-/four-coordinate COT derivative **6** (−85 ppm).[5] The asymmetric coordination environment found in the solid-state structure of **3** is not reflected by the solution-state ^{1}H NMR measurements, which show a single resonance for the Cp ring at 5.85 ppm, similar to values originally reported for E(η^5-Cp)$_2$ (E = Ge, 5.96 ppm; Sn, 5.81 ppm).[11] It is thus likely that the rings are fluxional, a phenomenon that has also been previously noted in the COT derivatives **5** and **6**.[5,12]

Analysis of the crude reaction mixture of either **1** or **2** with 1 equiv of CpH using ^{1}H NMR spectroscopy (C_6D_6) showed quantitative conversion to **3** (within 5 min at room temperature) or **4** (with 24 h), respectively, and free H_2 (δ 4.47 ppm). In order to explore the possibility for the micro-reverse of this reaction, solutions of **3** and **4** were exposed to 5 psi D_2; however, no H/D exchange was observed, as evidenced by a lack of change in the integral value for the C_5H_5−*H* resonances in the ^{1}H NMR spectra.

Further investigations with the less reactive substrate c-C_5H_8 gave no reaction with distannyne **2**, but remarkably **2** equiv reacted with digermyne **1** in 12 h to give the same Cp-containing species **3**, albeit in lower recrystallized yield (31%), as confirmed by NMR and X-ray methods. Analysis of the crude reaction mixture using ^{1}H NMR did not give any evidence for either evolved H_2 or free CpH but indicated the presence of a complex mixture of signals which we have not unequivocally characterized.

No reaction was observed between CHD and **2**, but 4 equiv of CHD reacted with **1** over 5 h to produce a mixture of the known hydride (Ar′GeH)$_2$ (24% isolated yield),[6] benzene (6% with respect to CHD by GC-MS), and an unusual new germanorbornene, Ar′Ge(c-C_6H_8)(c-C_6H_9) (**7**, 47% isolated yield), which contains an additional Ge-bound cyclohexene ligand (Scheme 1).

Investigations using the more saturated olefin cyclohexene did not show any evidence for reactivity with either **1** or **2**.

Structural determination of **7** showed a tetrahedral coordination environment around the Ge atom, which is bound in a bicyclic fashion to a 1,4-cyclohex-2-enyl fragment to give a 7-germabicyclo[2.2.1]hept-2-ene moiety and also bound through one carbon to a disordered 1-cyclohex-2-enyl ligand (Figure 2). The geometry of the former is similar to that of a silicon analogue that has been reported to arise from a [4+1] cycloaddition between a cyclotrisilane and 1,3-cyclohexadiene.[13] The data were of sufficient quality to freely refine all H atoms and clearly showed an CH_2−CH_2 moiety (C2−C3 1.550(3) Å) directed toward the terphenyl ligand and an unsaturated CH=CH group (C5−C6 1.330(3) Å) *syn* to the 1-cyclohex-2-enyl fragment, similar to that found in a tin derivative. ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy (C_6D_6) of **7** gave data consistent with this formulation, with no evidence for the enantiomer in recrystallized samples. A full discussion of the spectroscopic and structural data can be found in the Supporting Information. The presence of (Ar′GeH)$_2$ was verified by ^{1}H NMR (C_6D_6) and IR spectroscopy of the crude reaction mixture (Ge−H δ 5.87 ppm; ν 2100, 2060 cm^{-1}), in addition to a unit cell determination for an isolated, crystalline sample.[6]

The results presented above demonstrate a highly unusual series of aliphatic C−H activations of cycloalkenes by dimetallynes, leading to aromatized carbocycles, which presumably provide a significant thermodynamic driving force for the transformations. They are surprising because these dimetallynes had been shown earlier to undergo cycloaddition reactions with alkenes,[2b,c,4] which are not observed in these cases, although the facile cleavage of the E≡E triple bond has been previously found for similar reactions with COT.[5] The lower reactivity of distannyne **2** compared with that of digermyne **1** appears to be of electronic origin: **2** may be more sterically unsaturated than **1**, but it has a lower singlet diradical character, as indicated by calculations.[14] In other words, we expect a higher kinetic barrier for the tin reactions than for those with germanium but a similar thermodynamic gain for both in terms of the energy of aromatization.

The reduction of CpH (BDE = 81.2 ± 2 kcal mol^{-1}, pK_a = 18)[15] under ambient conditions to give the aromatic Cp anion and H$_2$ is known only for highly reducing species: alkali metals,[16] calcium metal,[17,18] metal carbonyls[16b] and low-valent f-element compounds.[19] In contrast to these relatively harsh conditions, the Diels−Alder [4+2] cycloaddition between CpH and π-bonded species (e.g., alkenes, alkynes, disilenes, diphosphenes, diarsenes)[20] is particularly facile due to the rigid *cisoid* conformation. Triply bonded dimetallynes are known to behave as dienophiles in Diels−Alder reactions.[21,22] It is therefore surprising to find that **1** and **2** do not react in such a manner and instead act as two-electron reducing agents toward two molecules of CpH.

The highly unusual dehydrogenation of c-C$_5$H$_8$ (BDE = 82.3 ± 1.1 kcal mol^{-1}, p$K_a \approx 46$)[23] to cyclopentadienyl, meanwhile, does not occur under highly reducing conditions (e.g., with alkali metals). This substrate is not easily deprotonated and is also more challenging as it involves the abstraction of three methylene hydrogens rather than one. Crabtree et al. were the first to demonstrate this transformation using an Ir hydride system that required either elevated temperatures or an additional alkene hydrogen "acceptor",[1d,e,24] and it has also been reported for a rhenium heptahydride species[25] which similarly dehydrogenates CpH and CHD by virtue of strongly basic hydride ligands.[26] Although this provides a parallel to some of the reactivity described here, previous investigations have shown that dimetallynes **1** and **2** possess relatively low basic character.[27] This, and the predicted singlet diradicaloid character of **1** and **2**, lead us to believe that the C−H activation reactions operate via a radical abstraction mechanism. In particular, the reaction described herein for **1** is likely to proceed by initial dehydrogenation of c-C$_5$H$_8$ to CpH, followed by a further C−H activation to give **3**. We have found no direct evidence of any free CpH, even if the reaction is carried out with substoichiometric amounts of c-C$_5$H$_8$. This is consistent with the C−H activation of c-C$_5$H$_8$ being slow with respect to that of CpH.

No reactions were observed with cyclohexene (BDE = 85 ± 1 kcal mol^{-1},[28] pK_a = 46[23b]), which may be attributed to the slightly stronger BDE of the methylene C−H groups. This is not the case for CHD (BDE 75 ± 2 kcal mol^{-1}),[29] the relatively facile dehydrogenation of which to benzene is used in organic synthesis to quench diradical intermediates (e.g., in Bergman cyclizations). With **1** we observed both oxidation products (benzene) and, simultaneously, reduction products 1,4-cyclohex-2-enyl and 1-cyclohex-2-enyl fragments, which are found coordinated to a single Ge atom in **7**. The latter are presumably derived from multiple addition of H radicals; the regiochemistry of the CHD is maintained in the 1,4-cyclohex-2-enyl moiety and would be a possible derivative of a C−H activation process with Ge at these positions. It is also possible that it is the product of [4+1] cycloaddition with the 1,3-cyclohexadiene isomer,[22] which would, however, necessitate an in situ 1,4 → 1,3 isomerization of CHD, known to be catalyzed by various organometallic species.[30]

Banaszak-Holl and co-workers have reported that single allylic C−H activations of a variety of alkenes, including c-C$_5$H$_8$, can occur with a germylene or stannylene/aryl halide reagent.[31] These reactions are believed to occur via a concerted mechanism in which oxidative addition of a phenyl halide to a tetryldiyl center creates an incipient phenyl radical capable of C−H activation.[32] This is in contrast to the reactions of germyl and stannyl radicals, which typically react directly at an unsaturated carbon−carbon bond.[33] Interestingly, Driess et al. have shown that a stable silylene can C$_{sp}$−H activate acetylene without additional reagents in preference to cycloaddition;[34,35] this species can also C$_{sp^2}$−H activate fluorobenzenes.[36] Intramolecular insertion into C$_{sp^2}$−H bonds of terphenyl ligands has been previously observed for unstable unsaturated borylene intermediates generated under reducing conditions.[37] Using the digermyne compound described here, we can control the reactivity of the p-block element center to selectively C$_{sp^3}$−H activate external hydrocarbon substrates under mild conditions. We are currently investigating the mechanism for these interesting transformations and exploring the possibility for catalytic activity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis and characterization of **3**, **4**, and **7**; tables of crystallographic data; full structural and NMR discussion for **7**; and X-ray crystallographic data, in CIF format, for **3** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
pppower@ucdavis.edu

■ ACKNOWLEDGMENT

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