Lithiation/silylation of ethyl 2-alkyl-1-trimethylsilylcycloprop-2-ene-1-carboxylate. Experimental and computational study

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The formation of novel trimethylsilyl-substituted allenes, including silyl ketene acetals incorporating an allenic moiety, by lithiation/silylation of ethyl 2-alkyl-1-trimethylsilylcycloprop-2-ene-1-carboxylate, is described. The reaction involves formation of silyl ketene acetal **3** (**3a**) which upon aqueous work-up gives diastereomeric allenes **4′** (**4′a**) and **4″** (**4″a**). Becke3LYP/6-311+G** calculations were also carried out to provide geometries, energies and insights into the electronic structure of the proposed reaction intermediates.

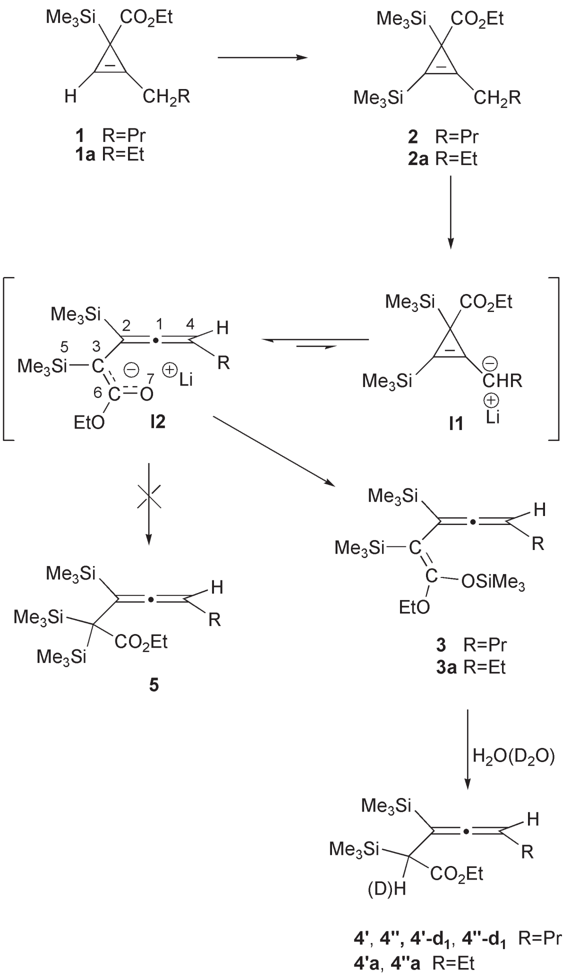
Introduction

Thermal and photochemical ring opening reactions of cyclopropene derivatives have attracted considerable attention from both experimental and theoretical points of view.[1–3] This is not surprising in view of their remarkable potential in organic synthesis[4] and interest for better understanding of the effect of various substituents on their mechanism.[5] Much less work has been done on rearrangements of cyclopropenyl anions or the corresponding organometallic equivalents, which are known to occur well below ambient temperature.[6,7] A typical example is provided by the ring opening of 1,2-dilithiocyclopropene to 1,1-dilithioallene reported by Binger *et al.*[6] More recently, we have shown that ethyl 1-trimethylsilylcycloprop-2-ene-1-carboxylate undergoes regioselective addition of an electrophile after ring opening upon lithiation with lithium diisopropylamide (LDA) in THF–TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), yielding upon quenching with trimethylsilyl or trimethylgermyl chloride the corresponding acetylene and/or allene derivatives.[7]

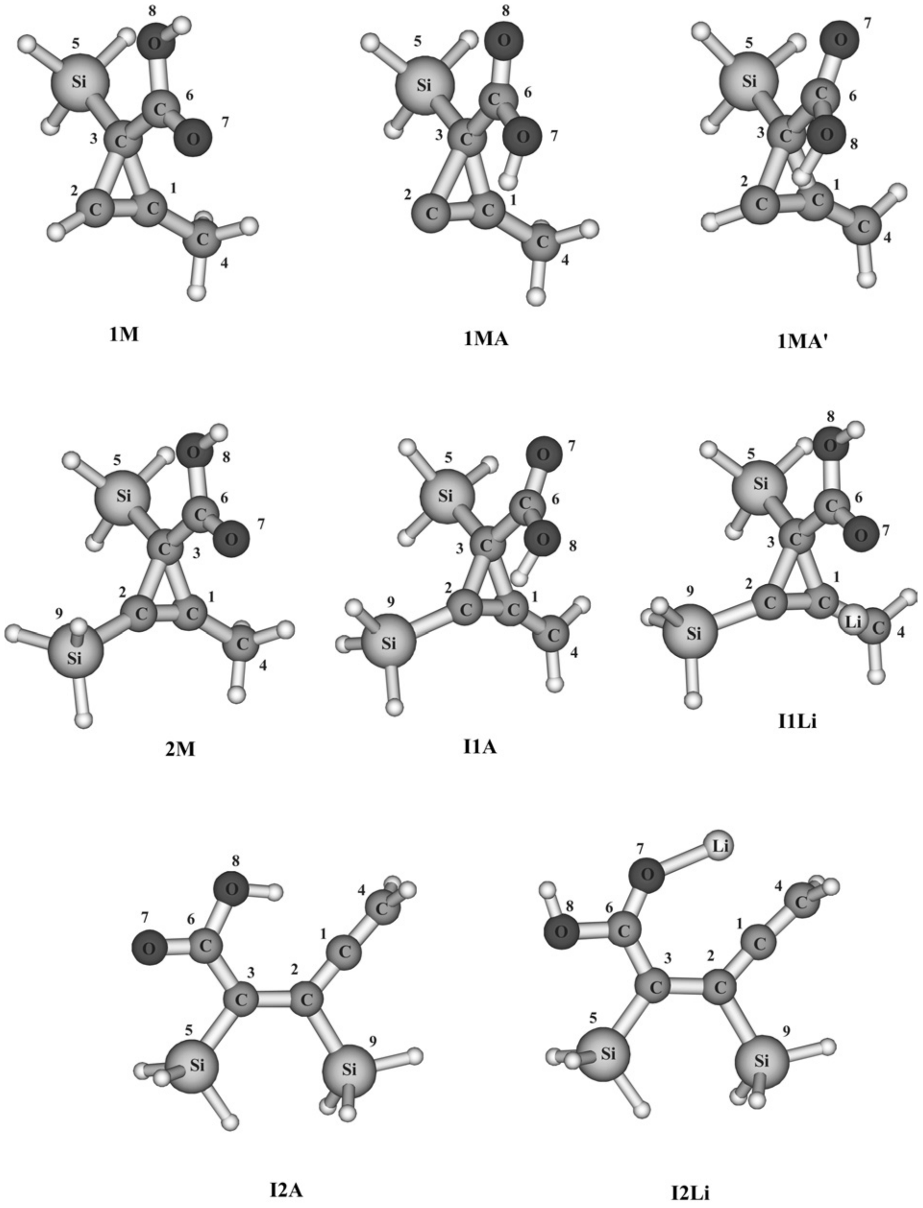
With the aim of gaining more information about the mechanism and synthetic scope of this reaction we turned our attention to more complex systems. In this paper we report the results of an experimental investigation of the metallation of several 2-alkyl derivatives of 1-trimethylsilylcycloprop-2-ene-1-carboxylate combined with quantum mechanical calculations on closely related model molecules and reaction intermediates (Schemes 1 and 2). Our main objectives in this study were to (a) elucidate the relative acidities of the vinylic ring proton and the protons of the methylenic group of the aliphatic chain attached to the vinylic position of the cyclopropene ring; (b) to explore the synthetic potential of this reaction and (c) to get insight into the molecular and electronic structure of the potential reaction intermediates and the key factors influencing their stability.

Results and discussion

Thus, in a preliminary experiment, treatment of ethyl 2-butyl-1-trimethylsilylcycloprop-2-ene-1-carboxylate (**1**) with 2.0 equivalents of LDA in THF–TMEDA at −60 °C, followed by addition of an excess of trimethylsilyl chloride (TMSCl) at −30 °C, warming the reaction to 0 °C and aqueous work up afforded a mixture of three products in an 1 : 2 : 1 ratio (Table 1, entry 1). The products were purified by vacuum distillation and subsequently subjected to column chromatography which resulted in full separation of the corresponding allenic diastereomers **4′** (**4′a**) and **4″** (**4a″**) (see Experimental



Scheme 1


1M 1MA 1MA'

2M I1A I1Li

I2A I2Li

Scheme 2 Schematic representation of the optimised geometries of the model compounds.

section). On the other hand, all attempts to isolate the third product, denoted hereafter as **3**, under similar conditions failed. Hence, its structure was proposed on the basis of NMR analysis of the crude reaction mixture by subtracting signals due to **4′** and **4″** and subsequently verified by its identity with an independently prepared sample of this compound (*vide infra*, Table 1). Under identical conditions **1a** gave a mixture of **3a**, **4′a** and **4″a** in a similar ratio.[8] Structures of allene derivatives of **4′** and **4″** were established unambiguously by spectroscopic analysis (see Experimental section). For instance, their ^{1}H NMR spectrum exhibits two strong signals (at 0.05 and 0.10 ppm and 0.06 and 0.11 ppm for **4′** and **4″**, respectively) each for nine hydrogens, as expected, for two nonequivalent Me_3Si groups. Another characteristic feature is the triplet at *ca.* 4.8 ppm for the vinylic proton which was proved to be the consequence of coupling ($J = 6.8$ Hz) with the neighbouring CH_2 group which appears as the multiplet at *ca.* 2.0 ppm. The ^{13}C NMR spectra showed a signal at *ca.* 208 ppm, *i.e.* in the region characteristic for the strongly deshielded central sp carbon of an allenic group. Similarly their IR spectra showed a typical C=C=C stretching band at 1906/1936 and 1936 cm^{-1} in **4′** and **4″**, as well as the C=O absorption at *ca.* 1730 cm^{-1}.

Table 1 Products ratios and yields of lithiation/silylation of cyclopropenes **1** and **2**

Entry	Starting cyclopropene (CP)	Molar ratio CP : LDA : Me_3SiCl	Work-up	Product(s)/product ratios[a]	Yield (%)
1	**1**	1 : 2.0 : 2	Aqueous	**3**, **4′**, **4″** (1 : 2 : 1)	—, 23, 16
2	**1**	1 : 2.0 : 6	Non-aqueous	**3**	70
3	**1**	1 : 2.0 : 6	Aqueous	**3**, **4′**, **4″** (1 : 1 : 1.4)	10, 13, 17
4	**1**	1 : 1.1 : 6	Non-aqueous	**1**, **2**, **3** (1 : 1 : 4.6)	—, 12, 40
5	**2**	1 : 2.0 : 6	Non-aqueous	**3**	81

[a] Monitored by GC analysis.

We next carried out the same reaction under somewhat different conditions, *i.e.* by adding the starting cyclopropene **1** to a mixture of LDA in the presence of an excess of TMSCl at −60 °C in THF–TMEDA (Table 1, entry 2). After *ca.* 10 minutes, GC analysis of the reaction mixture revealed the presence only of **3** which was isolated as the sole product after non-aqueous work up in the very good yield of 70%. Under identical reaction conditions and an aqueous work-up (Table 1, entry 3) a mixture of **3**, **4′** and **4″** in 10%, 13% and 17% isolated yields was obtained. These results constitute firm evidence that silyl ketene acetal **3** (**3a**) is an intermediate in the transformation of **1** (**1a**) into diastereomeric allenes **4′** (**4′a**) and **4″** (**4″a**). Finally, we performed the same reaction using a 1 : 1.1 : 6 molar ratio of **1** : LDA : TMSCl. After *ca.* 5 min and non-aqueous work up, the reaction led to a mixture of **2** (12%) and **3** (40%), along with the starting cyclopropene **1** (Table 1, entry 4). From this mixture, **2** was isolated by column chromatography after fraction distillation of the reaction mixture under low pressure, and its structure was verified by spectral analysis (see Experimental section).

The above experimental results are accounted for by the reaction pathway shown in Scheme 1.

It involves deprotonation of the unsubstituted ring position in **1** and subsequent interception of the so formed intermediate (not shown in Scheme 1) with TMSCl leading to ethyl 2-butyl-1,3-bis(trimethylsilyl)-cycloprop-2-ene-1-carboxylate (**2**). Once formed, the latter compound is easily deprotonated by LDA to give the allylic-type carbanion **I1**,[9] which subsequently undergoes ring-opening to its acyclic counterpart **I2**. As expected, reaction of the intermediate **I2** with a second equivalent of TMSCl occurs at the oxygen atom O7, which possesses the largest concentration of negative charge within a formally ambient enolate subunit (C3–C6–O7). The attack of TMSCl on C3 which would lead to the tris(trimethylsilylated) allene **5** can be excluded, since **5** was not observed under our reaction conditions. Finally, hydrolysis of **3** (**3a**) gives the corresponding enol which rearranges into the more stable esters represented by **4′** (**4′a**) and **4″** (**4″a**), respectively. Decomposition of **3** was also carried out in the presence of deuterium oxide (D_2O), which afforded monodeuteriated allenes **4′-d$_1$** and **4″-d$_1$**.[10] The location of deuterium was assigned on the basis of ^{13}C NMR analysis, which showed triplets ($^1J_{CD}$ = 19.9 Hz) in the proton decoupled spectrum for the carbon atom labelled with deuterium, as well as a small upfield (36.70 ppm) shift for the corresponding resonance.

Additional confirmation of involvement of **2** in the first step of the reaction is adduced by treating **2** with LDA and TMSCl (Table 1, entry 5) under identical conditions as described for **1**. This reaction after non-aqueous work up afforded **3** as the sole product in a high isolated yield of 81%, thus providing additional support in favour of the proposed mechanism.

Computational studies

With our experimental knowledge about the described reaction, we turned to theoretical calculations in order to elucidate the pertinent factors contributing to the stability of the proposed reaction intermediates. Optimizations were carried out for the model compounds shown in Scheme 2 at the B3LYP/6-311+G** level of theory, which is well documented to provide reliable descriptions of organolithium compounds related to those under study here.[11] It should be noted that in all of the model compounds methyl groups at the silicon atom were replaced by hydrogen atoms. Similarly the ethyl and the *n*-butyl groups were replaced by hydrogen atom(s) and methyl group(s), respectively. For the sake of clarity we have adopted the following convention: the model compounds which correspond to the neutrals **1** and **2** are identified by the number of the corresponding neutral followed by **M** (**1M** and **2M**, respectively). The anions derived from **1M** are named by the number of the corresponding model compound followed by **A**, if deprotonation takes place at the position C2 and by **A′** if deprotonation takes place at the C4 atom. A similar convention is adopted for model compounds related to the reaction intermediates **I1** and **I2** in Scheme 1; *i.e.* they are identified by the name of a given intermediate followed by **A** for the anions and **Li** for the lithium salts (**I1A**, **I1Li**, *etc.*). The optimized geometries of all model compounds considered in this study are shown in Scheme 2, whereas the selected structural parameters are given in Table 2. Among a variety of conformations of the studied model molecules considered here, only the most stable ones are shown and will be discussed in some detail. The total energies and ZPVEs of

Table 2 Selected structural parameters of model compounds **1M** and **2M** their anions **1MA**, **1MA′**, **I1A**, **I2A** and Li-salts **I1Li** and **I2Li** calculated at B3LYP/6-311+G** level. Bond lengths are given in Å and angles in °[a]

	Molecule							
Bond or angle	**1M**	**1MA**	**1MA′**	**2M**	**I1A**	**I1Li**	**I2A**	**I2Li**
C1–C2	1.280	1.303	1.391	1.289	1.381	1.363	1.329	1.319
C1–C3	1.542	1.506	1.516	1.520	1.519	1.531	–	–
C2–C3	1.536	1.737	1.571	1.573	1.564	1.594	1.452	1.459
C1–C4	1.473	1.485	1.344	1.473	1.346	1.356	1.315	1.326
C3–C6	1.500	1.466	1.502	1.497	1.502	1.472	1.433	1.392
C6–O7	1.208	1.224	1.221	1.208	1.218	1.236	1.236	1.274
C3–Si5	1.898	1.860	1.870	1.896	1.879	1.891	1.841	1.866
C2–Si9	—	—	—	1.849	1.812	1.831	1.893	1.915
C1–Li	—	—	—	—	—	2.098	—	2.298
C2–Li	—	—	—	—	—	2.171	—	3.097
C4–Li	—	—	—	—	—	2.475	—	2.216
O7–Li	—	—	—	—	—	1.901	—	1.719
C1–C2–C3	65.7	57.3	61.2	63.2	61.8	61.8	129.8	130.5
C2–C3–C1	49.2	46.7	53.5	49.2	53.2	51.7	—	—
C3–C1–C2	65.2	76.0	65.3	67.5	65.1	66.6	—	—
C4–C1–C2	154.5	149.2	156.3	152.3	156.4	152.5	178.8	175.3
C1–C3–C6	114.6	119.7	119.1	114.8	117.7	114.5	—	—
C6–O8–H	107.5	105.1	101.2	107.5	102.8	108.1	110.1	107.0
C3–C6–O7	126.7	125.2	124.3	126.7	124.1	125.3	123.0	128.8
C6–O7–Li	—	—	—	—	—	105.2	—	135.9

[a] For numbering of atoms see Scheme 2.

the latter are summarized in Table 3, whereas Table 4 shows results of natural bond orbital (NBO) analysis.

Like the cyclopropene **1**, the model molecule **1M** possesses two alternative deprotonation sites, the vinylic atom (C2) and the CH_2 group of the alkyl chain attached to the ring, denoted here as C4. Experimental data discussed above indicate that first deprotonation in **1** takes place at the vinylic position leading to **2**. Interestingly, our computational results for **1M** predict that the deprotonation energy of protons attached to the C4 carbon atom (leading to the anion **1MA′**) is 6.5 kcal mol^{-1} higher than that of the vinylic proton at the C2 position (resulting in the anion **1MA** (360.2 kcal mol^{-1} *vs.* 353.7 kcal mol^{-1}), being thus in disagreement with the exclusive formation of **2** observed experimentally. This in turn suggests that the relative acidities of vinylic and allylic positions in **1** are drastically different in condensed media, presumably due to the diminished importance of delocalization.[12] Similar results were found earlier for *e.g.* deprotonation of propyne, which is deprotonated exclusively at the acetylenic carbon in the liquid phase, but a roughly 1 : 1 mixture of acetylenic and propargylic (allenic) anions are obtained upon reaction with hydroxide in the gas phase.[13] Another interesting question concerns the effect of lithium counterions on the stability ordering of these anions. Therefore, we optimized also the structures of the lithium salts of both ions (not shown in Scheme 2). It turned out that lithiation slightly reduces the difference in stabilities of the anionic species (by 0.6 kcal mol^{-1}), but does not influence their stability ordering. Concomitantly, we tentatively conclude that formation of silylated product **2** under experimental conditions is driven by different solvation and aggregation effects of reaction intermediates.[11*b*,11*c*]

A few comments on the geometries of the carbanions **1MA** and **1MA′** (Scheme 2, Table 2) also are warranted. Deprotonation of **1M** at the vinylic positions of the cyclopropene ring leading to carbanion **1MA** induces hybridization change at the deprotonation site leading to a dramatic decrease in s-character of the C2–C3 bond, which in turn assumes a highly pronounced p-character (Table 4). As a consequence, the C1–C2–C3 angle becomes smaller by 8.4° (Table 2). The lone pair produced by deprotonation has a high s character (58.9%) as expected. Redistribution of atomic charges is also of interest. Somewhat surprisingly, the formal atomic charge at the anionic center C2 is decreased by only 0.1 $|e|$ implying that the excess electron is distributed all over the molecule. The largest gain in the electron density ($-0.28\ |e|$) is obtained at the C1 atom which was positively charged in the neutral molecule, thus being the most electropositive before deprotonation. The rest of the anionic electron is distributed over the C3 atom and the carboxylic group. The most striking structural characteristic is elongated C2–C3 bond, which becomes very long particularly for the three membered ring (1.737 Å).[14] Taking into account that the carbon–carbon bond is elongated in going from *e.g.* cyclopropane to propane followed by a strain relief, one is tempted to conclude that the same takes place in this compound too. Deprotonation of the methyl group in **1M** resulting in formation of anion **1MA′**, gives rise to a pronounced contraction of the C1–C4 bond (by 0.129 Å) and its strengthening by an increase in the double bond character. In contrast, the C1=C2 double bond is stretched (0.111 Å) and weakened compared to **1M** (Table 2). Nevertheless, it is an interesting hyperconjugative interplay between the π-double bond of the allylic fragment and the C2–H bond. The latter is a consequence of the large out-of-plane twist angle (*ca.* 70°) of the vinylic hydrogen at the C2 center calculated from the plane of the cyclopropenyl ring (Table 2).

Table 3 Total energies of the model compounds **1M** - **I2Li** calculated on the B3LYP/6-311+G** level of theory

Molecules	E^a (a.u.)	ZPVE^b (a.u.)
1M	−635.23326	0.11371
1MA	−634.66961	0.10063
1MA′	−634.68067	0.09969
2M	−925.95009	0.12936
I1A	−925.40477	0.11577
I1Li	−932.92149	0.11960
I2A	−925.42209	0.11581
I2Li	−932.95020	0.11974

[a] Total enegies are corrected for ZPV energies. [b] Not scaled.

Table 4 Natural bond orbital[a] atomic charges, hybridizations and bond orders for **1M**–**I2Li**. Mayer's bond orders are given in parentheses[b]

Molecules	Atoms	NBO Atomic charges	Bonds	s-Characters (%)	NBO b.o. (Mayer. b.o.)[c]
1M	C1	0.07	C1–C2	37.9–37.8	1.931 (1.941)
	C2	−0.15	C1–C3	20.5–19.0	0.883 (0.885)
	C3	−0.63	C2–C3	21.8–18.3	0.894 (0.920)
	C4	−0.73	C1–C4	41.3–26.8	1.048 (0.950)
	C6	0.80	C3–C6	28.4–39.3	0.997 (0.971)
	O7	−0.62	C6–O7	33.8–41.3	1.739 (1.829)
1MA	C1	−0.21	C1–C2	38.9–35.7	1.929 (1.924)
	C2	−0.25	C1–C3	22.9–27.0	0.912 (0.880)
	C3	−0.74	C2–C3	5.4–9.6	0.695 (0.693)
	C4	−0.70	C1–C4	38.1–28.8	1.020 (0.954)
	C6	0.78	C3–C6	30.0–41.1	1.104 (1.067)
	O7	−0.67	C6–O7	32.0–40.0	1.635 (1.696)
1MA′	C1	0.01	C1–C2	34.3–32.1	1.248 (1.153)
	C2	−0.58	C1–C3	20.3–21.5	0.901 (0.857)
	C3	−0.68	C2–C3	23.9–18.9	0.881 (0.911)
	C4	−0.62	C1–C4	45.2–37.9	1.728 (1.787)
	C6	0.81	C3–C6	27.0–38.7	0.999 (0.982)
	O7	−0.67	C6–O7	33.2–41.0	1.658 (1.716)
2M	C1	0.10	C1–C2	37.5–37.1	1.888 (1.772)
	C2	−0.39	C1–C3	21.7–20.7	0.900 (0.896)
	C3	−0.61	C2–C3	19.0–16.6	0.858 (0.875)
	C4	−0.72	C1–C4	40.5–26.9	1.045 (0.950)
	C6	0.80	C3–C6	28.4–39.4	1.003 (0.978)
	O7	−0.62	C6–O7	33.8–41.3	1.743 (1.818)
I1A	C1	0.03	C1–C2	34.5–31.5	1.258 (1.101)
	C2	−0.81	C1–C3	20.0–21.0	0.890 (0.856)
	C3	−0.63	C2–C3	21.7–19.4	0.884 (0.897)
	C4	−0.63	C1–C4	45.1–37.5	1.708 (1.769)
	C6	0.81	C3–C6	27.3–39.0	1.003 (0.981)
	O7	−0.65	C6–O7	33.1–41.0	1.673 (1.730)
I1Li	C1	−0.04	C1–C2	35.1–33.0	1.342 (1.134)
	C2	−0.80	C1–C3	19.8–20.5	0.869 (0.868)
	C3	−0.62	C2–C3	17.6–17.3	0.832 (0.845)
	C4	−0.69	C1–C4	44.8–35.8	1.638 (1.565)
	C6	0.83	C3–C6	27.9–40.8	1.066 (1.032)
	O7	−0.75	C6–O7	31.7–40.0	1.562 (1.444)
I2A	C1	−0.07	C1–C2	49.8–35.4	1.716 (1.681)
	C2	−0.47	C1–C3	–	–
	C3	−0.81	C2–C3	38.2–34.6	1.185 (1.126)
	C4	−0.56	C1–C4	49.9–38.4	1.930 (1.910)
	C6	0.75	C3–C6	31.4–42.3	1.255 (1.235)
	O7	−0.70	C6–O7	32.2–40.0	1.548 (1.602)
I2Li	C1	−0.01	C1–C2	50.3–35.7	1.787 (1.778)
	C2	−0.44	C1–C3	–	–
	C3	−0.73	C2–C3	38.2–33.1	1.150 (1.114)
	C4	−0.70	C1–C4	49.6–37.3	1.863 (1.657)
	C6	0.74	C3–C6	32.1–43.9	1.411 (1.452)
	O7	−0.91	C6–O7	30.5–40.2	1.312 (1.201)

[a] All NBO calculations were performed using B3LYP/6-31+G*//B3LYP/6-311+G** method. [b] For numbering of atoms see Scheme 2. [c] Mayer's bond orders were calculated using HF/6-31 G*//B3LYP/6-311+G** level of theory.

Replacement of the vinylic proton in **1M** with the SiH_3 group leading to the molecule **2M** enhances acidity of the methylenic protons by an additional 3 kcal mol^{-1}. The so formed anion **I1A** (which closely resembles the anionic part of intermediate **I1** in Scheme 1) is, however, found to be less stable by *ca.* 10.9 kcal mol^{-1} than its rearranged counterpart **I2A** (modelling anionic fragment of intermediate **I2**). Lithiation of **I1A** and **I2A**, leading to lithium salts **I1Li** and **I2Li**, respectively, enlarges this difference by an additional 7.1 kcal mol^{-1} (Table 3).

The optimized geometry of the lithiated species, consistent with previously published data,[15] demonstrates that the lithium atom is coordinated not only to the carbanionic center(s), but also to the carbonyl-type oxygen atom of the carboxylic group at the C3 position. For instance, position of the lithium atom in the geometry obtained for **I1Li** shows complexation to the oxygen atom O7 and the carbon atoms C1 and C2 (Table 2), with the O7 being in closest proximity to the lithium cation. Interestingly, the complexation pattern to the carbon atoms does not appear to follow neither the charges calculated by NBO method (Table 4) nor the HOMO coefficients in the free anion. Both the molecular orbital coefficients of the HOMO and the charges of the carbons C1, C2 and C4 suggest that coordination should be at carbons C2 and C4. This discrepancy seems to be a consequence of steric effects caused by the presence of the bulky SiH_3 and COOH substituents at the C3 atom and the orientation of the COOH group relative to the plane of the cyclopropene ring (see Scheme 2).

Similarly, in the geometry obtained for **I2Li**, the lithium atom is closest to the oxygen atom O7 (1.719 Å), whereas the distance from the lithium atom to carbon atoms of the allenyl subunit are in the range of 1.901–2.475 Å. It is interesting to note that likewise in **I1Li**, the strength of complexation of the lithium to the carbon atoms do not correlate either with the negative charges of the carbon atoms forming the allenyl subunit or the symmetry of the corresponding HOMO orbital (Table 4). In other words, the distance between lithium and the C1 and C4 atoms is smaller than the separation between Li and C2 (Table 2), which in turn is more negatively charged than C1. The most plausible reason behind this seemingly counterintuitive result lies in the geometrical features of the calculated structures, which appear to be the result of an interplay of electrostatic and conjugative interactions.[16] As a consequence the carboxylic group rotates by 180° relative to its position in the free anion and the C6–O7–Li angle widens by almost 30° relative to the corresponding angle in the free anion.

Generally, the structures of the anionic part in the Li-salts **I1Li** and **I2Li** are similar to those of the corresponding free anions **I1A** and **I2A**, with some notable exceptions. The most remarkable difference concerns a change in orientation of the COOH group which occurs in a way to maximize the electrostatic attractions between the formal anionic center C4 and the O7 atom with the lithium counterion. The differences in bond distances for most of the bonds are within 0.02 Å (Table 2). An exception is provided by the bond C3–C6 which shortens by *ca.* 0.03 Å and 0.04 Å in **I1Li** and **I2Li** relative to the corresponding anions, respectively, indicating a sizeable conjugative interaction of the p-lone pair at the O7 atom with the π*-orbital of the C3–C6 bond. This is corroborated by elongation of the C6–O7 bond in both of the lithiated compounds relative to the free anions (Table 2). Analysis based on the calculated NBO bond orders fully supports this view (Table 4).

Finally it is worth noting that the lithium atom in both structures has nearly one unit of the positive charge obtained by NBO analysis (Table 4), indicating that the O–Li bond is essentially completely ionic. The electrostatic charge localizing effect of the lithium atom is also responsible for the greater negative charges at the O7 and the C4 atoms in the lithiated species compared to the corresponding free anions.

Conclusions

In this paper we have described the synthesis of novel trimethylsilyl-substituted allenes **4′**(**4′a**) and **4″**(**4″a**), starting from easily available new ethyl 2-alkyl-1-trimethylsilylcycloprop-2-ene carboxylates (**1**, **1a** and **2**). The silyl ketene acetals incorporating an allenic moiety **3** (**3a**) described in this work might have vast potential in various organic synthetic applications.[17] The mechanism of reaction, based on experimental and computational results, is also discussed, and clearly shows that the reaction proceeds through allenic type intermediates. The calculations provide evidence that the latter species are *ca.* 10–20 kcal mol^{-1} more stable than their cyclic counterparts.

Experimental

Trimethylsilyl diazoacetate was synthesized according to a previously reported procedure.[18] *n*-Butyllithium 1.6 M solution in hexane, diisopropylamine and TMEDA, deuterium oxide (D_2O) was purchased from Aldrich. Diisopropylamine and TMEDA were dried before use by refluxing over sodium. Solvents were dried by distillation under argon or nitrogen from the appropriate drying agent.[19] TLC was done on Merck silica gel plates (25 DC-Alufolien Kiesegel 60F-254). Column chromatography was performed on Aldrich silica gel 60 (63–200 μm) with petroleum ether–Et_2O mixtures as eluent. Infrared spectra (IR, in cm^{-1}) were recorded on a Perkin-Elmer 297 or Perkin-Elmer FT 2000 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer. Chemical shifts are reported in parts per million (δ/ppm) downfield from tetramethylsilane using the residual solvent signal as an internal standard. High resolution mass spectra (HRMS) were obtained at EXTREL FTMS 2001 DD spectrometer. GC analysis was carried out on Varian 3300 gas chromatograph. All reactions involving air sensitive reagents were performed under argon in oven-dried glassware by syringe/septum cap technique. Photochemical reactions were carried out in Rayonet Chamber RPR-100 photochemical reactor with 16 PRP-3500A lamps.

Ethyl 2-butyl-1-trimethylsilylcycloprop-2-ene-1-carboxylate (1)[20]

Ethyl (trimethylsilyl)diazoacetate (1.86 g, 0.01 mol) and 1-hexyne (50.5 ml, 0.44 mol) were placed in a Pyrex photolysis tube and the mixture was degassed with argon at 0 °C for one hour. The mixture was irradiated using 16 lamps ($\lambda_{max} = 350$ nm) for 7 hours. The unreacted 1-hexyne was recovered by distillation under reduced pressure (10 mmHg/25 °C). The residue was filtered through a short column of Florisil R (60–100 mesh) (petroleum ether–Et_2O 30 : 1 as eluents) to afford 1.87 g of pure **1** (78%). ^{1}H NMR ($CDCl_3$), δ: 0.00 (s, 9H), 0.88–0.93 (t, 3H, $J = 7.2$ Hz), 1.20–1.25 (t, 3H, $J = 7.1$ Hz), 1.35–1.42 (m, 2H), 1.50–1.57 (m, 2H), 2.44–2.49 (t, 2H, $J = 7.1$ Hz), 4.04–4.12 (dq, 2H, $J_1 = 7.1$ Hz, $J = 3.2$ Hz, $J_2 = 7.2$ Hz, $J = 3.3$ Hz), 6.27 (s, 1H); ^{13}C NMR ($CDCl_3$), δ: −1.47 (q), 13.60 (q), 14.18 (q), 19.70 (s), 22.16 (t), 25.17 (t), 29.00 (t), 59.86 (t), 94.46 (d), 116.36 (s), 178.19 (s); IR (KBr), ν: 1704/1717 (C=O), 1806 (C=C); HRMS (EI) m/z calc. for $C_{13}H_{24}O_2Si$ (M^+) 240.1540, found. 240.1505.

Synthesis of 3, 4′ and 4″. General procedure

LDA was prepared by adding 1.6 M of BuLi (2.51 mL, 4.0 mmol) to a mixture of dry diisopropylamine (0.56 mL, 4.0 mmol) and dry TMEDA (0.27 mL) in 2 mL dry THF at 0 °C under argon. Cyclopropene **1** (485 mg, 1.95 mmol) and TMSCl (1.55 mL, 12 mmol) were added quickly to the freshly prepared solution of LDA at −60 °C under argon.

The reaction mixture was stirred for about 10 minutes at the same temperature and allowed to warm up to 0 °C (*ca.* 10 minutes).

1-Ethoxy-1-trimethylsiloxy-2,3-bis(trimethylsilyl)octa-1,3,4-triene (3)

The solvent was removed from the reaction mixture with a rotary evaporator and the resulting mixture was filtrated with suction through a Celite pad and washed with dry hexane. The hexane was removed by evaporation and the residue was distilled under reduced pressure (40–50 °C/10^{-5} mmHg) to give pure **3** (527 mg, 70.4%).

^{1}H NMR (CDCl$_3$), δ: 0.07 (18H, s), 0.20 (9H, s), 0.90–0.95 (t, 3H, J = 7.4 Hz), 1.21–1.26 (t, 3H, J = 7.0 Hz), 1.35–1.47 (2H, m), 1.94–2.01 (2H, q, J_1 = 7.3 Hz, J_2 = 7.4 Hz), 3.72–3.82 (2H, m), 4.61–4.66 (1H, t, J = 7.4 Hz); ^{13}C NMR (CDCl$_3$), δ: −0.71 (q), 0.02 (q), 0.11 (q), 13.68 (q), 14.54 (q), 23.64 (t), 30.68 (t), 63.68 (t), 83.46 (d), 90.49 (s), 95.39 (s), 155.36 (s), 205.74 (s); IR (KBr), v: 1616 (C=C), 1929 (C=C=C); HRMS (EI) m/z calc. for $C_{19}H_{40}O_2Si_3$ (M^+) 384.2331, found 384.2320.

Diastereoisomers of ethyl 2,3-bis(trimethylsilyl)octa-3,4-dienoate (4′ and 4″)

Cold water was added to the reaction mixture, and organics were extracted with Et$_2$O. The organic phase was washed with 1 M aqueous of HCl, saturated brine and aqueous $Na_2S_2O_3$. The crude reaction products were purified by fractional distillation at 0.05 and 10^{-5} mmHg/40–50 °C to obtain a mixture of diastereoisomers **4′** and **4″** and pure **3** (74.9 mg, 10%), respectively. The mixture of diastereoisomers was separated by column chromatography (petroleum ether–Et$_2$O = 12 : 1) yielding **4′** (79.1 mg, 13%) and **4″** (103.5 mg, 17%). Spectroscopic data of **4′**: ^{1}H NMR (CDCl$_3$), δ: 0.05 (s, 9H), 0.10 (s, 9H), 0.91–0.96 (t, 3H, J = 7.4 Hz), 1.21–1.26 (t, 3H, J = 7.2 Hz), 1.41–1.49(m, 2H), 1.98–2.04 (m, 2H), 2.47 (s, 1H), 4.06–4.13 (q, 2H, J_1 = 6.9 Hz, J_2 = 7.2 Hz), 4.83–4.88 (t, 1H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$), δ: −1.80 (q), −1.74 (q), 13.74 (q), 14.21 (q), 22.62 (t), 30.41 (t), 37.27 (d), 59.86 (t), 86.68 (d), 90.99 (s), 173.50 (s), 208.64 (s); IR (KBr), v: 1728 (C=O), 1906/1936 (C=C=C); HRMS (EI) m/z calc. for $C_{16}H_{32}O_2Si_2$(M^+) 312.1935, found 312.1951. Spectroscopic data for **4″**: ^{1}H NMR (CDCl$_3$), δ: 0.06 (s, 9H), 0.11 (s, 9H), 0.91–0.95 (t, 3H, J = 7.4 Hz), 1.21–1.26 (t, 3H, J = 7.4 Hz), 1.36–1.46 (m, 2H), 1.95–2.02 (m, 2H), 2.50 (s, 1H), 4.06–4.13 (q, 2H, J_1 = 6.9 Hz, J_2 = 7.2 Hz), 4.92–4.97 (t, 1H, J = 6.8); ^{13}C NMR (CDCl$_3$), δ: −1.86 (q), −1.61 (q), 13.86 (q), 14.33 (q), 23.08 (t), 30.95 (t), 37.03 (d), 59.98 (t), 86.23 (d), 90.61 (s), 173.51 (s), 207.87 (s); IR(KBr), v: 1730 (C=O), 1936 (C=C=C); HRMS (EI) m/z calc. for $C_{16}H_{32}O_2Si_2$(M^+) 312.1935, found 312.1901.

Ethyl 2-butyl-1,3-bis(trimethylsilyl)cycloprop-2-ene-1-carboxylate (2)

Compound **2** was obtained from cyclopropene **1** (800 mg, 3.3 mmol), LDA (3.7 mmol) and TMSCl (2.5 mL, 19.8 mmol) as described for compound **3**. This reaction, after non-aqueous work-up, afforded a mixture of **2** and **3**, along with the starting cyclopropene **1**. The crude reaction mixture was purified by fractional distillation at 0.05 and 10^{-5} mmHg/40–50 °C to afford a mixture of **1** and **2** and pure **3** (507 mg, 40%), respectively. The mixture of **1** and **2** was separated by column chromatography (petroleum ether–Et$_2$O = 12 : 1) to give **2** (123.6 mg, 10%).

Spectroscopic data for **2**: ^{1}H NMR (CDCl$_3$), δ: 0.01 (s, 9H), 0.19 (s, 9H), 0.91–0.95 (t, 3H, J = 7.2 Hz), 1.19–1.24 (t, 3H, J = 7.02 Hz), 1.37–1.45 (m, 2H), 1.54–1.61 (m, 2H), 2.46–2.52 (m, 2H), 4.02–4.09 (q, 2H, J_1 = 7.0 Hz, J_2 = 7.1 Hz); ^{13}C NMR (CDCl$_3$), δ: −1.1 (q), 1.0 (q), 13.69 (q), 14.26 (q), 19.58 (s), 22.23 (t), 26.70 (t), 29.35 (t), 59.46 (t), 103.66 (s), 128.64 (s), 178.16 (s); IR (KBr), v: 1704 (C=O), 1834 (C=C); HRMS (EI) m/z calc. for $C_{16}H_{32}O_2Si_2$ (M^+) 312.1935, found 312.1960.

Computational studies. All computations were carried out using Gaussian94[21] or Gaussian98[22] program packages on LINUX-based PCs. Structures were optimized with density functional method using Becke3LYP hybrid functional[23,24] and the 6-311+G**[25] basis set. DFT calculations on a variety of organolithium compounds have recently been shown to reproduce accurately experimental data.[26] All stationary points were characterized to be minima by calculation of their vibrational frequencies. The reported energies (Table 3) are corrected for ZPV energies. Natural charges, s-characters and bond orders were calculated by using the natural bond orbital (NBO) method.[27]

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References

1 For recent review articles see, *e.g.* (*a*) M. S. Baird, in *Carbocyclic Three- and Four-Membered Compounds*, ed. A. de Meijere, Houben-Weyl, Thieme, Stuttgart, 1997, vol. E. 17d, pp. 2781–2790; (*b*) W. E. Billups, M. M. Haley and G.-A. Lee, *Chem. Rev.*, 1989, **89**, 1147; (*c*) M. G. Steinmetz, R. Srinivasan and W. J. Leigh, *Rev. Chem. Intermed.*, 1984, **5**, 57.

2 For more recent papers see, *e.g.* (*a*) M. Eckert-Maksić and M. Golić, *J. Chem. Soc. Perkin Trans. 2*, 1993, 2325; (*b*) R. Walsh, S. Untiedt and A. de Meijere, *Chem. Ber.*, 1994, **127**, 237; (*c*) R. Walsh, C. Wolf, S. Untiedt and A. de Meijere, *J. Chem. Soc., Chem. Commun.*, 1992, **127**, 421; (*d*) R. Walsh, C. Wolf, S. Untiedt and A. de Meijere, *J. Chem. Soc., Chem. Commun.*, 1992, **127**, 422; (*e*) H. Hopf, W. Graf v. d. Schulenburg and R. Walsh, *Angew. Chem.*, 1997, **109**, 415; *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 381; (*f*) W. Graf v. d. Schulenburg, H. Hopf and R. Walsh, *Chem. Eur. J.*, 2000, **6**, 1963 and references cited therein.

3 (*a*) A. Padwa, M. Akiba, C. S. Chou and L. Cohen, *J. Org. Chem.*, 1982, **47**, 183; (*b*) A. Padwa, T. J. Blacklock, D. M. Cordova and R. Loza, *J. Am. Chem. Soc.*, 1980, **102**, 5648 and references cited therein.

4 M. S. Baird, in *Topics in Current Chemistry*, Springer-Verlag, Berlin, Heidelberg, vol. 144, 1988, pp. 137–209.

5 *e.g.* A. de Meijere, D. Faber, U. Heinecke, R. Walsh, T. Müller and Y. Apeloig, *Eur. J. Org. Chem.*, 2001, 663.

6 P. Binger, P. Müller, R. Wenz and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1037.

7 I. Zrinski, PhD Thesis, University of Zagreb, 2000.

8 Similarly, reaction of ethyl 2-propyl-1-trimethylsilylcycloprop-2-ene-1-carboxylate (**1a**) under identical condition afforded a mixture of diastereomeric allenes **4′a** and **4″a**, accompanied by the corresponding silyl ketene acetal **3a**.

9 (*a*) G. Fraenkel, J. Cabral, C. Lanter and J. Wang, *J. Org. Chem.*, 1999, **64**, 1302; (*b*) G. Fraenkel and F. Qiu, *J. Am. Chem. Soc.*, 2000, **122**, 12 806.

10 Characteristic spectroscopic data of **4′**-d$_1$: ^{13}C NMR (CDCl$_3$), δ/ppm: −1.86 (q), −1.59 (q), 13.87 (q), 14.35 (q), 23.10 (t), 30.97 (t), 36.70 (t, $^1J_{CD}$ = 19.9 Hz), 59.95 (t), 86.25 (d), 90.59 (s), 173.44 (s), 207.89 (s).; HRMS (EI) m/z calc. for $C_{16}H_{31}DO_2Si_2$ (M^+) 313.1998, found 313.1963, deuteriated 68.9%.

11 (*a*) T. D. Power and J. F. Sebastian, *Tetrahedron*, 1998, **54**, 8371; (*b*) K. Sorger, P. v. R. Schleyer and D. Stalke, *J. Am. Chem. Soc.*, 1996, **118**, 1086; (*c*) C. Lambert and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1129.

12 *e.g.* L. Moore, R. Lubinski, M. C. Baschky, G. D. Dahlke, M. Hare, T. Arrowood, Z. Glasovac, M. Eckert-Maksić and S. R. Kass, *J. Org. Chem.*, 1997, **62**, 7390.

13 (*a*) J. M. Oakes and G. B. Ellison, *J. Am. Chem. Soc.*, 1983, **105**, 2969; (*b*) J. H. Stewart, R. H. Shapiro, C. H. DePuy and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1977, **99**, 7650; (*c*) J. H. J. Dawson, T. A. M. Kaandorp and N. M. M. Nibbering, *Org. Mass. Spectrom.*, 1977, **12**, 330.

14 S. Ikuta, *J. Mol. Struct. (Theochem)*, 1998, **434**, 121.

15 (*a*) N. J. Harris and J. F. Sebastian, *Tetrahedron Lett.*, 1991, **32**, 6069; (*b*) C. Lambert, P. v. R. Schleyer and E.-U. Würthwein, *J. Org. Chem.*, 1993, **58**, 6377.

16 (*a*) P. Dem'yanov, G. Boche, M. Marsch, K. Harms, G. Fyodorova and V. Petrosyan, *Liebigs Ann.*, 1995, 457; (*b*) W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353.

17 For reviews, see (*a*) P. Brownbridge, *Synthesis*, 1983, **1**, 85; (*b*) K. Hattori and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 5301; (*c*) M. A. Hena, S. Terauchi, C.-S. Kim, M. Horiike and S.-I. Kiyooka, *Tetrahedron: Asymmetry*, 1998, **9**, 1883; (*d*) P. H. Dussault, T. K. Trullinger and S. Cho-Shultz, *Tetrahedron*, 2000, **56**, 9213; (*e*) M. Bellassoued, S. Mouelhi and N. Lensen, *J. Org. Chem.*, 2001, **66**, 5054.

18 T. Allspach, H. Gümbel and M. Regitz, *J. Organomet. Chem.*, 1985, **290**, 33.

19 B. S. Furnis, A. J. Hanaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Pratical Organic Chemistry*, 4th edn., Longman, London, 1987.

20 **1** was also prepared by thermolysis of ethyl (trimethylsilyl)diazoacetate in the presence of a catalytic amount of rhodium(II) octanoate and a large excess of acetylene. This recation, however, afforded **1** in very poor yield (20%).

21 Gaussian 94, Revision D.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheesman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburg, PA, 1995.

22 Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

23 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785; (*c*) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200; (*d*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11 623.

24 (*a*) R. G. Parr and W. Yang, *Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989; (*b*) W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, 2000.

25 See *e.g.* J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd edn., Gaussian, Inc., Pittsburgh, USA, 1996.

26 L. Pratt and I. M. Khan, *J. Comput. Chem.*, 1995, **16**, 1067.

27 (*a*) A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; (*b*) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.