Cyclization/Hydrogermylation of Functionalized 1,6-Dienes Catalyzed by Cationic Palladium Complexes

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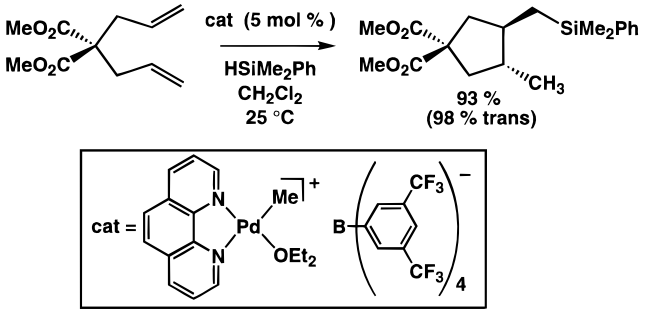
A 1:1 mixture of the palladium phenanthroline complex (phen)Pd(Me)Cl and $NaBAr_4$ (phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$) catalyzed the reaction of 4,4-disubstituted 1,6-dienes with trialkylgermanes at 80 °C in 1,2-dichloroethane (DCE) to form R_3GeCH_2-substituted cyclopentanes in good yield with high trans selectivity.

Introduction

We recently reported several related protocols for the cyclization/hydrosilylation of 1,6-[1,2] and 1,7-dienes[2,3] and for the asymmetric cyclization/hydrosilylation of 1,6-dienes[4] catalyzed by cationic palladium complexes (Scheme 1). These procedures were characterized by high activity, good stereoselectivity and functional group compatibility, and low air and moisture sensitivity. Cyclization/hydrosilyation[5] constitutes a subset of a larger body of catalytic cyclization/addition protocols which employ $HSnBu_3$,[6] X−CN (X = $SiMe_3$,[7] $GeMe_3$[8]), X−SiR_3 (X = SiR_3,[9] SnR_3,[9] BR_2[10]), or X−SnR_3 (X = SnR_3,[9] BR_2[11]) as stoichiometric reductants. Although procedures for the transition-metal-catalyzed hydrogermylation of alkynes,[12,13] alkenes,[14] and allenes[15] have been developed, cyclization/hydrogermylation has not been demonstrated. For this reason, we have investigated the potential of palladium-catalyzed cyclization/hydrogermylation and report our results herein.

Scheme 1



Results and Discussion

Our initial attempt to effect cyclization/hydrogermylation of dimethyl diallylmalonate (**1**) employed a procedure analogous to our optimized procedure for palladium-catalyzed cyclization/hydrosilylation.[2] For example, reaction of **1** and $HGeEt_3$ (1.2 equiv) in the presence of a 1:1 mixture of (phen)Pd(Me)Cl and $NaBAr_4$[16] (5 mol %) (phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$) in 1,2-dichloroethane (DCE) at room temperature for 1 h formed a 9:1 mixture of *trans*-1,1-dicarbomethoxy-3-[(triethylgermyl)methyl]-4-methylcyclopentane (**2**) and 1,1-dicarbomethoxy-3,4-dimethylcyclopentane (**3**) along with traces of isomers of **1** (∼5%), as determined by GC/MS analysis of the crude reaction mixture (Table 1, entry 1).[17] Evaporation of solvent and flash chromatography of the residue gave pure **2** in 67% yield as a single stereoisomer. The trans stereochemistry of **2** was assigned by analogy to the palladium-catalyzed cycliza-

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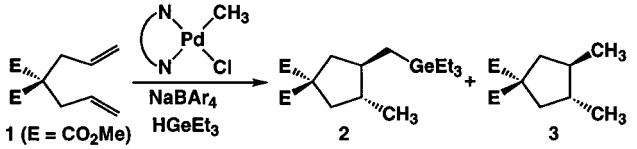
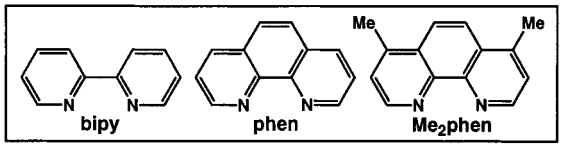
Table 1. Cyclization/Hydrogermylation of 1 and $HGeEt_3$ (1.2 Equiv) Catalyzed by a 1:1 Mixture of (N−N)Pd(Me)Cl and $NaBAr_4$ (5 mol %)



entry	solvent	N N	temp (°C)	time (min)	2:3[a]	yield 2 (%)[b]
1	DCE	phen	25	60	9:1	67
2	DCE	bipy	25	30	11:1	70
3	DCE	Me_2phen	25	60	11:1	73
4	CH_2Cl_2	phen	25	20	14:1	79
5	DCE	phen	80	5	26:1	79



[a] Ratio determined by GC analysis of the crude reaction mixture. [b] Yield refers to isolated material of >95% purity.

tion/hydrosilylation of **1** and $HSiEt_3$, which gave exclusively *trans*-1,1-dicarbomethoxy-3-[(triethylsilyl)methyl]-4-methylcyclopentane (**4**),[1] and by the close similarity between the NMR spectra of carbocycles **2** and **4**.[18]

The efficiency of cyclization/hydrogermylation was probed as a function of ligand, solvent, and temperature in an effort to improve chemoselectivity and yield. For example, use of (2,2′-bipyridine)Pd(Me)Cl or the more electron-rich complex (Me_2phen)Pd(Me)Cl (Me_2phen = 4,7-dimethyl-1,10-phenanthroline) as precatalysts led to slight improvements in selectivity and yield (Table 1, entries 2 and 3). More substantial improvement was observed upon substitution of CH_2Cl_2 for DCE, which increased the chemoselectivity to 14:1 and improved the yield of **2** to 79% (Table 1, entry 4). Alternatively, the selectivity and yield increased with increasing temperature, and at 80 °C in DCE, a 26:1 ratio of **2** to **3** and an 79% isolated yield of **2** were obtained (Table 1, entry 5). Attempts to employ <5 mol % of catalyst led to incomplete conversion.

The scope of the cyclization/hydrogermylation protocol was probed with respect to the diene and germane at 80 °C in DCE employing a 1:1 mixture of (phen)Pd(Me)Cl and $NaBAr_4$. For example, while trialkylgermanes such as $HGeEt_3$ and $HGeBu_3$ reacted efficiently with **1** in the presence of the palladium catalyst (Table 2, entry 1), germanes such as $HGe(SiMe_3)_3$ and $HGePh_3$ failed to react under these conditions. Cyclization/hydrogermylation required the presence of a homoallylic ester, ketone, or ether directing group on the diene to effect cyclization, as was observed for the corresponding cyclization/hydrosilylation procedure.[2] For example, dienes which possessed a homoallylic carbomethoxy, carbobenzyloxy, acetyl, benzoyl, methoxymethyl, acetoxymethyl, or (trimethylacetoxy)methyl group underwent cyclization/hydrogermylation with $HGeEt_3$ in good yield and with good trans selectivity (Table 2, entries 2−8). In the case of dienes which possessed two dissimilar homoallylic substituents, cyclization/hydrosilylation led to the formation of mixtures of C-1 diastereomers (Table 2, entries 3−5).

The palladium-catalyzed cyclization/hydrogermylation procedure tolerated allylic substitution. For example, reaction of $HGeEt_3$ with 4,4-dicarbomethoxy-3-methyl-1,6-heptadiene led to the isolation of the corresponding carbocycle as a 1:1 mixture of C-2 diastereomers along with traces (~3%) of a third isomer (Table 2, entry 9). By analogy to palladium-catalyzed cyclization/hydrosilylation,[1−4] the major regioisomer is presumably that generated from transfer of the germyl group to the less hindered olefin.[19] In a similar manner, 4,4-dicarbomethoxy-3,3-dimethyl-1,6-heptadiene, which possesses a single disubstituted allylic carbon atom, underwent cyclization/hydrogermylation with excellent regio- and diastereoselectivity (Table 2, entry 10). Dienes which possessed olefinic substitution failed to undergo cyclization/hydrogermylation, in contrast to the corresponding protocol employing hydrosilanes.[20]

Cationic late-transition-metal alkyl complexes,[21] including palladium phenanthroline complexes,[22] react with hydrosilanes to form metal−silyl complexes with loss of alkane. As a result, we have previously invoked palladium−silyl complexes as intermediates in the palladium-catalyzed cyclization/hydrosilylation of dienes.[1−4] By analogy, we propose a plausible mechanism for diene cyclization/hydrogermylation initiated by reaction of the cationic palladium−methyl complex **I** (L = solvent or other ligand)[16] with the hydrogermane to generate the palladium−germyl intermediate **II** (Scheme 2). β-Migratory insertion of an olefin of the diene into the Pd−Ge bond of **II** would form the palladium−alkyl intermediate **III**. Olefin coordination followed by β-migratory insertion into the Pd−C bond of **IV** would generate the palladium−alkyl intermediate **V**. Reaction of **V** with R_3GeH could then release the carbocycle and regenerate the palladium germyl complex **II** (Scheme 2).[23] In support of the proposed mechanism, several transition-metal germyl complexes have been isolated,[13,24,25] and the β-migratory insertion of both alkynes[25] and styrene[26] into a Pd−Ge bond has been observed.

In summary, mixtures of (phen)Pd(Me)Cl and $NaBAr_4$ catalyze the cyclization/hydrogermylation of functionalized 1,6-dienes to form germylated carbocycles in good

(18) Specifically, the ^{1}H NMR spectrum of **2** displayed a pair of one proton doublet of doublets at δ 1.03 (J = 2.4, 13.6 Hz) and δ 0.44 (J = 11.0, 13.7 Hz) assigned to the exocyclic methylene group which is indicative of the *trans*-C(3)−C(4) product: Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348.

(19) The minor isomer presumably results from transfer of the germyl group to the allylic-substituted olefin.

(20) 1,7-Dienes failed to undergo cyclization/hydrogermylation.

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(23) Although the mechanism by which the homoallylic functional groups promote cyclization has not yet been elucidated,[2] the oxygen atom may serve to fill the open coordination site generated by β-migratory insertion in the converstion of **II** to **III** or of **IV** to **V**.

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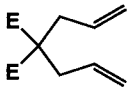
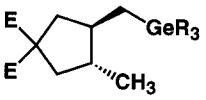
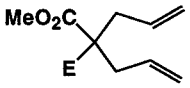
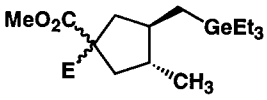
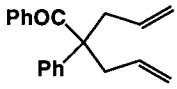
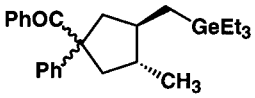
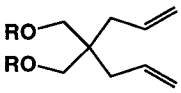
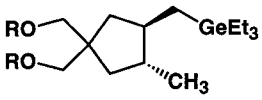
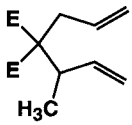
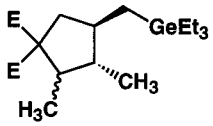
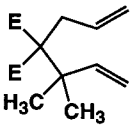
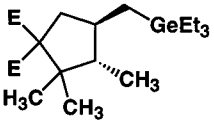
Table 2. Cyclization/Hydrogermylation of Functionalized Dienes Catalyzed by a 1:1 Mixture of (phen)Pd(Me)Cl and $NaBAr_4$ in DCE at 80 °C

entry	diene	germane	catalyst load (%)	carbocycle	yield (%)[a]	isomer ratio[b]
						
1	E = CO_2Me	$HGeBu_3$	5		77	>50:1
2	E = CO_2Bn	$HGeEt_3$	5		77	>50:1
						
3	E = Ph		5		79	2.5:1
4	E = COMe		5		72	1:1
						
5			10		79[c]	2.0:1
						
6	R = Me		5		84	>50:1
7	R = COMe		10		57	>50:1
8	R = CO*t*-Bu		5		73[d]	>50:1
						
9	E = CO_2Et		5		69	1:1[e]
						
10	E = CO_2Me		10		62	30:1

[a] Yields refer to isolated material which was >95% pure as determined by ^1H NMR, GC and elemental analysis. [b] Determined by capillary GC analysis of the crude reaction mixture. [c] Product contained 5% reduced diene. Analytically pure compound was obtained in 30% yield as a 10:1 mixture of diastereomers. [d] Gave 79% yield with 10% catalyst loading. [e] Also contained ~3% of a third isomer.

yield with excellent trans selectivity. The protocol displays several similarities with palladium-catalyzed cyclization/hydrosilylation, most notably the requirement of a homoallylic directing group. However, palladium-catalyzed cyclization/hydrogermylation is considerably slower, requires higher catalyst loading, and displays less generality than does palladium-catalyzed cyclization/hydrosilylation.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained on a General Electric QE 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C in $CDCl_3$, unless otherwise noted. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Flash chromatography was performed employing 200−400 mesh silica gel (EM) with mixtures of hexane and ethyl acetate as eluents. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). CH_2Cl_2 and DCE were distilled from CaH_2 under nitrogen. Germanes (Gelest), dimethyl diallylmalonate (Lancaster), and nitrogen ligands (Aldrich) were used as received. The syntheses of remaining dienes have been reported.[1−4] Precatalysts (N−N)PdMe(Cl) (N−N = phen, bipy, 4,7-dimethyl-1,10-phenanthroline) were prepared from the reaction of the appropriate ligand with (COD)Pd(Me)Cl[27] (COD = 1,5-cyclooctadiene) in benzene.[28] $NaB[3,5\text{-}C_6H_3(CF_3)_2]_4$ was prepared by a known procedure.[29]

***trans*-1,1-Dicarbomethoxy-3-[(triethylgermyl)methyl]-4-methylcyclopentane (2).** DCE (10 mL) was added via syringe to a mixture of (phen)Pd(Me)Cl (7 mg, 0.022 mmol) and $NaB[3,5\text{-}C_6H_3(CF_3)_2]_4$ (24 mg, 0.024 mmol) at 0 °C. Diene **1** (100 mg, 0.47 mmol) and triethylgermane (100 mg, 0.62 mmol) were added sequentially via syringe, and the resulting

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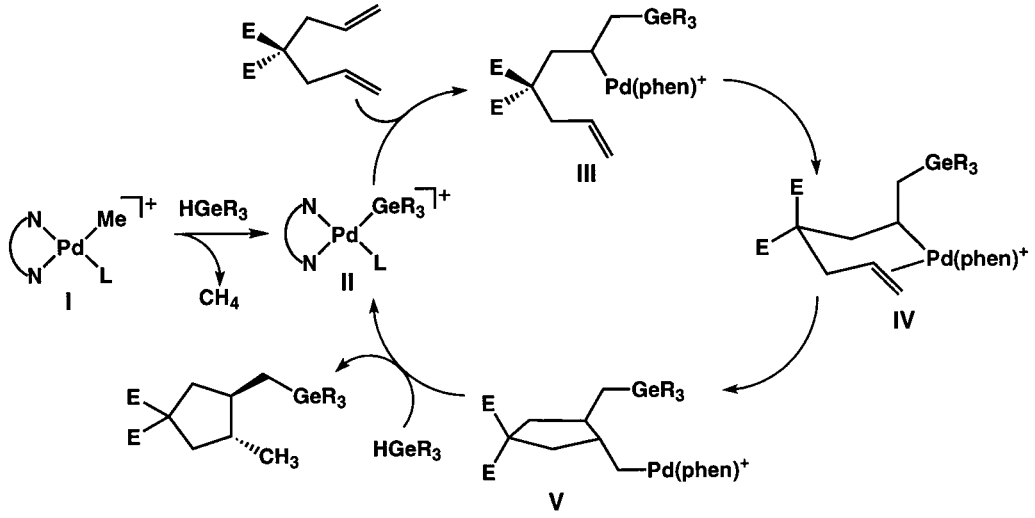
Scheme 2



solution was heated at 80 °C for 5 min to form a dark brown solution. Solvent was evaporated under vacuum, and the oily residue was chromatographed (SiO_2, 24:1 hexane/EtOAc) to give **2** (138 mg, 79%) as a colorless oil. ^{1}H NMR: δ 3.69 (s, 6 H), 2.52 (td, J = 6.7, 13.7 Hz, 2 H), 1.72−1.66 (m, 2 H), 1.5−1.4 (m, 2 H), 1.03 (dd, J = 2.4, 13.6 Hz, 1 H), 0.99 (t, J = 8.0 Hz, 9 H), 0.95 (d, J = 6.0 Hz, 3 H), 0.71 (q, J = 8.0 Hz, 6 H), 0.44 (dd, J = 11.0, 13.7 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.6, 58.2, 52.8, 44.7, 43.8, 43.2, 42.5, 17.5, 15.1, 9.2, 4.7. IR (neat, cm^{-1}): 2953, 1736, 1458, 1256, 1017. Anal. Calcd (found) for $C_{17}H_{32}GeO_4$: H, 8.65 (8.89); C, 54.74 (54.92).

3-[(Tributylgermyl)methyl]-1,1-dicarbomethoxy-4-methylcyclopentane (Table 2, Entry 1). ^{1}H NMR: δ 3.69 (s, 6 H), 2.51 (ddd, J = 6.5, 9.4, 13.3, 2 H), 1.67 (td, J = 10.7, 13.3 Hz, 2 H), 1.45 (m, 2 H), 1.30 (m, 12 H), 1.02 (dd, J = 2.4, 13.8 Hz, 1 H), 0.98 (d, J = 6.0 Hz, 3 H), 0.87 (br t, J = 6.8 Hz, 9 H), 0.70 (m, 6 H), 0.43 (dd, J = 11.0, 13.7 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.3, 57.3, 51.8, 43.7, 42.8, 42.2, 41.5, 26.7, 25.9, 16.6, 13.4, 13.0, 12.3. IR (neat, cm^{-1}): 2954, 1737, 1457, 1254, 1143. Anal. Calcd (found) for $C_{23}H_{44}GeO_4$: H, 9.70 (9.69); C, 60.42 (60.29).

1,1-Dicarbobenzyloxy-3-[(trimethylgermyl)methyl]-4-methylcyclopentane (Table 2, Entry 2). ^{1}H NMR: δ 7.30 (m, 10 H), 5.10 (m, 4 H), 2.53 (td, J = 6.9, 13.7 Hz, 2 H), 1.69 (dt, J = 10.8, 13.1 Hz, 2 H), 1.45 (m, 2 H), 0.97 (t, J = 7.9 Hz, 9 H), 0.94 (d, J = 5.7 Hz, 3 H), 0.68 (q, J = 8.0 Hz, 6 H), 0.41 (dd, J = 10.9, 13.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.4, 135.5, 128.3, 128.0, 127.8, 127.7, 66.8, 58.1, 44.3, 43.4, 42.8, 42.1, 17.2, 14.7, 8.8, 4.3. Anal. Calcd (found) for $C_{29}H_{40}GeO_4$: H, 7.68 (7.88); C, 66.32 (66.04).

1-Carbomethoxy-3-[(triethylgermyl)methyl]-4-methyl-1-phenylcyclopentane (Table 2, Entry 3). ^{1}H NMR: δ 7.28 (m, 5 H), 3.60 (s, 3 H), 2.9−2.8 (m, 1 H), 2.30 (m, 2 H), 1.02 (t, J = 7.9 Hz, 9 H), 1.01 (d, J = 6.3 Hz, 3 H), [0.75 (q, J = 8.0 Hz), 0.74 (q, J = 8.0 Hz), (2.5:1), 6 H], [0.62 (dd, J = 11.1, 13.5 Hz), 0.49 (dd, J = 10.5, 13.6 Hz), (1:2.5), 1 H]. ^{13}C{^{1}H} NMR: δ 175.8, 144.0, 127.6, 125.8, 104.9, 56.3, [51.7, 51.6 (1:2.5)], [45.5, 45.0 (2.5:1)], [44.0, 43.8 (1:2.5)], [43.4, 43.2 (2.5:1)], 42.5, [18.2, 17.3 (2.5:1)], [15.9, 15.0 (1:2.5)], 8.3, 3.9. IR (neat, cm^{-1}): 2869, 1760, 1495, 1141, 1018. Anal. Calcd (found) for $C_{21}H_{34}GeO_2$: H, 8.76 (9.08); C, 64.49 (64.79).

1-Acetyl-1-carbomethoxy-3-[(triethylgermyl)methyl]-4-methylcyclopentane (Table 2, Entry 4). ^{1}H NMR (400 MHz): δ 3.68 (s, 3 H), [2.49 (dd, J = 7.2, 13.2 Hz), 2.43 (dd, J = 6.4, 12.8 Hz), 1:1, 2 H], [2.09 (s), 2.08 (s), 1:1, 3 H], 1.60−1.45 (m, 2 H), 1.4−1.25 (m, 2 H), [0.99 (t, J = 8.0 Hz), 0.98 (t, J = 8.0 Hz) 1:1, 9 H], 0.93 (d, J = 6.4 Hz, 3 H), 0.70 (q, J = 8.0 Hz, 6 H), [0.42 (dd, J = 11.2, 13.6 Hz), 0.40 (dd, J = 11.2, 14.0 Hz) 1:1, 1 H)]. ^{13}C{^{1}H} NMR (100 MHz): δ 203.7, 174.5, 64.8, 52.8, [44.8, 44.5 (1:1)], [43.9, 43.6 (1:1)], [41.8, 41.3 (1:1)], [41.2, 40.7 (1:1)], 26.4, [17.5, 17.4 (1:1)], [15.1, 15.0 (1:1)], 9.2, 4.7. IR (neat, cm^{-1}): 2871, 1756, 1458, 1253, 1018. HRMS (CI) calcd (found) for $C_{17}H_{33}GeO_3$ (MH^+): 359.1641 (359.1653).

1-Benzyloxy-3-[(triethylgermyl)methyl]-4-methyl-1-phenylcyclopentane (Table 2, Entry 5). ^{1}H NMR: δ 7.63 (m, 2 H), 7.23 (m, 8 H), 3.03 (dd, J = 5.3, 11.9 Hz, 1 H), 2.56 (dd, J = 7.4, 13.7 Hz, 1 H), 1.99 (dd, J = 10.6, 13.8 Hz, 1 H), 1.60 (m, 1 H), 1.50−1.40 (m, 2 H), 1.08 (dd, J = 2.5, 13.6 Hz, 1 H), 0.98 (d, J = 6.6 Hz, 3 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.69 (q, J = 7.6 Hz, 6 H), 0.45 (dd, J = 11.1, 13.7 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 201.7, 146.7, 135.8, 132.0, 130.5, 129.2, 128.2, 126.4, 125.8, 61.0, 48.2, 46.1, 45.0, 44.6, 18.1, 15.3, 9.3, 4.7. IR (neat, cm^{-1}): 2950, 2869, 1678, 1374, 1227, 1015. HRMS (CI) calcd (found) for $C_{26}H_{35}GeO$ ($M - H^+$): 439.1900 (439.2062).

3-[(Triethylgermyl)methyl]-1,1-bis(methoxymethyl)-4-methylcyclopentane (Table 2, Entry 6). ^{1}H NMR: δ 3.31 (s, 6 H), 3.16 (m, 4 H), 1.70 (ddd, J = 6.5, 8.6, 13.1 Hz, 2 H), 1.4−1.3 (m, 2 H), 0.99 (t, J = 7.8 Hz, 9 H), 0.90 (d, J = 5.8 Hz, 3 H), 0.69 (q, J = 7.8 Hz, 6 H), 0.38 (dd, J = 11.0, 13.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 77.4, 77.3, 58.5, 44.3, 43.3, 42.5, 41.2, 40.7, 17.1, 14.6, 8.3, 3.8. IR (neat, cm^{-1}): 2948, 2822, 1460, 1198, 1110, 1018, 966. Anal. Calcd (found) for $C_{17}H_{36}GeO_2$: H, 10.52 (10.69); C, 59.17 (58.94).

1,1-Bis(acetoxymethyl)-3-[(triethylgermyl)methyl]-4-methylcyclopentane (Table 2, Entry 7). ^{1}H NMR: δ 3.90 (s, 4 H), 2.02 (s, 6 H), 1.74 (td, J = 6.4, 13.2 Hz, 2 H), 1.45−1.33 (M, 2 H), 1.05 (dd, J = 2.2, 13.7 Hz, 1 H), 0.99 (t, J = 7.7 Hz, 9 H), 0.93 (d, J = 5.8 Hz, 3 H), 0.68 (q, J = 7.8 Hz, 6 H), 0.38 (dd, J = 10.9, 13.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 170.5, 67.7, 67.6, 43.3, 42.4, 40.9, 40.2, 20.2, 16.9, 14.5, 8.2, 3.8. IR (neat, cm^{-1}): 2950, 2871, 1745, 1240, 1037. Anal. Calcd (found) for $C_{19}H_{36}GeO_4$: H, 9.05 (9.25); C, 56.90 (57.14).

1,1-Bis[(trimethylacetoxy)methyl]-3-[(triethylgermyl)-methyl]-4-methylcyclopentane (Table 2, Entry 8). ^{1}H NMR: δ 3.88 (m, 4 H), 1.75 (dt, J = 6.5, 14.3 Hz, 2 H), 1.42−1.35 (m, 2 H), 1.17 (s, 18 H), 1.07 (dd, J = 2.3, 13.1 Hz, 1 H), 0.98 (t, J = 7.9 Hz, 9 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.68 (q, J = 7.9 Hz, 6 H), 0.38 (dd, J = 11.0, 13.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 178.7, 68.5, 68.4, 44.2, 43.7, 43.5, 41.9, 41.1, 39.1, 27.4, 17.9, 15.4, 9.2, 4.8. IR (neat, cm^{-1}): 2953, 1731, 1480, 1461, 1282, 1148, 1034. Anal. Calcd (found) for $C_{25}H_{48}GeO_4$: H, 9.97 (10.10); C, 61.88 (61.74).

1,1-Dicarbomethoxy-4-[(triethylgermyl)methyl]-2,3-dimethylcyclopentane (Table 2, Entry 9). ^{13}C{^{1}H} NMR: δ [172.3, 171.2 (1:1)], [61.8, 60.3 (1:1)], [60.2, 60.1 (1:1)], 49.3, [46.2, 46.0 (1:1)], [42.0, 41.0 (1:1)], [40.4, 40.3 (1:1)], 39.7, [16.0,

15.4 (1:1)], [14.6, 14.1 (1:1)], [13.4, 13.3 (1:1)], 8.2, 3.8. Resonances assigned to a minor isomer were observed at δ 170.5, 62.9, 50.1, 46.5, 40.6, 17.7, 13.9, 10.2, 4.3. IR (neat, cm^{-1}): 2871, 1729, 1458, 1252, 1020. Anal. Calcd (found) for $C_{20}H_{38}GeO_4$: H, 9.23 (9.47); C, 57.87 (57.78).

1,1-Dicarbomethoxy-4-[(triethylgermyl)methyl]-2,2,3-trimethylcyclopentane (Table 2, Entry 10). ^1H NMR: δ 3.70 (s, 3 H), 3.65 (s, 3 H), 2.70 (m, 1 H), 1.90 (m, 1 H), 1.60 (m, 2 H), 1.13 (s, 3 H), 0.99 (t, J = 7.9 Hz, 9 H), 0.82 (d, J = 6.8 Hz, 3 H), 0.74 (s, 3 H), 0.70 (q, J = 7.9 Hz, 6 H); $CHCH_2$-$GeEt_3$ protons not observed. $^{13}C\{^1H\}$ NMR: δ 173.3, 171.9, 67.1, 52.2, 51.7, 48.0, 39.8, 22.8, 19.2, 17.4, 12.4, 9.2, 4.7. IR (neat, cm^{-1}): 2871, 1731, 1456, 1432, 1389, 1369, 1051. Anal. Calcd (found) for $C_{19}H_{34}GeO_4$: H, 8.59 (8.87); C, 57.19 (56.94).

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