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Unusual Electrocyclic Rearrangements with Group 14 Element Compounds: Reversible Isomerization of a π -Aromatic Digermyl Complex with Carbon–Carbon and Germanium–Germanium Multiple Bond Cleavage

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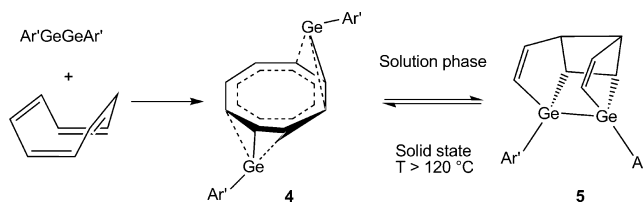
Abstract: Reaction of a digermine with cyclooctatetraene (cot) gave two isomeric products. A Ge(II) inverse sandwich is formed as the kinetic product, which was a result of complete Ge≡Ge bond cleavage and the formation of a π -bound cot ring. This isomerized in solution at room temperature over a period of 5 days to give the thermodynamic product, a tetracyclic diene-digermene, in which a single-bonded Ge–Ge moiety has inserted into a C=C bond of the cot carbocycle. Kinetic studies afforded an activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) of 14.9 kcal mol^{−1} and −6.2 cal mol^{−1} K^{−1} respectively. Heating crystals of the thermodynamic product at ca. 120 °C cleanly regenerated the original inverse sandwich isomer.

The selective cleavage of unstrained hydrocarbon C–C bonds under mild conditions is an attractive goal that would enable the conversion of basic petroleum products into higher value compounds.¹ However, this objective presents significant challenges: C–C bonds are typically strong (85 kcal/mol)² and kinetically inert with respect to competitive C–H activation. Despite this, direct metal insertion into nonactivated C–C bonds is known in a number of instances, involving C_{sp(n)}–C_{sp³} ($n = 1–3$),^{3–5} C_{sp²}–C_{sp²} (aromatic),^{6,7} and C_{sp}≡C_{sp} bonds.⁸ Highly reactive main group species can also be used to effect C–C bond cleavage, e.g. in ozonolysis of C_{sp²}=C_{sp²} bonds,⁹ or in the insertion of silylenes into aromatic C–C bonds with heat or UV radiation.¹⁰ An alternative approach to this problem is to achieve oxidative addition of an unstrained C–C bond *across* a multiple-bonded fragment (L)_nM–M(L)_n, which would involve a smaller oxidation state change at each M atom. Mutual scission of M≡M and C≡C bonds was first shown by Schrock et al. for group 6 metals (the “chop–chop” metathesis reaction)^{11a} and Cummins et al. for Mo≡Mo/N≡N metathesis.¹² However, these solution-phase activation routes have yet to be observed for other transition metal or inorganic main group element species or for alkenes.^{11b} Gas-phase investigations have given evidence for C_{sp³}–C_{sp³} cleavage of pentanenitrile by uncomplexed Ni₂⁺ cations.¹³

Our investigations with multiple bonded heavier group 14 alkyne analogues ArEEAr (E = group 14 element) have shown that they have a very high reactivity toward small molecules that is more typical of transition metal complexes than of their lighter RC≡CR congeners.¹⁴ This is due to their strained geometry and partial singlet diradical, virtually open-shell character which enables reactions that would be otherwise symmetry-forbidden. For example, the distannyne Ar'SnSnAr' (**1**) (Ar' = C₆H₃-2,6-(C₆H₃-2,6-

*i*Pr₂)₂) reversibly complexes ethylene and norbornadiene at room temperature¹⁵ and reacts in an electron-transfer process with the olefinic bonds of cot (1,3,5,7-cyclooctatetraene) to give an antibimetallic (Ar'Sn)₂(μ_2 - η^2 : η^3 -cot) (**2**)¹⁶ which contains a π -bound cot dianion and has resulted from complete Sn≡Sn cleavage.

Scheme 1. Overall Reaction for the Formation of **4** and **5** from Digermine



In this paper we report the results of the more complex reaction between the digermine Ar'GeGeAr' (**3**)¹⁷ and cot, which gives an isomeric mixture of both a germanium inverse sandwich cot species as the primary kinetic product and a tetracyclic cage-like digermene as the thermodynamic product that can be isolated in quantitative yield. Remarkably, the formation of the latter species resulted from cleavage of an unstrained C=C bond in C₈H₈ that appears to have occurred via oxidative addition across a multiple Ge–Ge bond.

Burgundy solutions of **3** reacted in hydrocarbon solvents with cot over a period of hours to give an orange solution that contains a mixture of two isomers by ¹H NMR spectroscopy. Pure samples of the initially dominant (kinetic) product (Ar'Ge)₂(μ_2 - η^2 : η^3 -cot) (**4**) precipitate as an air-sensitive yellow powder in 58% yield if the reaction is performed in diethyl ether. Structural studies using X-ray diffraction revealed an inverse sandwich structure somewhat different from that previously seen for (Ar'Sn)₂(μ_2 - η^2 : η^3 -cot) **2**, with Ge–Ar' moieties held on opposite sides of a cot ring that exhibits somewhat greater deviation from planarity than that in **2** (Figure 1). The average C–C distance 1.417(3) Å and C–C–C angle 133.2(2)°, although they are both consistent with an aromatic ring structure,¹⁸ also display differences from those in the tin compound (1.411(6) Å and 134.4(4)°).¹⁶ In addition, unlike in **2**, each Ge atom is bound primarily to two carbons with Ge1–C2 = 2.207(2) Å and Ge1–C3 = 2.239(2) Å and less strongly to an adjacent carbon Ge1–C1 2.433(2) Å. The Ge atoms are slipped toward each other, accounting for some of the small differences of C–C distances within the ring. NMR data are consistent with a fluxional, aromatic unit: the ¹H and ¹³C{¹H} NMR spectra taken immediately after dissolution of **4** (C₆D₆) gave a single resonance at δ 5.32 and 100.0 ppm respectively. These shifts may be compared to those found in the tin analogue **2** (δ 5.66 and 97.1 ppm) and suggest a diminution of the aromatic character of the C₈H₈ moiety, which is consistent with the structural changes between the tin and germanium

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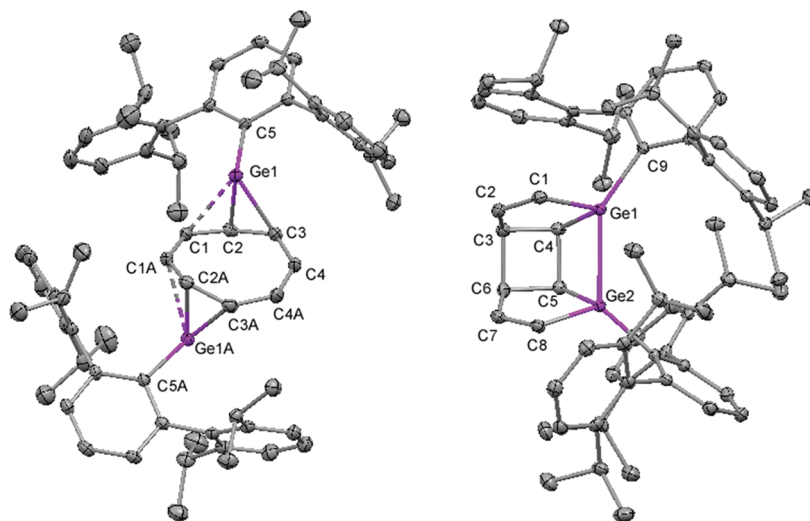


Figure 1. Thermal ellipsoid (50%) plots of **4** (left) and **5** (right). H atoms are not shown. Selected bond lengths [Å] and bond angles [deg] for **4**: Ge1–C1 2.433(2), Ge1–C2 2.207(2), Ge1–C3 2.035(2), C1A–C1 1.444(3), C1–C2 1.401(2), C2–C3 1.429(2), C3–C4 1.443(2), C4–C4A 1.347(3); C1A–C1–C2 133.9(1), C1–C2–C3 131.3(2), C2–C3–C4 133.3(2), C3–C4–C4A 134.1(1). **5**: Ge1–Ge2 2.5663(2), Ge1–C1 1.956(2), Ge2–C8 1.950(2), Ge1–C9 1.969(2), Ge2–C9 2.004(2), Ge1–C4 1.979(2), Ge2–C5 1.985(2), C1–C2 1.323(2), C7–C8 1.330(2), C2–C3 1.510(2), C7–C6 1.495(2), C3–C6 1.602(2), C3–C4 1.558(2), C4–C5 1.561(2), C5–C6 1.556(2); Ge1–C1–C2 109.9(1), Ge2–C8–C7 110.1(1), C6–C7–C8 120.9(1), C1–C2–C3 120.5(1).

derivative noted above.¹⁶ No decoalescence of the signal at temperatures as low as $-60\text{ }^{\circ}\text{C}$ was observed. A single absorption is found in the UV–vis spectrum at 290 nm, at higher energy than the transition found in **2** (340 nm) representative of a larger HOMO–LUMO gap expected for a germylene vs stannylene.¹⁹ It seems probable that the initial step of the reaction is a [2 + 2] addition to afford a 1,2-digermanacyclobutene species which because of the strained geometry and steric congestion rapidly dissociates the Ge=Ge bond²⁰ and permits reorientation of the germyl groups to form **4**.

Although solid samples of **4** are indefinitely stable under an inert atmosphere, solutions under N_2 fade from bright yellow to colorless over a period of days (with or without external sources of light)²¹ and a new set of resonances is observed in the ^1H NMR spectrum attributable to the thermodynamic product $(\text{Ar}'\text{Ge})_2(\text{C}_8\text{H}_8)$ (**5**). At room temperature clean conversion of a 2.0 mM solution of **4** to **5** is achieved in 5 days; pure samples of **5** are also obtained from the original reaction mixture after a similar time. This reaction is accelerated by mild heating, and full conversion is observed after 6 h at $60\text{ }^{\circ}\text{C}$. **5** is a colorless, air stable solid that can be recrystallized from Et_2O . X-ray data reveal that **5** is an isomer of **4** in which the cot has undergone internal cyclizations and C–C bond cleavage to give a diene cage molecule that can be considered a heavy group 14 element analogue of hypostrophene ($\text{C}_{10}\text{H}_{10}$),²² with replacement of two C–H groups with two Ge–Ar' moieties at the 3,10-positions (Figure 1). Unlike in **4**, the tetravalent Ge atoms in **5** are bound to each other by a single bond at 2.566(1) Å which is considerably longer than the 2.44 Å in elemental germanium and is suggestive of weakness. The molecule contains two unsaturated C=C bonds (C1–C2 1.323(2) Å and C7–C8 1.330(2) Å) each of which are directly bound to a Ge atom as part of an internal five-membered ring. The Ge–C_{sp²} distances of Ge1–C1 1.956(2) Å and Ge2–C8 1.950(2) Å are in accord with previously reported values for this type of bond (1.927–2.016 Å)^{23,24} and very slightly shorter than the Ge–C_{sp³} distances of Ge1–C4 1.979(2) Å and Ge2–C5 1.985(2) Å. A slight elongation of the C3–C6 bond in the four-membered carbocycle is observed due to the allylic character of these carbons (C3–C6 1.602(2) Å versus C3–C4 1.558(2) Å, C4–C5 1.561(2) Å, C5–C6 1.556(2)

Å). The ^1H and ^{13}C NMR spectra (C_6D_6) of **5** are both consistent with this structure.

The UV–vis spectrum of **5** showed a single absorbance at 260 nm, a higher energy than that for **4**. Monitoring the reaction by ^1H NMR spectroscopy shows that the reaction displays first-order kinetics ($t_{1/2} = 60\text{ h}$ at 293 K, 1.9 mM **4** in C_6D_6) with activation parameters $\Delta H^\ddagger = 14.9\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -6.2\text{ cal mol}^{-1}\text{ K}^{-1}$. The negative entropy change suggests a more ordered transition state at the rate-determining step and is inconsistent with a multistep route between several intermediates of high energy (i.e., at the rate-determining transition). Remarkably, we have found this reaction to be fully reversible: the heating of solid samples of **5** under an inert atmosphere to temperatures above $120\text{ }^{\circ}\text{C}$ results in quantitative conversion to **4**, as measured subsequently by ^1H NMR spectroscopy. Reversible coordination of substrates to heavy group 14 element centers has been recently documented with ethylene (see above)¹⁵ and isonitriles,²⁵ and reversible photochemical isomerization in these types of compounds has been shown between a thermally unstable bicycletetrasilane derivative and its preferred cyclo-tetrasilene form.²⁶ The transformation of **4** \leftrightarrow **5** is unusual in that a significant electronic and structural change occurs that involves the multiple formation/cleavage of C–C and Ge–Ge bonds, and either form can be isolated and stored indefinitely at room temperature.

In order to clarify these initial findings, we carried out a series of DFT calculations at the B3LYP/LANL2DZ²⁷ level on simplified model systems in which the Ar' groups have been substituted by phenyl groups. The most relevant geometrical parameters are summarized in Figure 2. Both structures, **4'** and **5'**, are local minima on the potential energy surface. For the structure **4'**, the computed Ge–C bond distances are in reasonable agreement with the experimental values. Note that the organic C_8H_8 ring in **4'** also exhibits a deviation from planarity, although the C–C bond lengths are consistent with an aromatic ring structure. Aromaticity was probed by computing nucleus-independent chemical shifts (NICS)^{28a} and the z-component of the induced magnetic field ($B_{\text{ind}}^{\text{z}}$)^{28b} at the ring center. The values for both descriptors (-10.9 and -15.9 ppm , respectively)^{28c} reveal aromatic character. In the case of **5'**, the calculated Ge–Ge and C–Ge bond lengths also

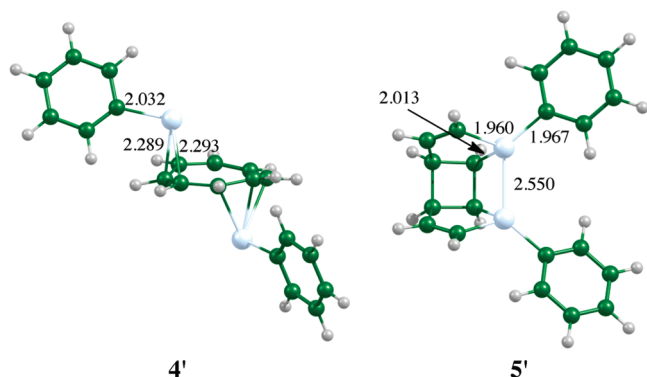


Figure 2. Selected internuclear distances in angstroms calculated for the model structures **4'** and **5'**.

closely match the experimental ones. The Wiberg bond index (WBI) values support the bonding description of **5**; i.e., the Ge–Ge (WBI_{Ge–Ge} = 0.80), Ge–C (WBI_{Ge–C} = 0.80), and all C–C (WBI_{C–C} = 0.93) bonds are single bonds. Computed HOMO/LUMO gaps (**4'** 358 nm; see Figure S5 for a depiction of these molecular orbitals; **5'** 245 nm) parallel the primary absorptions observed experimentally in the UV–vis spectra (cf. **4** 290 nm; **5** 260 nm). The calculations also indicate that **5'** is more stable than **4'** by 16.2 kcal mol^{−1} (including the zero-point energy) supporting the experimental determination that **5** is the thermodynamic product. Interestingly, our DFT calculations show that, in the case of the Sn analogue, it is the inverse sandwich structure **2'** that is more stable than its diene cage isomer by 37.1 kcal mol^{−1}. This is consistent with the fact that the cage form is not observed when distannyne **1** reacts with cot.¹⁶

The presence of a Ge–Ge bond in **5** suggests that this product derives from either an intermolecular reaction of the digermynes **3** with C₈H₈ in an intermediate state or an intramolecular rearrangement of **4** in which germynyl fragments on opposite faces of a cot ring participate in both C–C cleavage and Ge–Ge σ bond formation. The former seems unlikely on the basis that adding an excess of digermynes **3** to solutions of **4** does not affect the rate of isomerization to **5**. Using DFT calculations we were able to locate the transition states related to the formation of species **5'** that give an initial insight into the mechanism of formation (see Scheme 1). Hypostrophene undergoes degenerate Cope rearrangement,²⁹ and a possible route to **5** may include a [3,3]-sigmatropic shift to give the most stable arrangement with GeAr' fragments in the 3,10-positions. Elegant work by Geiger and co-workers has shown that under applied voltage the metal centers in *anti*-(CpM)₂(μ_2 -cot) (M = Co, Ru) can insert reversibly into a C–C bond of the cot dianion with concomitant M–M bond formation presumably via so-called “flyover” complexes (CpM)₂C₈H₈.^{30,31} Nonetheless, this mechanism does not directly apply to the reactions of **4** as further internal cyclizations would be necessary to create the tetracyclic framework of **5**. Detailed quantum chemical calculations to explore the conversion of **4** to **5** are in progress.

In conclusion, the reaction between digermynes **3** and cot has yielded two interconvertible isomers. Complete cleavage of the Ge≡Ge bond in **3** gave a new Ge(II) inverse sandwich cot complex **4** as the kinetic product, which slowly isomerizes in solution to give a tetracyclic diene-digermene **5**. Conversion back to **4** is achieved by heating solid samples of **5**. The metalloid character of low-valent germanium is reflected in the redox reaction to form a π -bound cot ligand in **4** which parallels low-valent metal chemistry (e.g., zerovalent s-block and lanthanide metals).^{18,32,33}

The spontaneous C–C cleavage reaction to give **5** has not been seen for structurally analogous transition metal compounds such as *syn*-(L)M₂(μ_2 : η^2 : η^2 -cot),³⁴ in which the cot contains two formal C=C bonds, whereas it occurs readily in the all-carbon congener hypostrophene, which undergoes a degenerate Cope rearrangement.^{29,35} The contrast between the behavior of **4** and the relative stability of its tin isomer is attributable mainly to the greater stabilization of the tin lone pairs.

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Supporting Information Available: Synthesis and characterization of **4** and **5**, tables of crystallographic data, details of kinetic measurements, complete ref 27, Cartesian coordinates of **4'** and **5'**, and CIFs for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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