

Supporting Information

C-H Activation of Cycloalkenes by Dimetallynes (Ge, Sn) under Ambient Conditions

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

Department of Chemistry, University of California, Davis, CA 95616, USA.

Fax: +1-520-752-8995

E-mail: pppower@ucdavis.edu

Experimental section

All reactions were performed with the use of modified Schlenk techniques under anaerobic and anhydrous conditions. Cyclopentene and 1,4-cyclohexadiene were purchased from Aldrich and distilled and dried (cyclopentene: sodium; 1,4-cyclohexadiene: molecular sieves) prior to use. Cyclopentadiene (CpH) was cracked immediately before use.

(Ar'Ge)₂ and cyclopentadiene; synthesis of Ar'GeCp (3): to a solution of (Ar'Ge)₂ (**1**) (0.200 g, 0.21 mmol)¹ in 50 mL pentane, cyclopentadiene (54 μ L, 0.63 mmol) was added via syringe, resulting in a color change from dark red to pale yellow after 2 minutes. Recrystallization at -20°C overnight gave colorless crystals of the product **3** (0.184 g, 0.34 mmol 81% yield). m.p. 155 °C; ¹H NMR (300 MHz, C₆D₆, 298K): δ = 1.05 (d, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.35 (d, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz) 3.01 (sept, 4H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 5.85 (s, 5H, C₅H₅), 7.10–7.38 ppm (m, 9H, *m*-C₆H₃, *p*-C₆H₃, *m*-Dipp, and *p*-Dipp; Dipp = 2,6-ⁱPr₂C₅H₃); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298K): δ = 22.9 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 31.2 (CH(CH₃)₂), 112.7 (C₅H₅), 123.6 (*m*-Dipp), 127.1 (*p*-C₆H₃), 129.0 (C_{sp2}H), 129.2 (*o*-Dipp), 138.0 (*m*-C₆H₃), 143.2 (*p*-Dipp), 147.5 (*i*-Dipp), 167.2 (*o*-C₆H₃).

(Ar'Sn)₂ and cyclopentadiene; synthesis of Ar'Sn(Cp) (4): (Ar'Sn)₂ (**2**) (0.250 g, 0.24 mmol)² and cyclopentadiene (61 μ L, 0.72 mmol) were reacted in a similar fashion as with digermynes **1** giving an immediate color change from green to red. The solution was stirred for 24 hours in which time the initial bright red color slowly faded to light yellow-orange. Washing with pentane and recrystallization at -20°C from toluene overnight gave the product Ar'Sn(η^1 -Cp) (**4**) as colorless blocks (0.208 g, 0.36 mmol, 74% yield). m.p. 185 °C (dec.); ¹H NMR (300 MHz, C₆D₆,

298K): δ = 1.05 (d, 12H, *o*-CH(CH₃)₂, $^3J_{\text{HH}}$ =6.9 Hz), 1.36 (d, 12H, *o*-CH(CH₃)₂, $^3J_{\text{HH}}$ =6.9 Hz) 3.01 (sept, 4H, CH(CH₃)₂, $^3J_{\text{HH}}$ =6.9 Hz), 5.85 (s, 5H, C₅H₅), 7.09–7.35 ppm (m, 9H, *m*-C₆H₃, *p*-C₆H₃, *m*-Dipp, and *p*-Dipp); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 100.6 MHz, 298K): δ = 22.8 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 30.8 (CH(CH₃)₂), 110.2 (C₅H₅), 123.5 (*o*-C₆H₃), 126.6 (*m*-Dipp), 129.0 (*p*-C₆H₃), 129.6 (*o*-Dipp), 138.9 (*m*-C₆H₃), 144.4 (*p*-Dipp), 147.2 (*i*-Dipp), 188.3 (*i*-C₆H₃); $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C₆D₆, 186.3 MHz, 298K) δ = 94 ppm.

Ar'Ge(Cp) (3) Metathesis Route: To a solid mixture of (Ar'GeCl)₂ (0.300 g, 0.30 mmol) and NaCp (0.040 g, 0.46 mmol), 50 mL of diethyl ether was added; the solution was stirred overnight. After removal of volatiles, the product was extracted with hexanes, filtered through a pad of celite and recrystallized at -20°C (0.216 g, 0.40 mmol, 68% yield).

Ar'Sn(Cp) (4) could be prepared by a similar route from (Ar'SnCl)₂ (0.250 g, 0.23 mmol) and NaCp (0.040 g, 0.46 mmol), albeit using toluene to extract and recrystallize rather than hexanes (0.205 g, 0.35 mmol, 78% yield).

(Ar'Ge)₂ and cyclopentene: To a solution of (Ar'Ge)₂ (**1**) (0.200 g, 0.21 mmol) in 50 mL pentane, cyclopentene (56 μL , 0.63 mmol) was added via syringe, resulting in a color change from dark red to emerald green over a period of 12 hours. Recrystallization at -20°C overnight gave colorless crystals of **3** (0.071 g, 0.13 mmol, 31% yield).

(Ar'Ge)₂ and 1,4-cyclohexadiene; synthesis of syn-7-cyclohex-2-ene-anti-(Ar')-7-germa-bicyclo[2.2.1]hept-2-ene (7): To a solution of (Ar'Ge)₂ (**1**) (0.400 g, 0.42 mmol) in 50 mL pentane, 1,4-cyclohexadiene (200 μL , 2.11 mmol) was added via syringe, resulting in a color change from dark red to yellow over a period of 5 hours. Reduction in volume to ca. 10 mL at room temperature induced precipitation of **7** as a colorless crystalline solid. After 12 hours at room temperature, the product was isolated from the mother liquor (0.249 g, 0.39 mmol, 47% with respect to Ge). Cooling of the mother liquor to -20°C overnight gave orange crystals of (Ar'GeH)₂ (0.092 g, 0.10 mmol, 24% with respect to Ge).³

Characterizing data for **7**: ^1H NMR (300 MHz, C₆D₆, 298K): δ = 0.95 (d, 3H, $^3J_{\text{HH}}$ =6.9 Hz), 0.97 (d, 3H, $^3J_{\text{HH}}$ =6.9 Hz), 1.04 (d, 3H, $^3J_{\text{HH}}$ =6.9 Hz), 1.10 (d, 3H, $^3J_{\text{HH}}$ =6.9 Hz), 1.30 (s, 1H), 1.34–1.37 (m, 8H), 1.44–1.55 (m, 1H), 1.63–1.69 (m, 1H), 1.75–1.83 (m, 1H), 1.89 (br, 1H), 2.91 (sept,

H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 3.01 (sept, 2H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 3.16 (sept, H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 4.90 (d, H, C₆H₈-H₂, ³J_{HH} = 10.3 Hz), 5.36 (dd, H, C₆H₈-H₃, ³J_{HH} = 3.3, 10.3 Hz), 6.07 (dt, 2H, C₆H₉-H₂, H₃, ³J_{HH} = 6.6, 6.6, 12.5 Hz), 6.98–7.35 ppm (m, 9H, *m*-C₆H₃, *p*-C₆H₃, *m*-Dipp); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298K): δ = 144.84, 139.41, 132.19, 130.13, 129.85, 128.36, 127.73, 122.60, 122.60, 122.08, 121.51, 121.08, 104.81, 33.67, 33.49, 29.97, 29.79, 28.89, 26.35, 25.53, 25.30, 25.01, 24.81, 23.89, 22.79, 22.72, 21.23, 20.60.

NMR discussion for 7: Three olefinic resonances were found, one at δ 6.07 ppm (dt) for the vinylic protons on the 1-cyclohex-2-enyl ligand, similar to the shift reported for (L)Sn(*c*-C₆H₉)(I) (δ 5.91 ppm).⁴ The vinylic protons on the Ge-bridged 1,4-cyclohex-2-enyl moiety meanwhile were found to exhibit diastereotopic resonances located upfield at δ 4.90 (d, ³J_{HH} = 10.3 Hz) and 5.36 ppm (dd, ³J_{HH} = 3.3, 10.3 Hz), confirmed to be coupled by COSY experiment. This inequivalence is due to the proximity of the 1-cyclohex-2-enyl group to the unsaturated bond in the germanorbornene moiety (see above) which induces an anisotropic effect according to the rotational conformation of the π bond in the 1-cyclohex-2-enyl ligand. This has been observed previously in *syn*-7-allylnorbornene compounds.⁵ It is surprising that coupling to the allylic CH proton is resolved at one methine position but not the other, however this type of behavior has been observed before in terphenyl-substituted germanium cage compounds.⁶ This asymmetry is further reflected by the observation of three diastereotopic resonances for the ⁱPr-CH protons on the Ar' ligand.

X- Ray Crystallography

Crystals of **5** and **7** were removed from a Schlenk tube under N₂ and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and quickly placed in a low temperature N₂ stream. The crystal structures were solved by direct methods using the SHELX version 6.1 program package. All non-hydrogen atoms were refined anisotropically. See below for more details.

Table S1. Crystal data and structure refinement for **5**.

Identification code	ots27fmi (JF2013)	
Empirical formula	C ₃₅ H ₄₂ Ge	
Formula weight	535.28	
Temperature	90(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 18.0854(15) Å	$\alpha = 90^\circ$.
	b = 10.1004(8) Å	$\beta = 92.544(2)^\circ$.
	c = 33.039(3) Å	$\gamma = 90^\circ$.
Volume	6029.3(8) Å ³	
Z	8	
Density (calculated)	1.179 Mg/m ³	
Absorption coefficient	1.508 mm ⁻¹	
F(000)	2272	
Crystal size	0.33 x 0.24 x 0.13 mm ³	
Crystal color and habit	Colourless Block	
Diffractometer	Bruker APEX-II Duo CCD	
Theta range for data collection	2.68 to 70.18°.	
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -37 ≤ l ≤ 39	
Reflections collected	13724	
Independent reflections	5553 [R(int) = 0.0243]	
Observed reflections (I > 2σ(I))	5502	
Completeness to theta = 70.18°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8258 and 0.6336	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	5553 / 0 / 493	
Goodness-of-fit on F ²	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0277, wR2 = 0.0757	
R indices (all data)	R1 = 0.0279, wR2 = 0.0758	
Largest diff. peak and hole	0.435 and -0.359 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **7**.

Identification code	ots34fmi (JF2031 Update)	
Empirical formula	C42 H54 Ge	
Formula weight	631.44	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 15.8497(12) Å	$\alpha = 90^\circ$.
	b = 25.8968(11) Å	$\beta = 95.87^\circ$.
	c = 17.0594(7) Å	$\gamma = 90^\circ$.
Volume	6965.4(7) Å ³	
Z	8	
Density (calculated)	1.204 Mg/m ³	
Absorption coefficient	0.907 mm ⁻¹	
F(000)	2704	
Crystal size	0.16 x 0.15 x 0.15 mm ³	
Crystal color and habit	Colorless Block	
Diffractometer	Bruker APEX-II CCD	
Theta range for data collection	2.29 to 27.50°.	
Index ranges	-20 ≤ h ≤ 20, -33 ≤ k ≤ 33, -22 ≤ l ≤ 22	
Reflections collected	29533	
Independent reflections	7988 [R(int) = 0.0447]	
Observed reflections (I > 2σ(I))	6494	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8775 and 0.8662	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	7988 / 8 / 491	
Goodness-of-fit on F ²	1.023	
Final R indices [I > 2σ(I)]	R1 = 0.0351, wR2 = 0.0740	
R indices (all data)	R1 = 0.0490, wR2 = 0.0790	
Largest diff. peak and hole	0.416 and -0.279 e.Å ⁻³	

Structural Discussion for 7

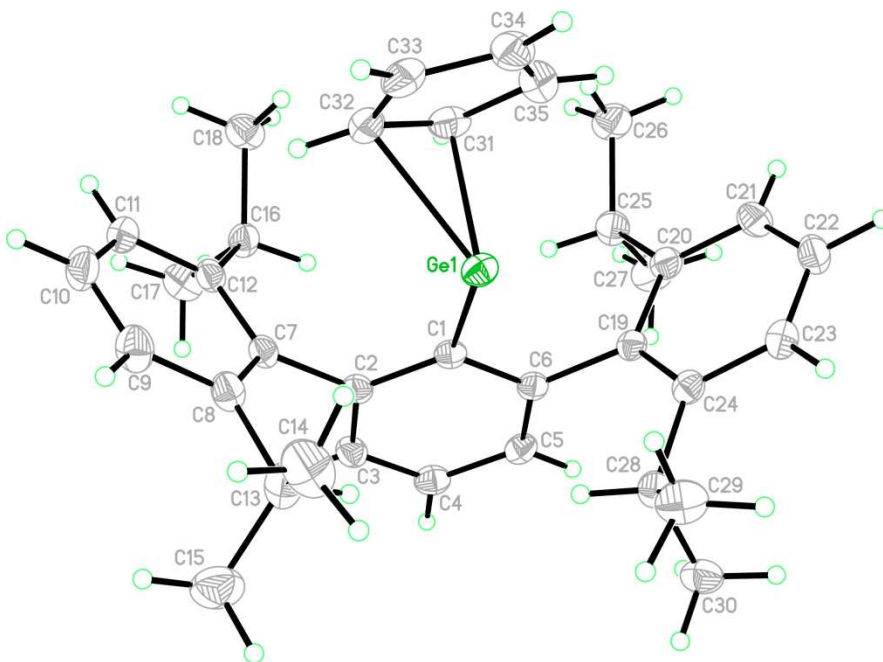
Structural determination of **7** showed a tetrahedral coordination environment around the Ge atom which is bound in a bicyclic fashion to a 1,4-cyclohex-2-enyl fragment to give a 7-germa-bicyclo[2.2.1]hept-2-ene moiety and also bound through one carbon to a disordered 1-cyclohex-2-enyl ligand. The geometry 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.⁷ The data were of sufficient quality to freely refine all H atoms, and clearly show an CH₂-CH₂ moiety (C2-C3 1.550(3) Å) directed towards the terphenyl ligand and an unsaturated CH=CH group (C5-C6 1.330(3) Å) *syn* to the 1-cyclohex-2-enyl fragment. The latter was found to be coordinated *pseudo*-equatorially to Ge and disordered in two rotational conformations approximately 180° to one another with virtually equal occupancy, similar to that previously observed in the structure of (L)Sn(*c*-C₆H₉)(Br) (L = C₂(SiMe₃)₄C₂H₄).⁸ Further disorder is also observed which could be due to libration of the aliphatic propylene backbone. This may be particularly facile in this compound due to the cavity created by the adjacent large ligands, leaving a space for the smaller C₆H₉ ligand to undergo rotational-vibrational motions. Unfortunately this has prevented us from determining the bond angles and distances in this fragment with a high degree of accuracy and may be a possible reason for the anomalously short single bond between C8 and C9 (1.46(3) Å). Nonetheless, short bonds between C11 and C12 (1.33(2) Å) and C8b and C9b (1.39(3) Å) are clearly visible and are accompanied by wider internal angles C_α-C_β-C_γ (114(2) and 119.5(16)°) and C_β-C_γ-C_δ (127.9(9) and 129.9(11)°) consistent with sp² hybridization and similar to those found in (L)Sn(*c*-C₆H₉)(Br) (122.9(3) and 125.4(5)°).⁸

JF2013 (OTS27)

A colorless block with approximate orthogonal dimensions 0.132 x 0.244 x 0.333 mm³ was placed and optically centered on the Bruker APEX Duo⁹ CCD system at -183°C (90K). Indexing of the unit cell was attempted using a random set of reflections collected from three series of 0.5° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Eighteen ω -scan and phi-scan data frame series were collected [CuK α] with 0.5° wide scans, 10, 15 or 20 seconds per frame dependent upon detector two theta angle. The crystal to detector distance was 4.96 cm, thus providing a complete sphere of data with processing to 2 θ_{max} = 140.36°.

Structural determination and Refinement:

All crystallographic calculations were performed on an iMac with 2.80GHz i7 quad core processor and 8GB of memory. A total of 23264 reflections were collected and corrected for Lorentz and polarization effects with SAINT⁹ and absorption using Blessing's method as incorporated into the program SADABS^{10,11} with 5847 unique. The



SHELXTL¹² program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences, and intensity statistics indicated the centrosymmetric non-standard monoclinic space group I2/a (no.15). The structure was determined by direct methods with the successful location of nearly all of the non-hydrogen atoms using the program XS¹². The structure was refined with XL¹³. The 23264 data collected were merged based upon identical indices to 14088 data [R(int)=0.0250] and then merged for least squares refinement to 5553 unique data [R(int)=0.0243]. A single least-squares difference-Fourier cycle was required to locate the remaining non-hydrogen atoms. Hydrogen atoms were initially idealized and then allowed to refine freely throughout the final refinement stages. The final structure was refined to convergence with R(F)=2.79%, wR(F²)=7.58%, GOF=1.062 for all 5553 unique reflections [R(F)=2.77%, wR(F²)=7.57% for those 5502 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

References.

- (1) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785-1787.
- (2) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930.
- (3) Spikes, G. H.; Fettingner, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005** *127*, 12232.
- (4) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 1041.
- (5) Holtsclaw, J.; Koreeda, M. *Org. Lett.* **2004**, *6*, 3719.
- (6) Summerscales, O. T.; Jiménez-Halla, J. O. C.; Merino, G.; Power, P. P. *J. Am. Chem. Soc.* **2011** *133*, 180.
- (7) Belzner, J.; Ihmels, H.; Kniesel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305.
- (8) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2008**, *27*, 1041.
- (9) Bruker (2010) APEX (Version 2010-1) and SAINT (Version 7.68a). Bruker AXS Inc., Madison, Wisconsin, USA.
- (10) An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). *Acta Cryst.*, *A51*, 33-38.
- (11) Sheldrick, G.M., SADABS (2008) Version 2008/2, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.
- (12) Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- (13) Sheldrick, G. M., (1997). SHELXS97 and SHELXL97. Universität Göttingen: Göttingen, Germany.