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 digermyne 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-digermane, 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 ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) 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_{sp^3} ($n = 1-3$),[3−5] C_{sp^2}−C_{sp^2} (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_{sp^2}=C_{sp^2} 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_{sp^3}−C_{sp^3} cleavage of pentanenitrile by uncomplexed Ni_2^+ 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 temperature[15] 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 Digermyne
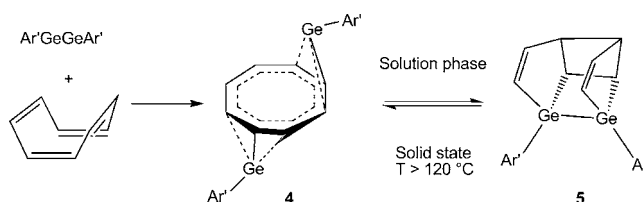
In this paper we report the results of the more complex reaction between the digermyne Ar′GeGeAr′ (**3**)[17] and cot, which gives an isomeric mixture of both a germanium inverse sandwich cot species as the primary kinetic product and a tetracyclic cage-like digermane as the thermodynamic product that can be isolated in quantitative yield. Remarkably, the formation of the latter species resulted from cleavage of an unstrained C=C bond in C_8H_8 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^2-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
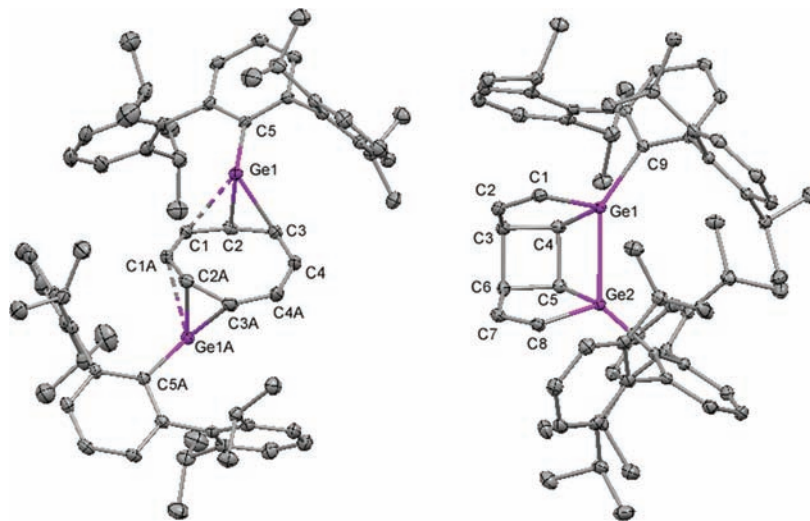
Figure 1. Thermal ellipsoid (50%) plots of **4** (left) and **5** (right). H atoms are not shown. Selected bond lengths [Å] and bond angles [deg] for **4**: Ge1−C1 2.433(2), Ge1−C2 2.207(2), Ge1−C3 2.239(2), Ge1−C5 2.035(2), C1A−C1 1.444(3), C1−C2 1.401(2), C2−C3 1.429(2), C3−C4 1.443(3), C4−C4A 1.347(3); 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−C39 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 °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 bond[20] 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 ^{1}H NMR spectrum attributable to the thermodynamic product $(Ar'Ge)_2(C_8H_8)$ (**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 °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 $(C_{10}H_{10})$,[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 $Ge-C_{sp^2}$ 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 $Ge-C_{sp^3}$ 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 ^{1}H 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 ^{1}H NMR spectroscopy shows that the reaction displays first-order kinetics ($t_{1/2}$ = 60 h at 293 K, 1.9 mM **4** in C_6D_6) with activation parameters $\Delta H^{\ddagger}$ = 14.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −6.2 cal mol^{-1} 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 °C results in quantitative conversion to **4**, as measured subsequently by ^{1}H 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 bicyclotetrasilane derivative and its preferred cyclotetrasilene form.[26] The transformation of **4** ↔ **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/LANL2DZ[27] 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^{ind}_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
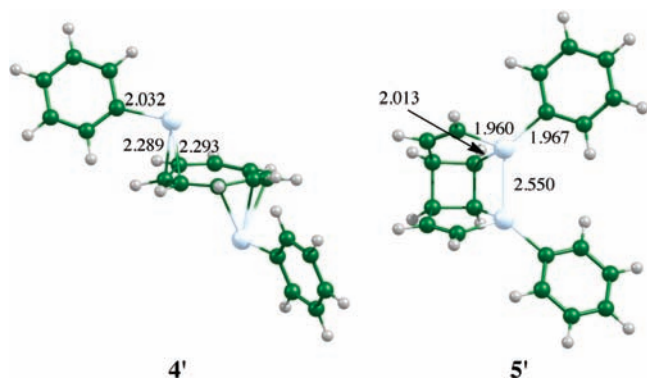
Figure 2. Selected internuclear distances in angstroms calculated for the model structures **4′** and **5′**.

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 digermyne **3** with C_8H_8 in an intermediate state or an intramolecular rearrangement of **4** in which germyl 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 digermyne **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)$_2$C$_8$H$_8$.[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 digermyne **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-digermane **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)M}$_2$(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.

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.

References

(1) (a) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870–883. (b) Jun, C. H. *Chem. Soc. Rev.* **2004**, *33*, 610–618. (c) Walter, M. D.; Tamm, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 3264–3266.
(2) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.
(3) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920–6922.
(4) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699–701.
(5) Gunay, A.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 8729–8735.
(6) Sattler, A.; Parkin, G. *Nature* **2010**, *463*, 523–526.
(7) Ellis, D.; McKay, D.; Macgregor, S. A.; Rosair, G. M.; Welch, A. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1–4.
(8) Park, J. T.; Shapley, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 6182–6184.
(9) Criegee, R. *Angew. Chem., Int. Ed.* **1975**, *14*, 745–752.
(10) (a) Suzuki, H.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11572–11573. (b) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **2002**, *124*, 3830–3831.
(11) (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291–4293. (b) Chisholm, M. H.; Davidson, E. R.; Quinlan, K. B. *J. Am. Chem. Soc.* **2002**, *124*, 15351–15358.
(12) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.
(13) Schlangen, M.; Schroder, D.; Schwarz, H. *Helv. Chim. Acta* **2005**, *88*, 1405–1420.
(14) Power, P. P. *Nature* **2010**, *463* (7278), 171–177.
(15) Peng, Y.; Ellis, B.; Wang, X.; Fettinger, J. C.; Power, P. P. *Science* **2009**, *325*, 1668–1670.
(16) Summerscales, O. T.; Wang, X.; Power, P. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 4788–4790.
(17) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785–1787.
(18) Hu, N.; Gong, L.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1988**, *352*, 61–66.
(19) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109* (9), 3479–3511.
(20) Some Ge−Ge bonds in digermenes are known to dissociate. See: (a) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. (b) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 239. (c) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.
(21) When the sample isomerizes under laboratory lighting, a slight red impurity is observed, which does not appear when the conversion occurs in the dark. This impurity is not significant and cannot be observed in the ^{1}H NMR.
(22) Pettit, R.; McKennis, J. S.; Brener, L.; Ward, J. S. *J. Am. Chem. Soc.* **1971**, *93*, 4957–4958.
(23) Hull, M. W.; Serov, S. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6695–6698.
(24) Yao, S.; Wüllen, C. V.; Driess, M. *Chem. Commun.* **2008**, 5393–5395.
(25) Peng, Y.; Wang, X. P.; Fettinger, J. C.; Power, P. P. *Chem. Commun.* **2010**, 943–945.
(26) Ueba-Ohshima, K.; Iwamoto, T.; Kira, M. *Organometallics* **2008**, *27*, 320–323.
(27) All calculations were done using the Gaussian 03: Frisch, M. J. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004 See Supporting Information for full reference.
(28) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Merino, G.; Heine, T.; Seifert, G. *Chem.—Eur. J.* **2004**, *10*, 4367. (c) The shielding tensors were calculated at the B3LYP/6-311++G(d,p) using the gauge-independent atomic orbital (GIAO) method.
(29) Tantillo, D. J.; Hoffman, R. *J. Org. Chem.* **2002**, *67*, 1419–1426.
(30) Geibel, W.; Wilke, G.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1978**, *160*, 139–147.
(31) (a) Edwin, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1987**, *109*, 7893–7894. (b) Geiger, W. E.; Salzer, A.; Edwin, J.; Philipsborn, W. V.; Piantini, U.;

Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113–7121. (c) Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314–2315.

(32) He, L.; Cheng, J.; Wang, T.; Li, C.; Gong, Z.; Liu, H.; Zeng, B.; Jiang, H.; Zhu, W. *Chem. Phys. Lett.* **2008**, *64*, 45–48.

(33) Hayes, R. G.; Thomas, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 6876.

(34) (a) Elschenbroich, C.; Heck, J.; Massa, W.; Schmidt, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 330–331. (b) Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905–2907. (c) Cotton, F. A.; Koch, S. A.; Schultz, A. J.; Williams, J. M. *Inorg. Chem.* **1978**, *17* (8), 2093–2098.

(35) Isolated samples of **5** do not undergo ambient Cope rearrangement, presumably due to the asymmetry induced by the Ge(Ar′) fragments and the consequent removal of degeneracy between isomeric forms.

JA107380P