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Photoelectron spectroscopic study of novel Group 14 functionalized vinylcyclopropenes

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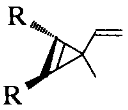
Abstract

Treatment of 3-methyl-3-vinylcyclopropene (1) with 2 equiv. of lithium diisopropylamide followed by 2 equiv. of Me_3ECl (E = Si, Ge, Sn) afforded 1,2-bis-(Me_3E)-3-methyl-3-vinylcyclopropenes (2–4) in moderate to good yield. The He(I) PE spectra of 2–4 have been recorded and interpreted in terms of inductive and conjugative abilities of the organometallic substituents, taking into account differences in the nature and the localization properties of the highest occupied levels in the parent molecule.

Keywords: Silicon; Germanium; Tin; Vinylcyclopropenes; Photoelectron spectra; MO calculations

1. Introduction

Compounds which incorporate the vinylcyclopropene moiety have been, and still are, a subject of intense research interest [1–7]. This is not surprising in view of their unique physical properties [1] and remarkable potential in organic syntheses [2]. Much attention in the past has been focused on their photochemical rearrangements [3], the effect of substituents on the electronic structure [4,5] and their conformational behaviour [6]. The motivation for the work presented here stemmed from our interest in the physicochemical properties of vinylcyclopropenes containing Group 14 elements other than carbon. In a recent paper, we described our results on the thermolysis reactions of two such compounds, namely 1,2-bis(trimethyl-silyl)- (2) and 1,2-bis(trimethylgermyl)-3-vinylcyclopropene (3) [7]. The present paper deals with their synthesis and photoelectron spectroscopic properties. In addition, the synthesis and electronic structure of 1,2-bis(trimethylstanyl)-3-methyl-3-vinylcyclopropene (4) are described. These form a rather interesting group for photoelectron (PE) spectroscopic investigation. They provide the opportunity to study the effect of the organometallic substituents on an olefinic π-system of considerably higher energy than that in the parent ethylene [8], and are at the same time appropriate models for studying the interaction between Group 14 elements and the high lying σ-MOs of the strained carbocyclic framework [9]. The consequences of the latter interaction on the geometry [10], IR frequencies [11] and some other properties of cyclopropane moiety [12] have received a great deal of attention recently, but studies concerned with these questions for cyclopropene derivatives are still scarce [13].



1 R = H
2 R = $SiMe_3$
3 R = $GeMe_3$
4 R = $SnMe_3$
5 R = SiH_3

2. Results and discussion

2.1. Syntheses of compounds 2–4

Metallation of olefinic carbon atoms within cyclopropene ring is commonly achieved by deprotonation followed by quenching with a suitable organometallic reagent [14,15]. An example involving the preparation

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of mono(trimethylsilyl)-derivatives of 3-methyl-3-vinylcyclopropene [16] by this procedure has been described [14]. We used the same method to prepare compounds **2**–**4**. Deprotonation of **1** was accomplished by using slightly more than 2 equiv. of lithium diisopropylamide (LDA), prepared in situ by reaction of ^{n}BuLi and ^{i}Pr$_2$NH in THF/TMEDA. Subsequent treatment of the mixture with slightly more than 2 equiv. (with respect to **1**) of Me$_3$ECl (E = Si, Ge, Sn), followed by conventional work-up gave the required compounds in moderate (**4**) to good (**2**, **3**) yield.

The structures of all three new compounds were confirmed by their IR, ^{1}H and ^{13}C NMR spectra and high-resolution mass spectra. Particular attention is drawn to the ^{13}C NMR data; comparison with the relevant data for the parent hydrocarbon reveals a downfield shift for all the carbon atoms except for the one at the terminal position of the vinyl group, which moves upfield. The largest shifts (ca. 20 ppm) are observed for the C-1 and C-2 carbon atoms, as expected. Another point of interest concerns the larger deshielding (ca. 2 ppm) of the C-1 and C-2 signals in the Sn derivative **4** compared with those in **2** or **3** (see Experimental detail). This is at variance with the expected change in electronegativity on varying the metal atoms [17], perhaps indicating that the paramagnetic contributions of the metal–carbon bonds [18] related to the existence of the low-lying metallic vacant MOs play a decisive role in this respect. A similar trend is observed in the IR spectra, which in **2** and **3** have the band for the presence of the cyclopropene double bond at ca. 1730 cm^{-1}, while the corresponding band in **4** is found at 1690 cm^{-1}.

2.2. Photoelectron spectra of 1–4

The He(I) photoelectron (PE) spectra of **1** and **2**–**4** are shown in Figs. 1 and 2, respectively. The vertical ionization energies (*IE*s) are listed in Table 1 and compared with the molecular orbital (MO) energies (ϵ_{MO}) calculated by the semi-empirical MNDO procedure [19], assuming the validity of Koopman's approximation [20]. Also included are the MO energies of **1** and the model compound **5** calculated at the HF/6-31G* level of theory [21]. In performing the calculations we assumed an *s-trans* orientation of the vinyl group with respect to the cyclopropene ring in all compounds. This is in accordance with conclusions drawn previously from the HF/6-31G* calculations [6] for **1** and the solid-phase molecular structure of compound **2**, as determined by an X-ray study [22].

Before discussing the PE spectra of compounds **2**–**4**, we make comment on the PE spectrum of the parent 3-methyl-3-vinylcyclopropene. The latter has been previously published by Plemenkov and coworkers [4] and discussed briefly by us [23]. The assignment proposed by Plemenkov was subsequently questioned by Boyarskaya et al. [24], who claimed that the published spectrum was not consistent with the vinylcyclopropene structure. We reached a similar conclusion in Ref. 23. Another interesting feature which emerged from our studies was that the PE spectrum of **1** underwent a profound change during PE measurements. This is illustrated by Fig. 1, which displays the PE spectrum recorded shortly after introducing the sample (Fig. 1a) and that obtained 10 min (Fig. 1b) and 30 min (Fig. 1c) later. Comparison of the PE spectrum shown in Fig. 1a with those of structurally related cyclopropene derivatives strongly supports the assignment of this spectrum

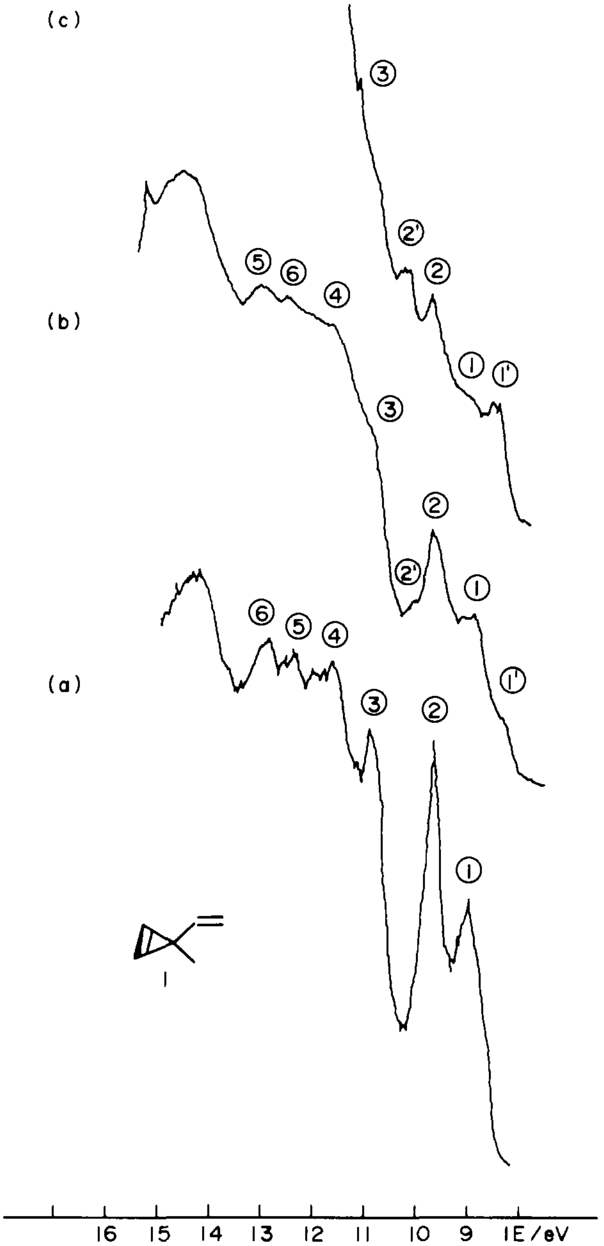


Fig. 1. Changes in the appearance of the He(I) PE spectrum of **1** within 30 min of recording.

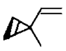
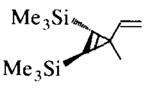
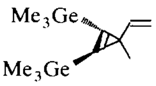
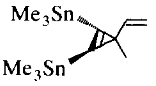
to **1**, as proposed in Ref. 23. Such an assignment is fully corroborated by the energy ordering of the highest occupied MOs of **1** obtained by calculations (Table 1), i.e. a small energy gap between the 4a″ and the 12a′ MOs followed by a considerably larger separation between the 12a′ and the lower lying MOs. Hence, the first PE band of **1** (① in Fig. 1a) is assigned to the out-of-phase linear combination of the vinylic π-MO (π_v) and the higher occupied Walsh-like σ-MO (W_a) of the cyclopropene moiety (4a″). For the next band (②) calculations predict ionization from the 12a′ MO, which is mainly localized in the region of the cyclopropene double bond (π_{cp}). By use of similar arguments, the bands ③ and ④ are assigned to the in-phase linear combination of the π_v and the W_a (3a″) and the symmetric Walsh-like MO (11a′) of the cyclopropene, respectively.

The approximate shapes of the uppermost orbitals of **1** as calculated by the MNDO procedure are indicated in Scheme 1.

The PE spectra shown in Figs. 1b and 1c exhibit in the two new bands (denoted by ①′ and ②′) low-energy region of the spectrum at 8.1 and 10.2 eV in addition to bands ① and ②. The latter bands gradually lose intensity, but retain the same relative intensities. The energies of the newly formed bands are consistent with the data obtained by Plemenkov (8.3 and 10.2 eV, respectively) within experimental error [4]. This strongly suggests that the PE spectrum published by these authors was that of the irreversible isomerization product of **1** [25] formed under the conditions in the target chamber of the PE spectrometer.

Starting from the assignment for **1** proposed above we are now in a position to discuss the effect of the Me_3E groups on the *IE*s of compounds **2–4** (Fig. 2). Of particular interest in this respect are the first two ionization events, because the MOs associated with them are expected to be influenced mostly by either the high-lying σ_{E-C} bond orbitals or the low-lying vacant metal orbitals of appropriate symmetry of the organometallic substituents. The latter type of interaction is usually disscussed in terms of p/d and/or $\sigma^*-\pi$ conjugation [26,27]. The data in Table 1 indicate that the respective ionization energies (IE_1 and IE_2, for **2–4** are lowered by a similar extent relative to that of **1**. In other words, within Koopmans' approximation, the 4a″ and 12a′ MOs of **1** experience nearly equal increases in energy upon introduction of the Me_3E groups at the C-1 and C-2 ring positions. Taking into account the differences in the nature and localization properties of 4a″ and 12a′ MOs in **1** (Scheme 1) it seems reasonable to assume that the net effect of

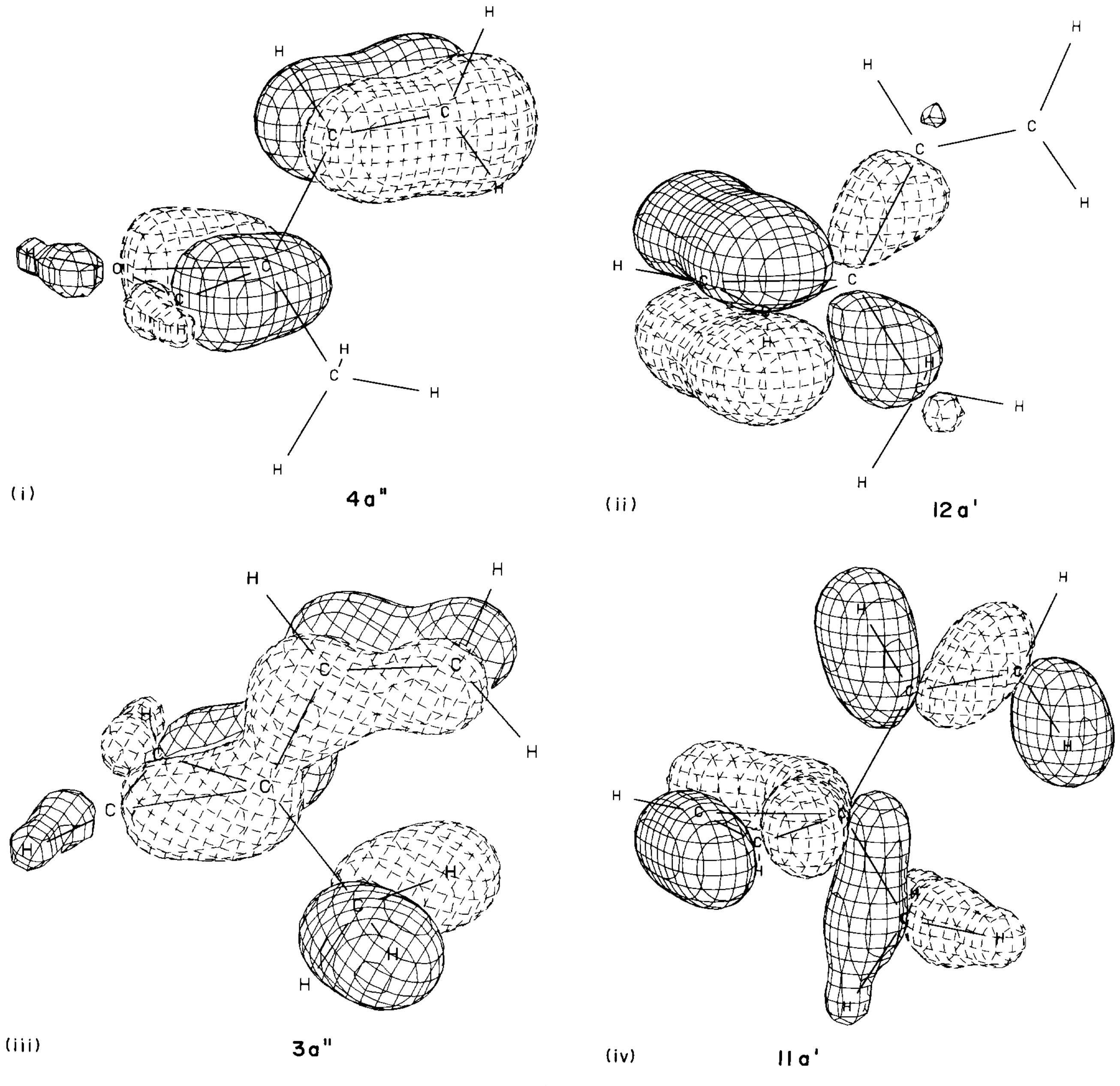
Table 1
Comparison between the first vertical ionization energies (IE_{vj}) and calculated orbital energies for compounds 1–4 [a]

Compound	Band (j)	IE_{vj} (eV)	Assignment	$-\epsilon_j$ (eV)	
				MNDO	HF/6-31G*
 **1** (C_s)	①	9.0	$W_a - \pi_v$ (4a″)	9.47	9.04
	②	9.7	π_{cp} (12a′)	10.03	9.89
	③	11.0	$W_a + \pi_v$ (3a″)	11.51	11.80
	④	11.8	W_s (11a′)	12.33	12.91
 **2**	①	8.1	$W_a - \pi_v$	9.35	8.86 [b]
	②	8.9	π_{cp}	9.97	9.82
	③–⑦	10.0–11.5	σ_{E-C}; $W_a + \pi_v$	11.02, 11.07, 11.30 11.42, 11.47	11.38, 12.25, 13.19, 13.37
	⑧	11.7	W_s	12.05	12.05
 **3**	①	7.9	$W_a - \pi_v$	9.31	
	②	8.6	π_{cp}	9.95	
	③–⑦	9.5–11.2	σ_{E-C}; $W_a + \pi_v$	11.02, 11.10, 11.32, 11.40, 11.45	
	⑧	11.5	W_s	11.86	
 **4**	①	7.6	$W_a - \pi_v$	9.03	
	②	8.5	π_{cp}	9.46	
	③–⑦	9.7–11.0	σ_{E-C}; $W_a + \pi_v$	10.70, 10.73, 11.03, 11.17, 11.25	
	⑧	11.6	W_s	11.82	

[a] The numbering (j) of the bands refers to Figs. 1 and 2. The values given for the bands ③–⑦ in 2–4 indicate the range of the composite band.
[b] Calculations were performed on the model compound **5**.

hyperconjugative interaction on the former MO is far less pronounced. Hence, the observed shift of this MO for **2–4** relative to that for **1** can be attributed mainly to the inductive influence of the Me_3E groups. This, in turn, suggests that most of the hyperconjugative destabilization of the 12a′ MO is counterbalanced by π-electron back-donation to the lower-lying vacant MOs of the proper symmetry of the Me_3E groups, irrespective of the nature of orbitals involved. It is noteworthy that the MNDO and HF/6-31G* procedures reproduce the experimentally observed pattern only qualitatively. Both methods underestimate the effect of the metallo-organic groups and predict a somewhat larger destabilization of the 4a″ relative to the 12a″ orbital.

Another noteworthy feature is that variation of the metal atom in the substituents on going from **2–4** slightly lowers (0.1–0.3 eV) both ionization events under scrutiny, reflecting the slight increase in the positive inductive effect on going from silicon to the heavier atoms of Group 14 [17]. Likewise, the near constancy of the energy gap between the first two bands over the series of compounds indicates that the net contribution (stabilizing vs. destabilizing) of the conjugative interaction remains nearly constant. The ob-



Scheme 1

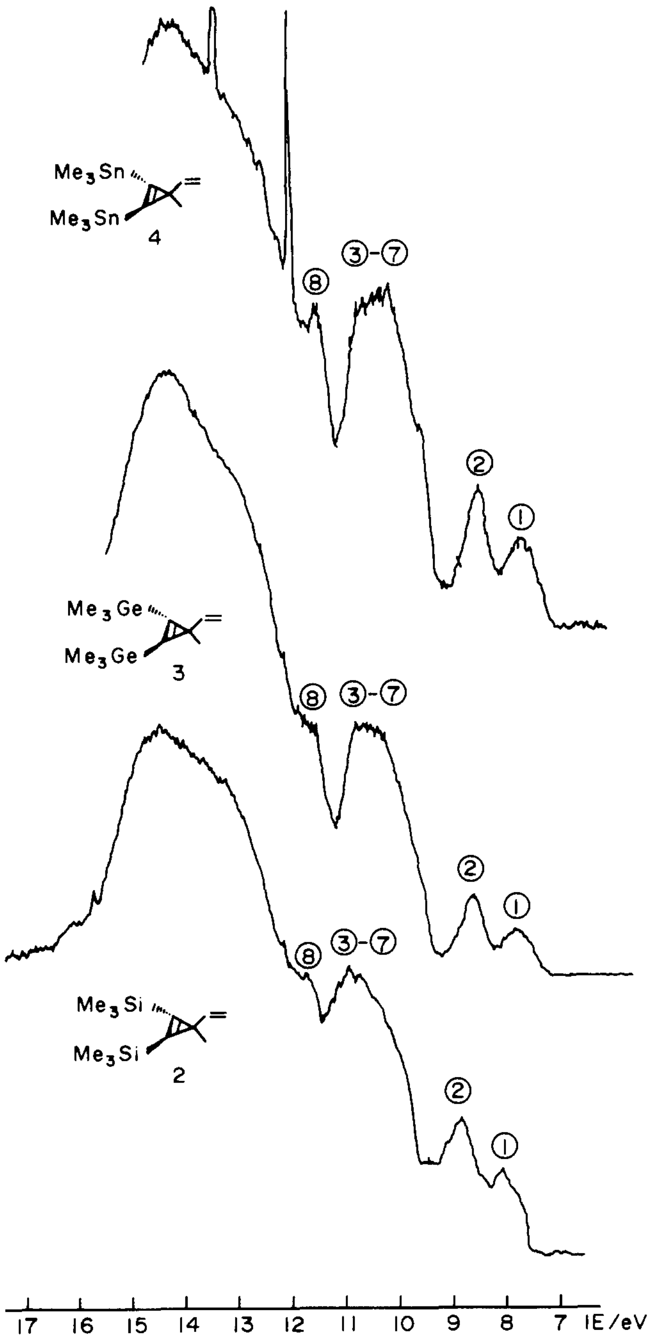


Fig. 2. The He(I) PE spectra of compounds **2–4**.

served pattern is fully consistent with the trends observed in other π-systems, such as $PhEMe_3$ [28] or 1-Me_3E- derivatives of naphthalene [29].

The ionization energy region above 10 eV in all three spectra shown in Fig. 2 is dominated by two large multiple ionization bands, with the space between them featuring an additional ionization event of low intensity. Comparison with data for related compounds involving Me_3E fragments suggests that the first composite band originates from MOs of essentially σ_{E-C} character, along with the ionization event arising from the MO of predominant $W_a + \pi_v$ character. This is in full accordance with the results of calculations (Table 1), which for this region predict five MOs within only 0.5 (**2** and **3**) to 0.7 (**4**) eV. Band ⑧ in all three compounds appears to arise from ionization from the W_s-type MO, highly localized within the ring. Its *IE* value changes negligably relative to that of **1**, indicating that inductive destabilization of the Me_3E groups on the MO in question is roughly compensated by its conjugative interaction with the higher-lying σ_{E-C} bond orbitals of the appropriate symmetry. Finally, the intense ionization system consisting of a series of highly overlapping bands between ca. 12.5 and 15.5 eV can be confidently assigned to the MOs strongly localized in the methyl groups [8,13,27–29].

The most important conclusion to be drawn from this work is that organometallic substituents involving Group 14 elements lower the first two ionization energies of the parent hydrocarbon **1** to a similar extent. Furthermore, the present results reveal that replacement of $SiMe_3$ by $GeMe_3$ or $SnMe_3$ groups affects the first two ionization energies only slightly. The observed trends can be rationalized in terms of the inductive and conjugative abilities of the organometallic substituents, taking into account the differences in the nature and localization properties of the highest occupied levels in the parent molecule.

3. Experimental details

All the He(I) spectra were recorded using a UVG3 Vacuum Generators instrument callibrated with xenon. The PE spectra of compounds **1–3** were recorded at room temperature, but **4** had to be heated to 50°C. Infrared spectra (IR, bands reported in cm^{-1}) were recorded on an FTIR Perkin-Elmer 1725X spectrometer. ^1H and ^{13}C nuclear magnetic resonance spectra (NMR signals reported in ppm) were recorded on a Varian Gemini 300 spectrometer. High resolution mass spectra were obtained with an EXTREL FTMS 2001 DD instrument. All reactions were carried out under Ar.

3.1. Preparation of 2–4. General procedure:

Compound **1** [16] (1.1 g, 12.5 mmol) was added dropwise to a solution of lithium diisopropylamide in THF/hexane at −60°C prepared in situ from n-butyllithium (30.2 mmol) and diisopropylamine (30.2 mmol). The mixture was stirred for ca. 3h as the temperature was allowed to rise to −10°C. It was then cooled to −30°C, Me_3ECl (30.2 mmol) slowly added, and the mixture stirred for an additional 2 h during which it was allowed to warm up to ambient temperature. It was then hydrolyzed with cold water and extracted with ether (2 × 100 ml). After separation, the organic phase was washed with dilute HCl (to pH 7), brine and then with saturated $Na_2S_2O_3$ solution, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by distillation under reduced pressure (10^{-4} mmHg).

1,2-bis(trimethylsilyl)-3-methyl-3-vinylcyclopropene (**2**): 3-methyl-3-vinylcyclopropene (**1**, 1.1 g, 12.5 mmol) and Me_3SiCl (3.3 g, 30.2 mmol) gave 2.15 g (69.7%) of **2**; IR cm^{-1}: ν 1727 (C=C, ring); 1616 (C=C, vinyl). ^1H NMR ($CDCl_3$) δ: 0.18 (18H, s, $Si(CH_3)_3$), 1.23 (3H, s, CH_3); 4.70–4.79 (2H, m, $=CH_2$), 5.44–5.53 (1H, dd, =CH) ppm. ^{13}C NMR ($CDCl_3$) δ: −1.02 (s, $Si(CH_3)_3$); 23.98 (s, CH_3); 24.91 (s, C-3), 108.47 (s, $=CH_2$); 142.78 (s, C-1 (C-2)); 151.35 (s, =CH) ppm. HRMS: 224.141 044 (Calc. for $C_{12}H_{24}Si_2$ 224.141 107).

1,2-bis-(trimethylgermyl)-3-methyl-3-vinylcyclopropene (**3**): 3-methyl-3-vinylcyclopropene (1.1 g, 12.5 mmol) and Me_3GeCl (4.6 g, 30.2 mmol) gave 1.69 g (39.3%) of **3**. IR cm^{-1}: 1730 (C=C, ring); 1615 (C=C, vinyl). ^1H NMR ($CDCl_3$) δ: 0.31 (18H, s, $Ge(CH_3)_3$); 24.51 (3H, s, CH_3); 4.67–4.77 (2H, m, $=CH_2$); 5.50–5.60 (1H, dd, =CH) ppm. ^{13}C NMR ($CDCl_3$) δ: −1.20 (s, $Ge(CH_3)_3$); 24.51 (s, CH_3); 25.08 (s, C-3); 108.34 (s, $=CH_2$); 142.31 (s, C-1 (C-2)); 152.32 (s, =CH) ppm. HRMS: 312.034 257 (Calc. for $C_{12}H_{24}Ge_2$ 312.033 229).

1,2-bis-(trimethylstanyl)-3-methyl-3-vinylcyclopropene (**4**): 3-methyl-3-vinylcyclopropene (1.1 g, 12.5 mmol) and Me_3SnCl (6.0 g, 30.2 mmol) gave 2.11 g (38.0%) of **4**. IR cm^{-1}. 1690 (C=C, ring); 1610 (C=C, vinyl). ^1H NMR ($CDCl_3$) δ: 0.26 (18H, s, $Sn(CH_3)_3$); 1.22 (3H, t, CH_3); 4.59–4.75 (2H, m, $=CH_2$); 5.62–5.71 (1H, dd, =CH) ppm. ^{13}C NMR ($CDCl_3$) δ: −8.79 (s, $Sn(CH_3)_3$); 23.37 (s, CH_3); 25.85 (s, C-3), 108.15 (s, $=CH_2$); 144.90 (s, C-1 (C-2)); 153.55 (s, =CH) ppm. HRMS: 407.996 518 (Calc. for $C_{12}H_{24}Sn_2$ 407.991 649).

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