On the Effect of 1,2-Disubstitution with Me_3M (M = Si, Ge, Sn) Groups upon the Electronic Structure of 3,3-Dimethylcyclopropene

Mirjana Eckert-Maksic*[a], Susanne Elbel[b], Michael Stohlmeier[c], Sven Untiedt[c], and Armin de Meijere*[c]

Department of Chemistry, Rudjer Boskovic Institute[a],
Bijenicka c. 54, 41001 Zagreb, Croatia

Technische Fachhochschule Berlin, FB 3[b],
Luxemburger Straße 10, D-13353 Berlin, Germany

Institut für Organische Chemie der Universität Göttingen[c],
Tammannstraße 2, D-37077 Göttingen, Germany

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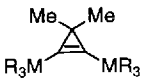
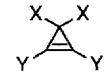
He(I) PE spectra of a series of 3,3-dimethylcyclopropenes bearing Me_3Si (**1**), Me_3Ge (**2**), and Me_3Sn (**3**) groups in the 1- and 2-positions, as well as the He(II) PE spectra of **1** and **3** were recorded. The changes in the lowest energy ionizations along the series are interpreted in terms of inductive and hyperconjugative interactions. The new compounds were prepared by reaction of lithiated 3,3-dimethylcyclopropene with the corresponding trimethylmetal chlorides.

To probe the substituent effects on the chemical and physical properties of three-membered ring compounds has been a long standing goal for us[1,2]. In recent years, we have been engaged in the study of substituent effects on the kinetics and the mechanism of thermal and photochemical rearrangements of cyclopropenes[2c,3]. Among others, trimethylsilyl and trimethylstannyl groups have been shown to exert a significant influence on the kinetics as well as the mechanism of thermal cyclopropene rearrangements[4]. This has mostly been attributed to a transition state stabilization or destabilization, and ground-state influences have not been considered. As photoelectron spectroscopy (PES) is a suitable method to probe electronic properties of molecules in the ground state – within the limits of Koopmans' approximation[5] – we have recorded the PE spectra of a series of 3,3-dimethylcyclopropenes bearing Me_3Si, Me_3Ge, and Me_3Sn groups in the 1,2-positions, as these compounds appeared to be suitable test cases for exploring the electronic effects of the R_3M groups[6] on their C=C double bonds which have a considerably higher π energy than the parent ethylene[7]. At the same time they are appropriate models for studying the interaction between the R_3M groups and the high-lying σ MOs of the strained ring[8]. The consequences of the latter interaction as to the geometry[9], the IR frequencies[10], and some other properties[11] of cyclopropene have received considerable attention in the past, while PES studies addressing this question are still limited[2c,6].

The cyclopropene moiety is particularly interesting in this regard due to the large difference in energy of the two highest occupied σ MOs[12], implying that in appropriately substituted cyclopropene derivatives one of them (W_A) might be higher, and the second one (W_S) lower in energy than the σ C–M bond orbitals[8]. Moreover, for similar reasons only the former MO is likely to experience, if any, counteracting influence of vacant metallic orbitals of appropriate symmetry, which provides a mechanism for delocalizing the parent MO with its concomitant stabilization[13–15]. We therefore recorded the photoelectron spectra of three tetrasubstituted cyclopropenes **1**–**3**, which have recently been prepared in another context[3b].



1 $R_3M = Me_3Si$
2 $R_3M = Me_3Ge$
3 $R_3M = Me_3Sn$



4 X = H, Y = SiH_3
5 X = Me, Y = H
6 X = Me, Y = SiH_3

Results and Discussion

The He(II) PE spectra of compounds **1** and **2** were recorded in addition to the He(I) PE spectra of **1**–**3** (see Figure 1) in the hope of getting supplementary information about the nature of the organometallic substituent orbitals involved in mixing with the uppermost occupied MOs of the cyclopropene ring. The vertical ionization energies, $I_{v,j}$, are collected in Table 1 and compared with the MO energies by assuming the validity of Koopmans' approximation[5]. The MO energies were calculated according to the semiempirical AM1[16a] method. MO energies for the model systems **4** and **6** were calculated at the ab initio Hartree-Fock level by employing the 6-31G* basis set[16b] for comparison. The same basis set was employed to derive wave functions of the highest occupied MOs in **4**, which are depicted in Figure 2. Geometries of all considered molecules were optimized under the C_{2v} symmetry constraint, with the methyl

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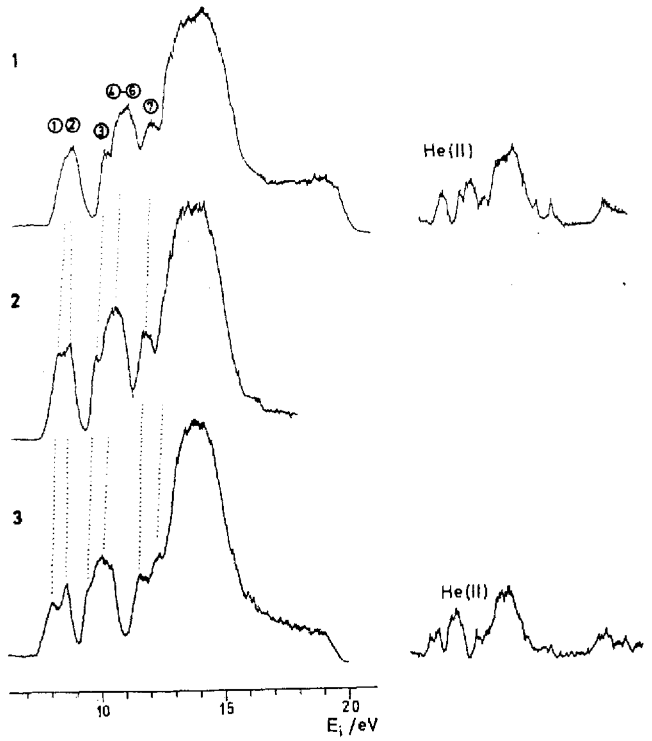
groups in **1**−**3** possessing local C_{3v} symmetry. Structures of model compounds **4**−**6** were also optimized employing ab initio Hartree-Fock model by using the standard 6-31G* basis set. Additional pilot calculations at the MP2(FC)/6-31G* level of theory have been performed on molecule **4** in order to examine the influence of the electron correlation on the molecular structure. The characteristic structural parameters of **4**−**6** obtained from ab initio calculations are summarized in Table 1.

Figure 1. He(I) and He(II) PE spectra of cyclopropene derivatives **1**−**3**



The important point to be emphasized with regard to the calculated structural features of **4** is that substitution by SiH_3 groups effects strongly only the C(1)−C(2) bond distance at both levels of theory. On the other hand, single bond distances [C(1)−C(3) and C(2)−C(3), resp.] within the ring increase only marginally relative to their values in the unsubstituted hydrocarbons[17b]. This result is a clear indication of a complex orbital interaction pattern. Thus, lengthening of the double bond is consistent with π electron flow from the substituents to the cyclopropene π orbital and π donation from the cyclopropene ring to the low lying unoccupied orbitals of the $SiMe_3$ groups, respectively. The influence of the latter type of interaction on the single bond distances within the ring seems to be counterbalanced by σ donation from the substituents to the W_A ring orbital.

Inspection of the measured He(I) photoelectron spectra (Figure 1) reveals that all three spectra are similar in a broad sense as they show three groups of bands of increasing intensity, with the interspace between the last two systems featuring one (compounds **1** and **2**, resp.) and two (compound **3**) ionization bands of considerably lower intensity. Nevertheless, they exhibit several significant and important differences. The most striking among them are related to a gradual enlargement of the energy gap between the first two ionization events (within the first band system) and to a decrease in the separation between the third and fourth ionization event within the second group of bands along the series. In addition, there is an apparent shift of all bands below 12.5 eV towards lower energies by replacing silicon by a heavier metal in the series as expected[6,18] (Figure 3).

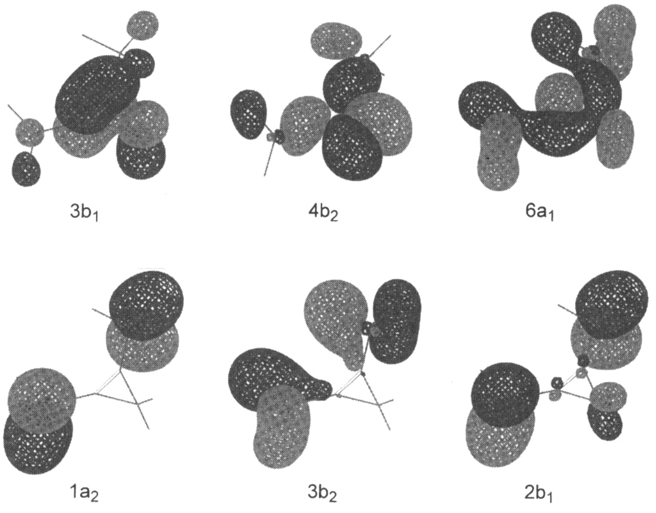
Table 1. Comparison of the computed structural parameters for cyclopropene and molecules **4**−**6**. Bond lengths in Å, bond angles in degrees

Molecule	Bond/Length	HF/6-31G*		MP2(FC)/ 6-31G*
	C(1)–C(2)	1.279[a]	(1.296 ±0.04)[b]	1.303
	C(1)–C(3)	1.494	(1.509 ±0.001)	1.507
	C(1)–H	1.068	(1.072 ±0.001)	1.079
	C(3)–H	1.083	(1.088 ±0.001)	1.091
	HC(3)H	112.9	(114.6 ±0.2)	113.5
	HC(1)C(2)	150.2	(149.8 ±0.1)	149.9
	C(1)C(3)C(2)	50.6	(50.84 ±0.05)	51.2
4	C(1)–C(2)	1.295		1.325
	C(1)–C(3)	1.499		1.512
	C(1)–Si	1.859		1.847
	C(3)–H	1.082		1.095
	Si–H	1.475		1.485
	HC(3)H	113.2		114.0
	SiC(1)C(2)	149.5		149.0
	C(1)C(3)C(2)	51.2		52.0
5	C(1)–C(2)	1.279		
	C(1)–C(3)	1.495		
	C(3)–C(Me)	1.531		
	C(1)–H	1.069		
	C(Me)–H	1.086		
	C(Me)CC(Me)	113.6		
	HC(1)C(2)	149.7		
	C(1)C(3)C(2)	50.7		
6	C(1)–C(2)	1.298		
	C(1)–C(3)	1.499		
	C(3)–C(Me)	1.529		
	C(1)–Si	1.857		
	C(Me)–H	1.086		
	Si–H	1.475		
	C(Me)C(3)C(Me)	114.0		
	SiC(1)C(2)	148.7		
	C(1)C(3)C(2)	51.3		

[a] Ref.[17a]. – [b] Ref.[17b].

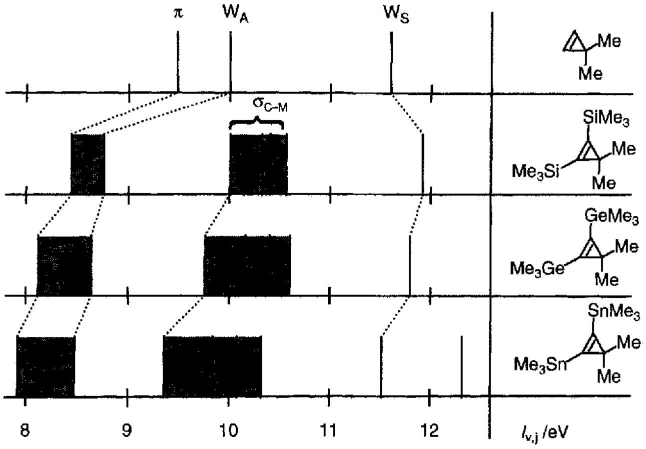
Comparison of the lower ionization energies of **1** and the parent molecule **5**[8,19] (Figure 3) reveals that attachment of the $SiMe_3$ groups to the olefinic ring positions leads to a pronounced destabilization of both the π ($9b_1$) and the highest occupied σ ($10b_2$, W_A) MOs. The latter appear to be influenced more severely, resulting in a near degeneracy of the two levels. Based on the results of AM1 calculations (Table 2) the first ionization event in **1** is ascribed to ionization from the $9b_1(\pi)$ and the second one to that from the $10b_2(W_A)$ MO. It is noteworthy that the same order results from ab initio calculations performed on the model molecule **6** employing a 6-31G* basis set, thus implying a participation of d functions. It should be also noted (Figure 2) that both MOs exhibit significant delocalization over the

Figure 2. Graphical illustrations of the highest occupied MOs of 1,2-disilylcyclopropene (**4**) as calculated with the 6-31G* basis set



TMS groups, indicating presence of hyperconjugative-type of interactions between the olefinic π system and the W_A MO with Si−C σ MOs of the substituents possessing appropriate symmetry[20]. Moreover, inspection of Figure 3 indicates a more efficient mixing between the latter, presumably due to the better energy matching of the interacting MOs[21,22].

Figure 3. Comparison between the first ionization energies of compounds **1**−**3** and those of 3,3-dimethylcyclopropene (**5**)



Another point of interest concerns the influence of vacant metallic orbitals on the energies of the HOMO and HOMO-1. Irrespective of the nature of the empty orbitals involved[6,18], this type of interaction should stabilize the π MO to a greater extent than W_A on account of the better energy matching[21] and larger coefficients at the sites of attachment of the $SiMe_3$ groups[22]. Interestingly, a closer analysis of the shape of the first ionization band system shows a lower intensity of the band related to ionization from the π band as compared to the W_A-related ionization feature. This is at variance with findings in PE studies of other cyclopropene derivative[8,23], perhaps indicating a significant change in the composition of the corresponding MOs due to introduction of the $SiMe_3$ groups. It is important to note, however, that switching to the He(II) excitation induces negligible changes in the relative intensities of the corresponding maxima[24], thus not allowing any conclusion as to the character of orbitals involved in the interaction pattern. In particular, it neither favors nor disfavors d-orbital participation.

Table 2. Comparison between the first vertical ionization energies (I_{vj}) and calculated orbital energies, ε_j, for compounds **1**−**3**. All values in eV

	Band	I_{vj}	Assn.	−ε (AM1)	−ε (6−31G*)[a]
	1	8.4(sh)	$9b_1$	9.72	9.53 ($5b_1$)
1	2	8.66	$10b_2$	9.80	9.83 ($5b_2$)
(C_{2v})	3	10.05	$13a_1$	10.76	12.02 ($8a_1$)
	4–6	10.1–11.3	$6a_2$	10.96	13.23 ($4b_1$)
			$9b_2$	10.97	13.29 ($2a_2$)
			$8b_1$	11.10	13.30 ($7a_1$)
	7	11.86	$12a_1$	11.55	13.59 ($3b_1$)
2	1	8.15	$9b_1$	9.70	
(C_{2v})	2	8.59	$10b_2$	9.76	
	3	9.66	$13a_1$	10.82	
	4–6	9.7–11.0	$6a_2$	10.99	
			$9b_2$	11.00	
			$8b_1$	11.09	
	7	11.69	$12a_1$		
3	1	7.88	$9b_1$	9.10	
(C_{2v})	2	8.45	$10b_2$	9.22	
	3	9.3(sh)	$13a_1$	10.21	
	4–6	9.4–10.7	$6a_2$	10.53	
			$9b_2$	10.55	
			$8b_1$	10.73	
	7	11.46	$12a_1$	11.13	
	8	12.30	$7b_1$	11.85	

[a] Calculations were performed on the model compound **6**.

The second group in the PE spectrum of **1** is related to four Si−C σ orbitals[6,14,15] (Table 2). Two of them, possessing π symmetry with respect to the plane of the cyclopropene ring, correspond to the antibonding and bonding ($6a_2$) linear combinations of the Si−C out-of-plane bond orbitals, whilst the other two are composed of σ Si−C orbitals lying in the plane of the ring. For the bonding ($9b_2$, $8b_1$) combinations of the latter, calculations predict profound destabilization due to the mixing with the cyclopropene W_S orbital, while for the remaining three linear combinations ($6a_2$, $9b_2$, and $8b_1$) calculations predict shift toward lower energy relative to the energy of the σ MO in Me_4Si[14]. The highest among them ($6a_2$) is of appropriate symmetry to interact with the low lying π* MO of the cyclopropene ring, while $9b_2$ and $8b_1$ are stabilized by mixing with the π and the W_A MO of the cyclopropene moiety, respectively. Their approximate shape in the model compound **4** is shown in Figure 2. The proposed assignment (Table 2) should be, however, considered only as tentative due to the unresolved structure of the second band system.

The same holds for the seventh ionization event observed at 11.86 eV (Figure 1), for which calculations predict ionization from the bonding linear combination of the W_S and σ Si−C orbitals of a_1 symmetry (Table 2). Finally, the broad intense set of bands between 12.5 and 15.5 eV in the PE spectrum of **1** can be assigned with confidence to ionization from the highest occupied methyl group orbitals[14,15]. This conjecture is corroborated by calculations and by a comparison with the PE spectra of related molecules[14,15] as well as by changes in relative intensities of the PE bands in the He(I) and He(II) spectra[24].

Replacement of the $SiMe_3$ by $GeMe_3$ and $SnMe_3$ groups effects, as expected, mostly the lowest ionization energies (Table 2, Figure 3)[6,18]. The changes in ionization energies related to the two highest occupied MOs are of particular interest in this respect. Both of them rise in energy, but to a different extent. Whereas the energy of the $10b_2$ MO changes only slightly within the series, the rise in energy of the $9b_1$ MO appears to be more pronounced. The observed trend is readily interpreted in terms of (i) an increase in the positive inductive effect of the Me_3M groups on passing from **1** to **3** and (ii) a weakening of conjugative type of interactions between the π and W_A MOs of the parent ring with the occupied as well as vacant MOs of the Me_3M groups[6,18]. The latter is anticipated due to the C−M bond lengthening[6,25]. For instance, AM1 estimates for the $M-C_1$ bond lengths in **1**, **2**, and **3** 1.778, 1.930, and 2.053 Å, respectively. The enlargement of the energy gap between the first two ionization events along the series suggests that both factors contribute to the increase in energy of the $9b_1$ MO, whilst in the case of $10b_2$ they operate in the opposite direction. This, in turn, offers additional evidence in favor of the more pronounced π-type back bonding in the former case as well as a more sizeable admixture of the Si−C σ MOs to the $10b_2$ MO. As a further point it should be noted that, similarly as in the case of **1**, the second and third set of bands appear to be significantly weakened upon He(II) excitation as expected on the basis of differences in the cross sections of the involved basis orbitals[24].

Conclusions

The most interesting result of the present study is photoelectron-spectroscopic evidence for the pronounced destabilization and near degeneracy of the highest occupied π and W_A levels in **1**. It should also be noted that replacement of the $SiMe_3$ by $GeMe_3$ and $SnMe_3$ groups results in further increase of the π and W_A ionization energies, with the former being slightly more pronounced. Another point worth of emphasizing is the computational finding that the presence of silyl groups in compounds considered has only marginal effect on the single bond lengths in the cyclopropene ring and consequently on their strength. This in turn suggests a similar reactivity of the two classes of compounds in the C−C bond cleavage reactions.

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Experimental

^1H NMR: Bruker AW 250 (250 MHz), WM 270 (270 MHz): δ = 7.15 for [D_6]benzene, 7.26 for $CDCl_3$. − ^{13}C NMR: Bruker AW 250 (62.9 MHz), WM 270 (67.9 MHz); δ = 77.0 for $CDCl_3$, 128.0 for [D_6]benzene. The multiplicities of ^{13}C-NMR signals were generally determined with the help of DEPT measurements and are designated as follows: CH_3, CH = (+), CH_2, C_{quat} (−). − IR: Perkin-Elmer 125, 297, 399. − MS: Varian MAT CH7 with Varian Aerograph 1740 and Varian MAT 112 with Varian Aerograph 1400 (GC with 25-m fused silica capillary Oribond SE-54, carrier gas He) and Varian MAT 311A (high resolution). − GC analytical: Siemens Sichromat 3 (25-m fused silica capillary CB-SE 54, carrier gas H_2). − GC preparative: Varian Aerograph 920 (carrier gas H_2, 3/8″ Teflon columns with Chromosorb W-AW-DMCS 60−80 mesh). − The He(I) and He(II) photoelectron spectra were recorded at room temperature with a 0078 Helectros spectrometer (H. J. Lempka, Beaconsfield, England) and were calibrated using the argon doublet and the He(+) line. Ionization energies are quoted to an estimated accuracy of ±0.10 eV. − M.p.: Melting point apparatus of Wagner & Munz; all values are uncorrected. − Elemental analyses: Mikroanalytisches Laboratorium, Institut für Organische Chemie, Universität Hamburg. − TLC: Alumina sheets with UV fluorescence indicator (E. Merck, Silica gel 60 F_{254}; Macherey & Nagel, aluminium oxide BF_{254}). − Column chromatography: 60−230 mesh silica gel from E. Merck, Darmstadt, 60−100 mesh Florisil (E. Merck, Fluka) or aluminium oxide (basic and neutral, respectively, activity III) from Woelm. − In reactions requiring anhydrous conditions, solvents were dried by distillation under argon or nitrogen from the appropriate drying agent, glassware was flame-dried under reduced pressure and afterwards cooled under a steady stream of argon or nitrogen.

3,3-Dimethyl-1-(trimethylsilyl)cyclopropene[26]: To a solution of 1.00 g (14.7 mmol) of 3,3-dimethylcyclopropene[27] in 8 ml of dry tetrahydrofuran (THF) was added dropwise at −60 °C 9.8 ml of a 1.5 M solution of lithium diisopropylamide (LDA, 14.7 mmol) in THF/hexane. The mixture was stirred for 3 h, while it warmed up to room temp. After heaving been cooled again to −40 °C, a solution of 1.60 g (14.7 mmol) of chlorotrimethylsilane in 10 ml of dry THF was added and the mixture stirred for an additional 15 h at room temp. It was subsequently hydrolyzed with 5 ml of a saturated ammonium chloride solution, the organic phase was separated and washed with three portions of 5 ml of H_2O each, then dried with $CaCl_2$. The solution was concentrated by distillation of the solvents over a 50-cm concentric tube column, until the column head had reached a temp. of 60 °C. According to the ^1H-NMR spectrum (270 MHz), the remaining solution consisted of THF (10%), 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (53%), and 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene (**1**) (37%). This corresponded to a yield of 1.23 g (60%) of the monosilylated compound, which could be purified by gas chromatography (Aerograph 920, 2 m 10% SE30, 25 °C, rel. retention time 4.3 with respect to diethyl ether). − IR (neat): $\tilde{\nu}$ = 2920 cm^{-1}, 2850, 1660 (C=C), 1450, 1355, 1240 ($Si-CH_3$), 1170, 1090, 1030, 860, 830, 750, 700. − ^1H NMR (270 MHz, C_6D_6): δ = 0.14 [s, 9H, $Si(CH_3)_3$], 1.26 (s, 6H, 2 × CH_3), 7.79 (s, 1H, 2-H). − ^{13}C NMR (67.9 MHz, C_6D_6, DEPT): δ = −0.86 [+, $Si(CH_3)_3$], 17.3 (C_{quat}, C-3), 29.0 [+, $C(CH_3)_2$], 134.2 (C_{quat}, C-1), 137.0 (+, C-2). − MS (70 eV), *m/z* (%): 140 (8) [M^+], 125 (16) [M − CH_3], 83 (28), 73 (100) [$Si(CH_3)_3^+$]. − $C_8H_{16}{}^{28}Si$: calcd. 140.10213; found 140.1021 (MS).

3,3-Dimethyl-1,2-bis(trimethylsilyl)cyclopropene (**1**): To a solution of 500 mg (3.5 mmol) of crude 3,3-dimethyl-1-(trimethylsilyl)-cyclopropene[27] in 10 ml of dry THF was added dropwise at −60 °C 2.3 ml (3.5 mmol) of a 1.5 M solution of LDA in THF, and the mixture was stirred for 3 h at −10 °C. After the mixture had been cooled again to −30 °C, a solution of 380 mg (3.5 mmol) of chlorotrimethylsilane in 5 ml of dry THF was added and the mixture then stirred for 15 h at room temp. It was subsequently hydrolyzed with 10 ml of a saturated ammonium chloride solution, the organic phase was separated, washed with three portions of 10 ml of H_2O each, then dried with $CaCl_2$ and concentrated in a rotary evaporator at room temp. The light yellow residue was trap-to-trap distilled under reduced pressure (0.01 mbar) to yield 335 mg (45%) of **1** as a colorless oil. − IR (neat): $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2900, 2850, 1695 (C=C), 1360, 1240 (Si−CH_3), 930, 830, 750, 620. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.15 [s, 18H, 2 × $Si(CH_3)_3$], 1.11 (s, 6H, 2 × CH_3). − MS (70 eV), *m/z* (%): 213 (2.6) [M + 1], 212 (11.4) [M^+], 197 (3.7) [M − CH_3], 155 (9.2) [M − CH_3SiCH_2], 124 (78) [M − SiC_4H_{12}], 73 (100) [$Si(CH_3)_3^+$]. − $C_{11}H_{24}Si_2$ (212.5): calcd. C 62.18, H 11.38; found C 62.12, H 11.28.

3,3-Dimethyl-1-(trimethylgermyl)cyclopropene: To a solution of 1.00 g (14.7 mmol) of 3,3-dimethylcyclopropene in 10 ml of dry THF was added dropwise at −78 °C 6.6 ml of a 1.5 M solution of LDA (10 mmol) in THF; the mixture was warmed to −30 °C within 2 h, then a solution of 1.53 g (10 mmol) of chlorotrimethylgermane in 5 ml of dry THF was added dropwise. After having been warmed up to room temp., the reaction mixture was hydrolyzed with 5 ml of H_2O, the organic phase was separated and dried with $CaCl_2$. The volatile components were distilled over a 25-cm concentric tube column, and the residue was separated by gas chromatography (Aerograph 920, 2 m 10% SE30, 50 °C) to give 100 mg (5.4%) of 3,3-dimethyl-1-(trimethylgermyl)cyclopropene (rel. retention time 10 with respect to THF) as a colorless liquid. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.30 [s, 9H, $Ge(CH_3)_3$], 1.13 (s, 6H, 2 × CH_3), 7.80 (s, 1H, 2-H). − $C_8H_{16}Ge$: calcd. 186.04635; found 186.0465 (MS).

3,3-Dimethyl-1,2-bis(trimethylgermyl)cyclopropene (**2**): − a) To a solution of 500 mg (2.7 mmol) of 3,3-dimethyl-1-(trimethylgermyl)-cyclopropene in 5 ml of dry THF was added at −78 °C 1.8 ml (2.7 mmol) of a 1.5 M solution of LDA in THF, and the mixture was stirred for 5 h while it was warmed up to −30 °C; then a solution of 420 mg (2.75 mmol) of chlorotrimethylgermane in 2 ml of dry THF was added. After hydrolysis of the reaction mixture with 5 ml of a saturated ammonium chloride solution, the organic phase was separated and washed with five portions of 5 ml of H_2O each, then dried with $CaCl_2$ and concentrated in a rotary evaporator. After gas chromatographic separation (Aerograph 920, 3 m 10% SE30, 70 °C, rel. retention time 7.9 with respect to THF) of the residue 75 mg (9.2%) of **2** was obtained as a colorless oil. − IR (neat): $\tilde{\nu}$ = 3000 cm^{-1}, 2925, 2860, 1690, 1410, 1360, 1240, 825, 760. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.31 [2, 18H, 2 × $Ge(CH_3)_3$], 1.11 (s, 6H, 2 × CH_3). − $C_{11}H_{24}Ge_2$: calcd. 304.03010; found 304.0305 (MS).

b) To a solution of 250 mg (3.67 mmol) of 3,3-dimethylcyclopropene in 5 ml of dry THF was added dropwise at −78 °C 5 ml of a 1.5 M solution of LDA (7.5 mmol) in THF/hexane; the mixture was stirred for 1 h at −30 °C, then 1.0 g (6.5 mmol) of chlorotrimethylgermane was added and the mixture stirred for an additional 15 h at room temp. After hydrolysis of the reaction mixture with 10 ml of a saturated sodium chloride solution, the solid material was filtered off, and the organic phase was separated and washed with 10 portions of 5 ml of H_2O each, then dried with $MgSO_4$ and concentrated in a rotary evaporator (12 mbar, 40 °C). Gas chromatographic separation (Aerograph 920, 3 m 10% SE30, 70 °C) of the residue gave 100 mg (8.9%) of **2** as a colorless oil.

3,3-Dimethyl-1-(trimethylstannyl)cyclopropene: To a solution of 2.28 g (8.69 mmol) of 1,1-dibromo-2-chloro-3,3-dimethylcyclopropane[26] in 15 ml of dry diethyl ether was added dropwise at −78 °C 12.4 ml (19.1 mmol) of a 1.54 M methyllithium solution in diethyl ether. The mixture was stirred for 15 min at room temp., cooled again to −78 °C, then 1.73 g (8.69 mmol) of chlorotrimethylstannane was added. After having been stirred for 8 h at room temp., the mixture was poured into 100 ml of an ice/water mixture. The aqueous phase was separated and extracted with three portions of 50 ml of diethyl ether each; the combined organic phases were dried with $MgSO_4$ and concentrated in a rotary evaporator to approx. 2 ml; this residue was trap-to-trap distilled under reduced pressure (0.10 mbar) at room temp. to give 1.86 g (93%) of 3,3-dimethyl-1-(trimethylstannyl)cyclopropene as a colorless oil. An analytically pure sample was obtained by gas chromatography. − IR (neat): $\tilde{\nu}$ = 2961 cm^{-1} (C−H), 2924, 1648 (C=C), 1449, 1363, 1264, 1192, 1029, 957, 773, 703, 532, 513, 461. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.25 [s, 9H, $Sn(CH_3)_3$], 1.12 (s, 6H, CH_3), 8.02 (bs, 1H, 2-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = −8.94 [+, $Sn(CH_3)_3$], 16.34 (C_{quat}, C-3), 29.68 (+, CH_3), 134.90 (C_{quat}, C-1), 139.58 (+, C-2). − MS (70 eV), *m/z* (%): 236/234/231/230/229/228 (4/3/6/17/5/10) [M^+], 169/167/164/163/162/161 (18/15/27/75/24/44) [$Sn(CH_3)_3^+$], 155/153/150/149/148/147 (4/4/6/18/5/11) [$HSn(CH_3)_2^+$], 141/139/136/135/134/133 (9/7/13/37/12/22) [$H_2SnCH_3^+$], 127/125/122/121/120/119 (2/2/3/8/2/7) [SnH_3^+], 83 (75), 55 (25). − $C_8H_{16}Sn$ (230.9): calcd. C 41.62, H 6.98; found C 41.88, H 6.98.

3,3-Dimethyl-1,2-bis(trimethylstannyl)cyclopropene (**3**): To a solution of 1.36 g (20 mmol) of 3,3-dimethylcyclopropene in 10 ml of dry diethyl ether was added dropwise at −78 °C 28 ml (42 mmol) of a 1.5 M solution of LDA in hexane/ether, and the mixture was stirred for 15 h at room temp. After the mixture had been cooled again to −30 °C, a solution of 9.0 g (45 mmol) of chlorotrimethylstannane in 20 ml of ether was added, and the mixture was stirred for 2 h while it warmed up to room temp. It was subsequently hydrolyzed with such an amount of H_2O that the precipitated lithium chloride just dissolved (ca. 14 ml). The phases were separated and the aqueous phase extracted with two portions of 20 ml of ether each. The combined organic phases were dried with $MgSO_4$, then concentrated in a rotary evaporator at room temp. (15 mbar), and the residue was separated by gas chromatography (Aerograph 920, 1.5 m 10% SE30, 40 °C) to give 4.3 g (55%) of **3** as a light yellow oil. − IR (neat): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 2850, 1660, 1360, 1240, 1195, 780. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.23 [s, 18H, 2 × $Sn(CH_3)_3$, $^2J_{Sn,H}$ = 49.4 Hz], 1.08 (s, 6H, 2 × CH_3). − $C_{11}H_{24}Sn_2$: calcd. 395.99206; found 395.9931 (MS).

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