Investigations on non-classical silylium ions leading to a cyclobutenyl cation†

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Instead of yielding the desired non-classical silylium ions, the reactions of different alkenes/alkynes with several [Me2Si]⁺ sources mostly led to oligomerization, or in the presence of Me3SiH – hydrosilylation of the alkenes/alkynes. Yet, from the reaction of 2-butyne with ion-like Me2Si–F–Al(OR)³ (R³ = CF3H) the salt of the silylated tetramethyl cyclobutenyl cation [Me4C4–SiMe3]+[al–f–a]⁻ 1 ([al–f–a]⁻ = [R¹O]¹Al–F–Al(OR)³]⁻) was obtained in good yield (NMR, scXRD, Raman, and IR). All the experimental and calculated evidence suggest a mechanism in which 1 was formed via a non-classical silylium ion as an intermediate. The removal of the [Me2Si]⁺ moiety from the cation in 1 was investigated as a means to provide free tetramethyl cyclobutadiene (CBD). However, the addition of [NMe4]F, in order to release Me2SiF and form CBD, led to the unexpected deprotonation of the cation. The addition of 4-dimethylaminopyridine to remove the [Me2Si]⁺ cation as a Lewis acid/base adduct, led to an adduct with the four-membered ring in the direct neighborhood of the Me2Si group. By the addition of Et2O to a solution of 1, the [F–Al(OR)³]⁻ anion (and Et2O–Al(OR)³) was generated from the [al–f–a]⁻ counterion. Subsequently, the [F–Al(OR)³]⁻ anion abstracted the [Me2Si]⁺ moiety from [Me4C4–SiMe3]⁺, probably releasing CBD. However, due to the immediate reaction of CBD with [Me4C4–SiMe3]⁺ and subsequent oligomerization, it was not possible to use CBD in follow-up chemistry.

However, it appears that the latter are only intermediates and react further by a methyl shift and formation of a vinyl silylium ion (Scheme 1c).6,7 By contrast, with substituted alkenes, classical carbenium ions as in Scheme 1b were calculated to be favored.6 Adducts of silylium ions with benzene or toluene could also be considered to possess non-classical structures, but crystallographic studies and also quantum-chemical calculations suggest a classical structure.8,9

The all-silicon analogue to the non-classical carbenium ions would be a silylium ion, which is coordinated by a disilene RSi=SiR₂ or by a (formal) disilyne RSi≡SiR. To the best of our knowledge, for the [Si,R₃]⁺ cations no experimental data exist and computational analyses are limited to thermodynamics and do not discuss structural properties.10 Reactions of silylium ions with di- and trisilenes yielded cycloketrasilenylium ions [(RSi)₂SiR₂]⁺ as part of more complicated rearrangement reactions (Scheme 1d; R = Bu₃MeSi, Bu).10,11 In any event, the stabilization of disilenes and disilynes against oligomerization requires large substituents R, which hinder their – classical or non-classical – coordination to a silylium ion.10,11,12 Although calculations at the MP2/def2-TZVPP level suggest a non-classical adduct between [Me₂Si]⁺ and the sterically hindered Me₆Si⁺ the disilene would not be isolable due to the discussed oligomerization. Therefore, we set out to synthesize non-classical silylium ions by reaction of sources of the small [Me₂Si]⁺ silylium ion with alkenes or alkynes. With small substituents,
Preliminary assessment of the stabilities of non-classical silylium ions

Calculations on the reaction of the free [Me3Si]+ cation with different alkenes and alkynes were performed at the MP2/def2-TZVPP level of theory according to eqn (1) and (2) (Table 1).

\[
[M_{e3}Si]^+ + R\equiv CR \rightarrow [M_{e3}Si(R\equiv CR)]^+ (R = H, Me, Ph) \tag{1}
\]

\[
[M_{e3}Si]^+ + R_2C\equiv CR_2 \rightarrow [M_{e3}Si(R_2C\equiv CR_2)]^+ (R = H, Me, Ph) \tag{2}
\]

For comparison, the structure of the [classical] benzene complex [Me3Si(C6H6)]+ is also included in Table 1. In order to evaluate whether the molecules are non-classical silylium ions or classical carbenium ions, we analyzed both relevant C–C–Si bond angles. For a classical carbenium ion, one of these angles is expected to be larger than at least 90°, while for non-classical silylium ions both angles should be (almost) equal and smaller than 90°. The complex \([Me3Si(Ph_2C\equiv CPh_2)]^+\) was calculated to be a classical carbenium ion stabilized by the \(\beta\)-Si effect with a C–C–Si angle of 93.8°, possibly due to the resonance of the phenyl moieties and also for steric reasons. The C–C–Si angles in the \(H_2C\equiv CH_2\) (73.4°), \(Me_3C\equiv CMe_2\) (72.9°), \(MeC\equiv Me\) (74.3°) and \(PhC\equiv CPh\) (74.3°) complexes combined with the symmetric C–Si distances suggest a non-classical structure for these cations. Regarding its structure, the [Me3Si(HC\equiv CH)]+ cation is a special case with asymmetric C–C–Si angles of 78.3° and 71.6°, most likely induced by steric repulsion of the H-atom with one methyl group. Yet, we will refer to its structure as being non-classical. It should be noted that the non-classical structure of this cation with symmetric C–C–Si angles is disfavored by only \(\DeltaG^0_{gas} = 0.01 \text{ kJ mol}^{-1}\) and therefore these two structures would be expected to be indistinguishable. The structures calculated at the simpler BP86-D3(BJ)/def-TZVP level of theory are similar, except for [Me3Si(PhC\equiv CPh)]+. Here, the PhC\equiv CPh adduct is calculated to be a classical carbenium ion. It was not possible to calculate similar classical structures for the other adducts, as these are not even local minima or transition states on the respective energy hypersurface. This was exemplarily verified by calculating the energy of [Me3Si(MeC\equiv CMe)]+ dependent on the C–C–Si angle in the range of 60 to 140° (see the ESI† for details). Therefore, classical starting structures also collapse to the non-classical structures. Thus no clear energy difference between a formally classical and a non-classical structure can be given.

Results and discussion

Before turning to the experiments, we investigated the principle feasibility of the planned reactions by assessing the cations sought for with DFT and \textit{ab initio} calculations and including solvation energies for the polar and weakly basic solvent ortho-difluorobenzene (\(\alpha\)-DFB, \(\varepsilon_r = 13.4\)).

Scheme 1  Classical and non-classical structures of (a) the 2-norbornyl cation and (b) analogous silylium ions (although we refer to “classical silylium ions” here, these are rather to be seen as carbenium ions stabilized by the \(\beta\)-Si effect); (c) the calculated methyl shift for the \([Me3Si(C_2H_3)]^+\) cation; (d) the reaction products of silylium ions with di- and trisilenes. 15,11

their \(\pi\) bond is more accessible than that in sterically hindered room temperature stable disilenes and disilynes. Additionally, alkenes and alkynes would allow for a homogeneous delocalization of the positive charge among the carbon atoms, which would require more reorganization for the disilenes/disilynes due to their trans-bent structure. However, the fluoride ion affinity (FIA), as a measure of Lewis acidity,\(^{14}\) of silylium ions is significantly higher than that of carbenium ions (FIA = 952 vs. 836 \(\text{kJ mol}^{-1}\) for [Me2E]+; \(E = Si, C\); calculated like in ref. 15; BP86/def-SV(P)). As a result, the addition of an alkene or alkyn to a silylium ion may also result in the formation of a carbenium ion that is stabilized in the \textit{classical} structure by the so-called \(\beta\)-Si effect. This implies a hyperconjugative stabilization due to electron density transfer from the occupied \(\sigma\)(Si–C) orbital into the empty \(\rho\)-orbital of the cationic C atom (Scheme 1b).

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The gas phase reaction enthalpies $\Delta H_{\text{gas}}^0$ and Gibbs energies $\Delta G_{\text{gas}}^0$ of the reaction \([\text{Me}_3\text{Si}]^+ + \text{L} \rightarrow \text{[Me}_3\text{Si][L]}^+\) calculated at the MP2/def2-TZVPP level of theory with thermal contributions from BP86-D3(BJ)/def2-TZVP calculations. The Gibbs solvation energy in o-DFB was calculated using the COSMO model ($\varepsilon = 13.4$) at the BP86-D3(BJ)/def2-TZVP level. Scheme: H (light gray), C (dark gray), Si (blue).

| Ligand L | $\frac{\Delta H_{\text{gas}}^0}{\Delta G_{\text{gas}}^0}$ (o-DFB) | dSC/pm | Gas phase structure |
|----------|---------------------------|--------|-------------------|
| H$_2$C==CH$_2$ | $-109/-60$ | 73.4 | |
| Me$_2$C==CMe$_2$ | $-174/-113$ | 72.9 | |
| Ph$_2$C==CPh$_2$ | $-143/-67$ | 93.8/54.6 | 221.6/271.4 |
| Ph==CPh | $-98/-53$ | 78.3/71.6 | |
| Me==CMe | $-157/-103$ | 74.3 | |
| Ph==CPh | $-188/-132$ | 74.3 | |
| C$_6$H$_6$ | $-134/-86$ | 98.3/51.3 | 217.3/275.8 |

Including COSMO$^{17}$ Gibbs solvation energies, all calculated reaction energies become less favored and the reaction of [Me$_3$Si]$^+$ with the larger PhC==CPh was also calculated to be less exergic than that with the smaller MeC==CMe. This is attributed to the fact that smaller ions are generally better solvated than larger ones. Since upon reaction with [Me$_3$Si]$^+$ the product cation always increases in size, reactions (1) and (2) become less favored the larger the ligand. Due to this effect, the formation of [Me$_3$Si(Ph$_2$C==CPh)$_2$]$^+$ was calculated to be endergonic in solution by $\Delta G_{\text{o-DFB}}^0 = +20$ kJ mol$^{-1}$.

### Reactions of Me$_3$Si-F—Al(OR$_3$)$_3$ with alkynes and alkenes

Since the calculations suggested that the formation of non-classical silylium ions should be possible, in part also in solution, we turned towards their synthesis. Ethylene and acetylene are gases and only weakly bound to [Me$_3$Si]$^+$ (cf. Table 1). Therefore, we performed the reactions of Me$_3$Si—F—Al(OR$_3$)$_3$ with the substituted compounds R$_3$C==C'R and RC==CR (R = Me, Ph). However, the reactions with Me$_2$C==CMe$_2$, Ph$_2$C==CPh$_2$ and PhC==CPh in o-DFB or CH$_2$Cl$_2$ and at r.t. or $-40$ °C did not yield any silylium ions, but only led to exergonic oligomerization of the alkenes and alkynes. However, this signals activation of the unsaturated hydrocarbons by Me$_3$Si—F—Al(OR$_3$)$_3$. By contrast, reactions with MeC==CMe in o-DFB or CH$_2$Cl$_2$ at various temperatures ($-40$ °C to r.t.; eqn (3), reproducibly gave a 28% yield of [Me$_3$C==SiMe$_3$][al-f-al]$^+$ 1 ([al-f-al]$^+ = [(R'OR)$_3$Al—F—Al(OR)$_3$]$^+$; NMR, scXRD, Raman, IR) after crystallization. This compound will be discussed later in more detail.

### Reactions of [Ph$_3$C]'[al-f-al]$^+$ with Me$_3$SiH and alkenes/alkynes

By exchanging Me$_3$Si—F—Al(OR$_3$)$_3$ for more reactive silylium ions, we hoped to form the desired products faster and thereby prevent oligomerization. In order to generate the [Me$_3$Si]$^+$ cation as an intermediate, we mixed the starting materials (liquid alkenes or alkynes) with [Ph$_3$C]'[al-f-al]$^+$ in the absence of solvent. An excess of Me$_3$SiH was condensed onto this mixture to generate silylium ions or their Me$_3$SiH adducts$^{18}$ in situ and allowed to warm to r.t. Although NMR spectra of these reaction mixtures in CD$_2$Cl$_2$ showed complete conversion of the starting materials, the non-classical silylium ions could not be detected. Instead, hydrosilylation of PhC==CPh and MeC==CMe$_2$ (see the ESI† for details) and formation of neutral 2 for...
MeC≡CMe were observed (eqn (4)). Upon reaction of MeC≡CMe with [Ph₃C][al-f-al] and Me₃SiH, presumably 1 was formed, which then reacted with excess Me₃SiH to yield 2 and [Me₃Si(solv)] (solv = Me₃SiH, CH₂Cl₂). Only after complete conversion of the alkenes and alkynes, the anion was attacked and decomposed. It should be noted that the evolving [Me₃Si–H–SiMe₃][al-f-al] is not isolable as a pure material. Yet, the [al-f-al] anion was shown to be fairly stable against silylium ions in CH₂Cl₂.

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Reactions of bromo-ethyl/vinyl silanes with Ag+[al-f-al]⁻

In order to prevent oligomerization of the alkenes and alkynes, we reacted bromo-ethyl and bromo-vinyl silanes with Ag+[al-f-al]⁻ in CH₂Cl₂ at −40 °C, respectively. The abstraction of Br⁻ from these silanes by Ag⁺ should result in the formation of ethylene/acetylene adducts of [Me₃Si]\(^+\) (cf. eqn (5a) for the bromo-ethyl example). Here the reaction with a second equivalent of an alkene/alkyne is not possible and the non-classical silylium ions should become isolable. Upon reaction, no solid AgBr visibly formed. Nevertheless, NMR spectra of these reactions did not show signals of the starting silanes, but of Me₃SiBr in both cases. This signal is slightly shifted to a lower field by 2 ppm and suggests a coordination of Me₃SiBr to Ag⁺. It seems likely that the non-classical silylium ions [Me₃Si(C₂H₄/C₂H₂)]⁺ were generated in situ (eqn (5a)). However, apparently these silylium ions then reacted further with the (solvated) AgBr under the formation of [[Me₃SiBr]Ag(solv)]⁺ and release of C₂H₄/C₂H₂ (see eqn (5b) for the ethene example; the evolving C₂H₄ could be identified by gas phase IR spectroscopy).

Similar silver-halosilane adducts were observed and structurally characterized upon reaction of “Bu₂SiBr with Ag⁺[al-f-al]⁻ – although halide abstraction and AgBr formation were desired. Additionally, partial decomposition of the anion and formation of Me₃SiF and Me₃SiCl were observed, which is further evidence for the generation of silylium ions.

Formation of [Me₃Si(MeC≡CMe)]⁺ vs. [Me₄C₄–SiMe₃]⁺

The reactions of 2-butyne with Me₃Si–F–Al(OR)₃ and silylium ions only yielded 1 and 2, respectively. Both compounds were formed from two 2-butyne units. This led to the question of whether it is at least theoretically possible to isolate the desired silylium ion [Me₃Si(MeC≡CMe)]⁺ by these routes, or if such non-classical ions reside in shallow potential wells that allow for a simple and low-barrier subsequent reaction with MeC≡CMe to give 1. Therefore, we calculated the reaction mechanism for the formation of [Me₄C₄–SiMe₃]⁺ (P-4) at the BP86-D3(BJ)/def-TZVP level of theory (Fig. 1). In order to reduce computational cost, we started from 2-butyne and [Me₃Si]⁺, instead of Me₃Si–F–Al(OR)₃.

Since 2-butyne itself does not dimerize under standard conditions, the silylation of 2-butyne can be assumed to be the first step in the formation of [Me₄C₄–SiMe₃]⁺. The Gibbs activation energy ΔG° (TS1) for this exothermic process was
calculated to be only 10 kJ mol\(^{-1}\). The silylated 2-butyne (\(\text{I}\)) then reacts with a second equivalent of 2-butyne to exothermically form the intermediate \(\text{II}\). We were not able to determine the Gibbs activation energy (TS2) for this reaction with the method used. This indicates that this barrier is either very small or not existent at all. Based on thermodynamics, this intermediate should rearrange to yield a 5-membered ring (P-5). However, the barrier for this rearrangement (TS3-5) was calculated to be 45 kJ mol\(^{-1}\) – which is almost triple the barrier (TS3-4) for the formation of the observed \([\text{Me}_4\text{C}_4\text{SiMe}_3]^+\) (P-4, 16 kJ mol\(^{-1}\)). Thus, the calculations are in agreement with the experimental observation and suggest that P-4 (=1) is the kinetic product.

When \([\text{Me}_4\text{Si}^+\text{F}\text{Al(OR)}^3]_2\) is used for the silylation of 2-butyne, the Gibbs activation energy (transition state similar to TS1) for this reaction is expected to be higher, due to its lower reactivity compared to \([\text{Me}_4\text{Si}]^+\). However, this will not change the entire picture. In conclusion it seems impossible to isolate the silylated 2-butyne (\(\text{I}\)) by use of \([\text{Me}_4\text{Si}^+\text{F}\text{Al(OR)}^3]_2\) or even (non-existent) free \([\text{Me}_4\text{Si}]^+\), as the reaction with the second molecule of 2-butyne appears to be much faster than the silylation.

**Properties of \([\text{Me}_4\text{C}_4\text{SiMe}_3]^-\,[\text{al-f-al}]^+\)**

From the reaction solution in o-DFB at r.t. single crystals of \(\text{I}\) were obtained by the addition of less polar CH\(_2\)Cl\(_2\). The molecular cation structure of salt \(\text{I}\) is shown in Fig. 2. With Si1–C1–C2/C2’ angles being 113°–118°, the stabilization of this cation by the β-silicon effect is not evident. Otherwise, these angles would be expected to lie around 90°.\(^{22}\)

This cation can be seen as a silylated cyclobutadiene and is closely related to the already known homoaromatic \([\text{R}_4\text{C}_4^–\text{H}]^+, [\text{R}_4\text{C}_4\text{Cl}^–\text{Cl}]^+, [\text{Bu}_4\text{C}_4\text{OH}]^–\) and the neutral \([\text{R}_4\text{C}_4\text{AlX}_3]\) (R = H, Me, ‘Bu, Ph; X = Cl, Br).\(^{23–29}\) Of these, the protonated cations \([\text{R}_4\text{C}_4\text{H}]^+\) with R = H, Me, Ph were only characterized by NMR at \(-40\) to \(-70\) °C,\(^{27}\) while with R = ‘Bu they were shown to be isolable with a large variety of anions, like \(\text{Br}^–\) or \([\text{SbF}_6]^–\).\(^{28}\) Also the chlorinated and hydroxylated cations \([\text{Ph}_4\text{C}_4\text{Cl}^–\text{Cl}]^–\) and \([\text{Bu}_4\text{C}_4\text{OH}]^–\) and the neutral \([\text{Me}_4\text{C}_4\text{AlCl}_3]\) were shown to be stable at r.t. and could be isolated.\(^{22,24–26,29}\)

A comparison of selected structural parameters, calculated NPA and PABOON partial charges and \(\pi^a(C_2\text{–C}_2\text{–C}_2’)\)-orbital energies of the compounds is found in Table 2. In order to allow for a better comparison, these calculations were performed on the methyl-substituted derivatives for all compounds. The \([\text{RSi}]_4\text{SiR}_3\) cations (R = ‘Bu,MeSi, ‘Bu) can also be seen as silicon analogues of these compounds but will not be discussed.\(^{30–33}\) When comparing the convolution angles (C1–C2–C2’–C3) of \(\text{I}, [\text{Bu}_4\text{C}_4\text{H}]^+, [\text{Ph}_4\text{C}_4\text{Cl}]^+, [\text{Bu}_4\text{C}_4\text{OH}]^–\) and \([\text{Me}_4\text{C}_4\text{AlX}_3]\), their absolute values are relatively similar and range between 37.3° and 31.5°, except for \([\text{Ph}_4\text{C}_4\text{Cl}][\text{Nb}_2\text{OCl}_6]\) with a dihedral angle of only 4.3°. However, the dihedral angles in \(\text{I}\) and \([\text{Me}_4\text{C}_4\text{AlX}_3]\) are positive, while in \([\text{Bu}_4\text{C}_4\text{H}]^+, [\text{Bu}_4\text{C}_4\text{OH}]^–\) and \([\text{Ph}_4\text{C}_4\text{Cl}]^–\) they are negative. This is a consequence of the (C2–)Me groups being bent, which leads to repulsion of the sterically most demanding group. The relatively small dihedral angle in \([\text{Ph}_4\text{C}_4\text{Cl}]^–\) results from resonance of the phenyl moieties with the (C2–C2’) orbitals, which is an intermediate between a σ and a π orbital. This leads to an increased C2–C2’ distance compared to that in the other compounds (203 vs. \(\approx 180\) pm).\(^{27,28}\)

When looking at the bonding \(\pi(C_2\text{–C}_2\text{–C}_2’\text{–C}_2’\text{–C}_3)\) orbitals of the methylated derivatives of the discussed compounds (Table 2), a correlation between their energies and the partial charge of the \(\text{Me}_4\text{C}_4\) moiety is evident, with a higher partial charge leading to lower orbital energies. From a frontier orbital point of view, this implies that the cations \([\text{Me}_4\text{C}_4\text{SiMe}_3]^+, [\text{R}_4\text{C}_4\text{H}]^+, [\text{R}_4\text{C}_4\text{Cl}^–\text{Cl}]^+, [\text{Bu}_4\text{C}_4\text{OH}]^–\) are more electron-deficient than the neutral \([\text{Me}_4\text{C}_4\text{AlX}_3]\). This is also evident when simply looking at the total charge of these molecules. Interestingly, the energies of the \(\pi^a(C_2\text{–C}_2\text{–C}_2’)\) orbitals seem to be less affected by the partial charge of the \(\text{Me}_4\text{C}_4\) moiety, but mostly by the total charge of the molecules. Therefore, the energy of this orbital is nearly the same for \([\text{Me}_4\text{C}_4\text{AlCl}_3]\) and \(\text{Me}_4\text{C}_4\), while for the cationic species it is lower by \(\approx 4\) eV.

**Fig. 2.** Molecular structure of the cation in \([\text{Me}_4\text{C}_4\text{SiMe}_3]^-\,[\text{al-f-al}]^+\) (1) with thermal ellipsoids set at 50% probability level. The [al-f-al]^- anion was omitted for clarity. Scheme: Si (yellow), C (grey), H (white). Selected distances (pm), bond angles (deg), and torsion angles (deg): Si1–C1 192.2(2), C1–C2 151.8(2), C1–C2’ 152.6(2), C2–C2’ 138.9(2), C2’–C3 138.5(2), C2–C2’ 179.4(2), Si1–C1–C2 117.9(1), Si1–C1–C2’ 113.0(1), C2–C1–C2’ 72.2(1), C2–C3–C2’ 80.6(1), and C1–C2–C3–C2’ 25.5(1).

**Evaluating the homoaromatic character of \([\text{R}_4\text{C}_4\text{E}]^{(1)}\)**

Since the structural parameters of the discussed compounds are very similar, especially \(d(C_2\text{–C}_2’\text{–C}_3)\) and \(d(C_2\text{–C}_2’\text{–C}_3)\), an unambiguous comparison of the C2–C2’ interactions is not possible (except for \([\text{Ph}_4\text{C}_4\text{Cl}^–\text{Cl}]^–\), which does not show this interaction). This interaction is a measure of homoaromaticity and can be determined from the difference in NMR chemical shifts between C2/C2’ and C3 (Table 3).\(^{26,27}\) In allylic systems, the terminal C atoms (here C2/C2’) bear a positive charge, resulting in the deshielding of these. The interaction between C2 and C2’ leads to their shielding, combined with the transfer of the positive charge to C3 (deshielding). For homoaromatic systems
a negative value for $\Delta (\delta_{13}^{\text{C}}(\text{C}_2) - \delta_{13}^{\text{C}}(\text{C}_3))$ is expected, while for allylic systems this difference should be positive.26

With [H4C4C(H)] and the cyclopentenylium cation [H4C4C(H)] being the prototypes for homoaromatic and allylic cations, respectively, the homoaromatic character of the discussed compounds and influence of the substituents can be evaluated. Exchanging the H substituents for Me moieties in [R4C4C(H)] leads to hyperconjugation of the C–H bond to C2. As a result, the C2–C2′ interactions are decreased and C2 is deshielded. Therefore the difference between $\delta_{13}^{\text{C}}(\text{C}_2)$ and $\delta_{13}^{\text{C}}(\text{C}_3)$ is more positive (0.0 vs. $-54.1$ ppm for [H4C4C(H)]). The methylated compounds [Me4C4C(SiMe3)+] and [Me4C4C(Cl)] show similar differences in the shielding of C2 and C3 and therefore are considered to have a similar homoaromatic character as [Me4C4C(H)]. Only [Me4C4C(AlCl3)] shows a comparatively high deshielding of C2 due to low homoaromaticity, which is a consequence of the hyperconjugation of the $\sigma$(C–C) orbital to the (C2–C2′) orbital.

When looking at the C2–C2′ interactions of [‘Bu4C4C(H)] and [‘Bu4C4C(OH)] they would be expected to be even weaker than in [Me4C4C(H)] and [Me4C4C(Cl)], respectively, due to the stronger electron-donating properties of the ‘Bu moieties. However, the NMR chemical shifts suggest a significantly increased homoaromatic character. We assign this to the bulkiness of the ‘Bu moieties leading to a repulsion of the C3–Bu and C2–Bu groups. As a result, the C1–C2–C2′–C3 dihedral angle is higher than that for the methylated derivatives (Table 2). Phenyl substituents seem to completely prevent the C2–C2′ interactions due to resonance and charge delocalization on the phenyl residue(s). This follows from the NMR chemical shifts of [Ph4C4C(H)] and from the structural parameters of [Ph4C4C(Cl)] (dihedral angle and $d$(C2–C2′)).

Taking a closer look at the dihedral angles in the discussed compounds, a correlation between these and $\Delta (\delta_{13}^{\text{C}}(\text{C}_2) - \delta_{13}^{\text{C}}(\text{C}_3))$ is evident. The higher the dihedral angle, the stronger the C2–C2′ interaction in the compound. For [H4C4C(H)] this angle was calculated to be $33.5^\circ$ (BP86-D3(BJ)/def-TZVP), which is in agreement with this thesis. Interestingly, the distances $d$(C2–C2′) and $d$(C2–C3) are only slightly affected by these C2–C2′ interactions (Table 2).

### Investigations towards release of Me4C4 from 1

While information on the reactivities of most of the discussed compounds is scarce, [R4C4C(AlCl3)] was shown to be a source of cyclobutadienes R4C4 (CBDs) by use of coordinating solvents, like DMSO, due to abstraction of AlCl3.28,32–34 Besides the discussed AlX3 adducts cyclobutane dicarboxylic acid anhydrides

### Table 2 Selected experimental (calculated) properties of different [R4C4C=–E]1+ compounds (E = SiMe3, H, Cl, OH, AlCl3, and AlBr3). Distances are given in pm, angles are given in ° and orbital energies are given in eV. The calculated values always refer to [Me4C4C=–E]1+ for better comparability; BP86-D3(BJ)/def-TZVP

| 1 | [‘Bu4C4C(H)]1+ | [Ph4C4C(Cl)]1+ | [‘Bu4C4C(OH)]1+ | [Me4C4C=–AlCl3]1+ | [Me4C4C=–AlBr3]1+ | Me4C4 |
|---|---|---|---|---|---|---|
| $d$(C1–C2) | 151.8/152.6/152.7 | 152.4/153.4 | 152.9/154.4/153.2 | 152.3/153.8/154.2 | 151.0/151.5 | 151.6 (159.1) |
| $d$(C2–C2′) | 179.4/183.2 | 180.6/187.5 | 203.3/195.5 | 183.3/190.7 | 179.8/183.1 | 184.4 (208.5) |
| $d$(C2–C3) | 138.5/138.9/140.2 | 140.7/140.2 | 138.7/140.4/140.6 | 139.4/139.6/140.2 | 138.7/140.2 | 140.2 (134.7) |
| C1–C2–C2′–C3 | 31.7 (29.3) | –37.3 (–27.7) | –4.3 (–22.1) | –36.3 (–26.2) | 31.5 (28.5) | 27.3 (0.0) |

### NPA/PABOON partial charges for the methyl derivatives [Me4C4C=–E]+

| | $\delta$(C1) | $\delta$(C2) | $\delta$(C3) | $\delta$(E) | $\delta$(C1) | $\delta$(C2) | $\delta$(C3) | $\delta$(E) |
|---|---|---|---|---|---|---|---|---|
| [H4C4C=–E]+ | $-0.45/-0.14$ | $-0.27/-0.05$ | $-0.09/0.09$ | $0.26/0.15$ | $-0.52/-0.14$ | $-0.54/-0.13$ | $0.03/0.01$ | $0.27/0.27$ |
| [Ph4C4C=–Cl]+ | $0.27/0.21$ | $0.28/0.19$ | $0.30/0.13$ | $0.17/0.15$ | $0.27/0.27$ | $0.28/0.27$ | $0.00/0.01$ | $0.00/0.01$ |
| [‘Bu4C4C=–OH]+ | $0.00/0.00$ | $0.02/0.01$ | $-0.01/0.01$ | $0.02/0.03$ | $-0.04/-0.05$ | $0.05/-0.05$ | $0.00/0.01$ | $0.00/0.01$ |
| [Me4C4C=–AlCl3]+ | $0.51/0.82$ | $0.75/0.90$ | $1.00/1.03$ | $1.16/1.01$ | $0.25/0.67$ | $0.25/0.67$ | $0.00/0.00$ | $0.00/0.00$ |
| [Me4C4C=–AlBr3]+ | $0.49/0.18$ | $0.25/0.10$ | $0.06/0.03$ | $-0.16/-0.01$ | $-0.25/-0.67$ | $-0.25/-0.67$ | $-0.25/-0.67$ | $-0.25/-0.67$ |

### Energies of the (anti)–bonding $\pi$(C2–C3–C2′)–orbitals of the methyl derivatives [Me4C4C=–E]+

| | $E_{\text{x}^2}$(C2–C3–C2′) | $E_{\text{x}^2}$(C2–C3–C2′) | $E_{\text{x}^2}$(C2–C3–C2′) |
|---|---|---|---|
| [H4C4C=–E]+ | $-1.5$ | $-0.61$ | $-0.61$ |
| [Ph4C4C=–Cl]+ | $-1.92$ | $-0.73$ | $-0.74$ |

### Table 3 Experimental 13C NMR chemical shifts of [R4C4C=–E]1+ in ppm (R = H, Me, ‘Bu, and Ph; E = SiMe3, H, Cl, OH, AlCl3, and AlBr3)

| Cation | $\delta$(C1) | $\delta$(C2/C2′) | $\delta$(C3) | $\delta$(C2) – $\delta$(C3) |
|---|---|---|---|---|
| [Me4C4C=–SiMe3]+ | 66.8 | 166.0 | 170.4 | 170.4 | 4.4 |
| [‘Bu4C4C=–OH]+ | 101.0 | 161.5 | 184.9 | 23.4 |
| [Me4C4C=–Cl]+ | 76.0 | 191.5 | 174.8 | 17.1 |
| [Me4C4C=–AlCl3]+ | 162.0 | 164.3 | 0.0 |
| [Me4C4C=–AlBr3]+ | 23.4 | 164.3 | 0.0 |

a Cyclopentenylium cation as reference for an allylic cation.
and \([\text{Fe(CO)}_3(\text{C}_4\text{H}_4)]\) can also be used for the generation of CBDS.\textsuperscript{25} CBDS are anti-aromatic and, therefore, unsubstituted CBD undergoes dimerization readily at \(T > 35\ \text{K}\).\textsuperscript{30} Thus, small CBDS have to be generated \textit{in situ}. Only when they bear large substituents, dimerization can be prevented.\textsuperscript{37}

By abstraction of the \([\text{Me}_3\text{Si}]^+\) moiety, \textbf{1} might be used as a tetramethylcyclobutadiene (\(\text{Me}_4\text{C}_4\)) donor as well. The advantage of \textbf{1} over \([\text{Me}_4\text{C}_4\text{–AlX}_3]\) as a CBD donor would be its increased stability, which allows for storage in a glove box for more than a year. NMR spectra of \([\text{Me}_4\text{C}_4\text{–AlX}_3]\) show partial coalescence of the signals already at 20 °C.\textsuperscript{29} In contrast, all signals of \textbf{1} are resolved, including the \(J_{\text{H1–H1}}\) coupling of 0.46 Hz. The increased stability very likely results from the higher Lewis acidity of \([\text{Me}_3\text{Si}]^+\) over \(\text{AlX}_3\) \((\text{FIA} = 539 \text{ vs.} 425/438 \text{ kJ mol}^{-1}, X = \text{Cl/Br})\). These FIA were calculated in an environment with the polarity of \(\text{CH}_2\text{Cl}_2\) \((\epsilon = 8.9)\) using COSMO.\textsuperscript{37} in order to account for the different charges of the Lewis acids. The effect is also evident by addition of \(\text{AlX}_3\) to \([\text{Me}_4\text{C}_4\text{–AlX}_3]\) in order to increase the Lewis acidity, \textit{i.e.} the formation of \([\text{Me}_4\text{C}_4\text{–Al}_2\text{X}_6]\). It shows an increased thermal stability and reduced coalescence compared to \([\text{Me}_4\text{C}_4\text{–AlX}_3]\).\textsuperscript{29}

**Reaction with \([\text{NMe}_4]^+\)\**

Due to the high stability of the Si–F bond, we reacted \textbf{1} with \([\text{NMe}_4]^+\) in \(\text{o-DFB/CH}_2\text{Cl}_2\) at r.t., in order to generate \(\text{Me}_3\text{SiF}\) and \(\text{Me}_4\text{C}_4\). However, only negligible amounts of \(\text{Me}_3\text{SiF}\) formed. The main products were \([\text{NMe}_4]^+[\text{F}_{1+1}\text{–Al}(\text{OR})_3]^-\) \((X = 0, 1)\), \(\text{HOR}\) and 3 due to deprotonation of \textbf{1} \((\text{eqn (6a)})\). The formation of the anions \([\text{F}_{1+1}\text{–Al}(\text{OR})_3]^-\) occurs due to the high Lewis acidity of \([\text{al-f-al}]^+\).\textsuperscript{37} The deprotonation of \textbf{1} suggested that a non-charged nucleophile, like 4-dimethylaminopyridine (DMAP), could be helpful to prevent deprotonation of the cation.

**Reaction with DMAP**

The reaction of \textbf{1} with an excess of DMAP in a mixture of \(\text{o-DFB and CH}_2\text{Cl}_2\) at r.t. yielded mainly DMAP–\(\text{Al(OR)}_3\)^\(2+\) \((\text{reaction with the anion})\) and the adduct of \([\text{Me}_4\text{C}_4\text{–SiMe}_3]\) with DMAP \((\text{eqn (6b)})\). We were able to obtain single crystals of both compounds at −40 °C from the reaction solution \((\text{see the ESI† for details})\). The crystal structure and NMR spectra of \textbf{4} showed that the cation is obtained as an enantiomeric mixture, with the DMAP and the \([\text{Me}_4\text{C}_4]^-\) moieties being in \textit{syn}-conformation, \textit{i.e.} in \((S,R)\) and \((R,S)\) configurations, which is attributed to the orientation of the LUMO \textbf{1} \((\text{see Fig. S-60†})\). A similar adduct between \(\text{Me}_4\text{C}_4\text{–AlCl}_3\) and \(\text{PPhCl}_2\) was already proposed as an intermediate in the synthesis of phosphine oxides.\textsuperscript{33} Due to the syn-

![Diagram](image-url)

**Reaction with diethylene**

Unexpectedly, one of the minor side products in the reaction of \textbf{1} with DMAP was \(\text{Me}_3\text{SiF}\), providing evidence for the reaction of \([\text{Me}_4\text{C}_4\text{–SiMe}_3]\) with a fluoride ion source. Since \textbf{1} is stable in \(\text{o-DFB over several days}, the Lewis basic \([\text{F–Al(OR)}_3^-]\)^\(1+\) anion \([\text{f-al}]^-\) \textsuperscript{38} has to be considered as the fluoride ion source. This is in agreement with the findings that the NMR spectra of \textbf{1} never showed the presence of \([\text{f-al}]^-\), independent of the reaction stoichiometry.\textsuperscript{38} Therefore, we dissolved \textbf{1} in \(\text{Et}_2\text{O at r.t.}, which is known to induce the dissociation of \([\text{al-f-al}]^-\) into \(\text{Et}_2\text{O–Al(OR)}_3\)\(^{2+}\) and \([\text{f-al}]^-\).\textsuperscript{38} NMR spectra of this reaction mixture revealed the formation of \(\text{Me}_3\text{SiF}\) and complete decomposition of \textbf{1} \((\text{eqn (6c)})\), but no evidence for the expected dimerization product of \(\text{Me}_4\text{C}_4\) could be found.\textsuperscript{34} Instead, the NMR spectra suggested the formation of oligomerization products. This reaction was performed in the presence of 2-butyne, partial formation of \(\text{C}_n\text{Me}_6\) was observed, similar to the reaction of \([\text{Me}_4\text{C}_4\text{–AlCl}_3]\) with 2-butyne and DMSO.\textsuperscript{44} Therefore, we assume this reaction is (weak) evidence for the intermediate release of CBD from \textbf{1}. However, analogous reactions of \textbf{1} with other electron-deficient or electron-rich dienophiles \((\text{MeO}_2\text{C}^-\text{C}==\text{C}–\text{CO}_2\text{Me}, \text{Me}_3\text{Si}–\text{C}==\text{SiMe}_3\) never gave the desired Diels–Alder products.\textsuperscript{29} but only the known oligomerization products and complete retention of the alkynes.

It should be noted that the reaction solution for the synthesis of \textbf{1} also contained \(\text{C}_6\text{Me}_6\) and these oligomerization products. The reason for this is that in the first stage of the reaction of \(\text{Me}_3\text{Si–F–Al(OR)}_3\)^\(1+\) with 2-butyne the \([\text{f-al}]^-\) anion is formed. Therefore, \([\text{f-al}]^-\) and 2-butyne are present in solution at the same time. Thus, \textbf{1} readily reacts with \([\text{f-al}]^-\) upon its initial synthesis, resulting in its decomposition and accounting for the relatively low yield of 28%. Eventually, the formation of \([\text{al-f-al}]^-\) from \([\text{f-al}]^-\) and \(\text{Me}_3\text{Si–F–Al(OR)}_3\)^\(1+\) suppresses this decomposition reaction.

**Rationalization**

Why is there such a difference in the reactivity of alkynes with \(\text{Me}_4\text{C}_4\) released from \textbf{1} and from \([\text{Me}_4\text{C}_4\text{–AlX}_3]\)? \(\text{Me}_4\text{C}_4\) is an electron-rich diene \((\text{high HOMO energy})\) and therefore should react with electron-deficient dienophiles \((\text{low LUMO energy})\). While the \(\pi\)-LUMO energy of −1.92 eV for \([\text{Me}_4\text{C}_4\text{–AlX}_3]\) is rather...
high and similar to that for free Me₄C₄, it is much lower for 1 with an energy of −5.60 eV (Table 1). For this reason [Me₂C₄−AlX₃] is a poor dienophile and the released Me₄C₄ alone undergoes Diels–Alder reactions with the added alkynes. In contrast, the π-LUMO energy of even very electron-deficient alkynes, like F₃C−C≡C–CF₃ (−2.70 eV), is significantly higher than that of 1. As a result, the evolving Me₄C₄ reacts with [Me₄C₄−SiMe₃]+ instead of other dienophiles, leading to oligomerization. The same problem is likely to arise when using the other cationic cyclobutenyl cations as their π-LUMO energies are expected to be in the same region as those of 1.

Conclusion

By the reaction of Me₃Si−F−Al(OR)₃ with different alkenes and alkynes the synthesis of non-classical silylium ions was investigated. However, most of these reactions only led to oligomerizations in which such silylium ions may be intermediates; they were assessed by calculations (Table 1). Replacing Me₃Si−F−Al(OR)₃ with silylium ions, generated in situ from [Ph₂C][al−f−al]− and Me₂SiH, also did not yield the desired non-classical silylium ions. Instead, hydrosilylation of the alkenes and alkynes was observed. Preliminary tests suggest that these hydrosilylation reactions can be performed with only catalytic amounts of [Ph₂C][al−f−al]−. However, this should be investigated in a separate study by specialists. Halide abstraction reactions from bromo-vinyl/alkyl silanes by Ag⁺[al−f−al]− seemed to be successful, but resulted in the formation of bromo silanes and C₂H₂/ C₂H₄ due to the reaction of the silylium ions with solvated AgBr. From the reaction of Me₃Si−F−Al(OR)₃ with 2-butyne, a salt of the stable silylated tetramethyl cyclobutylcycnion cation [Me₄C₄−SiMe₃]+ was obtained. Attempts to release the CBD Me₄C₄ from this compound did not result in the planned Diels–Alder reactions, but only in oligomerization products. We attribute this to the comparatively low π-LUMO energy of [Me₄C₄−SiMe₃]+, leading to the reaction of this cation with the evolving Me₄C₄.

Conflicts of interest

There are no conflicts to declare.

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References

1 (a) G. A. Olah and G. K. Surya Prakash, ed. Carbocation Chemistry, John Wiley & Sons, Hoboken, New Jersey, 2004; (b) H. Meerwein and K. van Emster, Ber. Dtsch. Chem. Ges. A/B, 1922, 55, 2500.
2 G. A. Olah, J. Am. Chem. Soc., 1972, 94, 808.
3 (a) P. v. R. Schleyer, D. Lenoir, P. Mison, G. Liang, G. K. S. Prakash and G. A. Olah, J. Am. Chem. Soc., 1980, 102, 683; (b) H. C. Brown, Acc. Chem. Res., 1986, 19, 34; (c) S. Winstead and D. S. Trifan, J. Am. Chem. Soc., 1949, 71, 2953; (d) H. C. Brown, The Nonclassical Ion Problem, Springer US, Boston, MA, 1977.
4 F. Scholz, D. Himmel, F. W. Heinemann, P. v. R. Schleyer, K. Meyer and I. Krossing, Science, 2013, 341, 62.
5 (a) B. Chiavarino, M. E. Crestoni, J. Lemaire, P. Maitre and S. Fornarini, J. Chem. Phys., 2013, 139, 71102; (b) O. Mó, M. Yáñez, J.-F. Gal, P. C. Maria and J.-C. Guillemin, J. Phys. Org. Chem., 2002, 15, 509; (c) B. Chiavarino, M. E. Crestoni and S. Fornarini, Chem. Commun., 2002, 1418.
6 X. Li and J. A. Stone, J. Am. Chem. Soc., 1989, 111, 5586.
7 H.-U. Siehl, S. Brixner, C. Coletti, N. Re, B. Chiavarino, M. E. Crestoni, A. de Petris and S. Fornarini, Int. J. Mass Spectrom., 2013, 334, 58.
8 M. F. Ibad, P. Langer, A. Schulz and A. Villinger, J. Am. Chem. Soc., 2011, 133, 21016.
9 (a) T. Müller, C. Bauch, M. Ostermeier, M. Bolte and N. Auner, J. Am. Chem. Soc., 2003, 125, 2158; (b) S. Duttwyler, Q.-Q. Do, A. Linden, K. K. Baldridge and J. S. Siegel, Angew. Chem., Int. Ed., 2008, 47, 1719; (c) J. B. Lambert, S. Zhang and S. M. Ciro, Organometallics, 1994, 13, 2430; (d) J. B. Lambert, S. Zhang, C. L. Stern and J. C. Huffman, Science, 1993, 260, 1917.
10 S. Inoue, M. Ichinohe, T. Yamaguchi and A. Sekiguchi, Organometallics, 2008, 27, 6056.
11 A. Sekiguchi, T. Matsuno and M. Ichinohe, J. Am. Chem. Soc., 2000, 122, 11250.
12 A. Burcat and E. Goos, Int. J. Chem. Kinet., 2018, 7, 793.
13 (a) A. Sekiguchi, Science, 2004, 305, 1755; (b) R. West, M. J. Fink and J. Michl, Science, 1981, 214, 1343; (c) I. Bejan and D. Scheschkewitz, Angew. Chem., Int. Ed., 2007, 46, 5783.
14 T. E. Mallouk, G. L. Rosenthal, G. Mueller, R. Brusasco and N. Bartlett, Inorg. Chem., 1984, 23, 3167.
15 K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy and J. A. Boatz, J. Fluorine Chem., 2000, 101, 151.
16 D. R. Lide, CRC Handbook of Chemistry and Physics, CRC Press/Taylor and Francis, Boca Raton, 90th edn, 2010.
17 A. Klant and G. Schuermann, J. Chem. Soc., Perkin Trans. 2, 1993, 799.
18 S. P. Hoffmann, T. Kato, F. S. Tham and C. A. Reed, Chem. Commun., 2006, 767.
19 A. Martens, P. Weis, M. C. Krummer, M. Kreuzer, A. Meierhöfer, S. C. Meier, J. Bohnenberger, H. Scherer, I. Riddlestone and I. Krossing, Chem. Sci., 2018, 9, 7058.
20 C. A. Reed, Acc. Chem. Res., 1998, 31, 325.
21 (a) V. G. Baonza, O. R. Montoro, M. Taravillo, M. Cáceres and J. Núñez, J. Chem. Phys., 2004, 121, 11156; (b) C. Mediavilla, J. Tortajada and V. G. Baonza, Chem. Phys. Lett., 2008, 454, 387.
22 S. G. Wierschke, J. Chandrasekhar and W. L. Jorgensen, J. Am. Chem. Soc., 1985, 107, 1496.
23 E. Hey, F. Weller and K. Dehnice, Z. Anorg. Allg. Chem., 1983, 502, 45.
24 R. F. Bryan, *J. Am. Chem. Soc.*, 1964, **86**, 733.
25 H. H. Freedman and A. E. Young, *J. Am. Chem. Soc.*, 1964, **86**, 734.
26 G. Maier, R. Emrich, K.-D. Malsch, K.-A. Schneider, M. Nидdorf and H. Irngartinger, *Chem. Ber.*, 1985, **118**, 2798.
27 G. A. Olah, J. S. Staral, R. J. Spear and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 5489.
28 J. B. Koster, G. J. Timmermans and H. van Bekkum, *Synthesis*, 1971, **1971**, 139.
29 P. B. J. Driessen and H. Hogeveen, *J. Am. Chem. Soc.*, 1978, **100**, 1193.
30 M. Simonetta and S. Weinstein, *J. Am. Chem. Soc.*, 1954, **76**, 18.
31 C. Krüger, P. J. Roberts, Y.-H. Tsay and J. B. Koster, *J. Organomet. Chem.*, 1974, **78**, 69.
32 (a) Š. Janková, J. Schulz, S. Hybelbauerová, I. Císařová, P. Šтepnička and M. Kotora, *Eur. J. Org. Chem.*, 2013, **2013**, 44; (b) P. B. J. Driessen and H. Hogeveen, *J. Organomet. Chem.*, 1978, **156**, 265; (c) M. J. Marsella, S. Estassi, L.-S. Wang and K. Yoon, *Synlett*, 2004, 192.
33 K. S. Fongers, H. Hogeveen and R. F. Kingma, *Tetrahedron Lett.*, 1983, **24**, 1423.
34 H. Hogeveen, H. Jorritsma, P. A. Wade, F. van Rantwijk, J. B. Koster, J. J. Prooi, A. Sinnema and H. van Bekkum, *Tetrahedron Lett.*, 1974, **15**, 3915.
35 T. Bally and S. Masamune, *Tetrahedron*, 1980, **36**, 343.
36 A. Fattahi, L. Lis, Z. Tian and S. R. Kass, *Angew. Chem., Int. Ed.*, 2006, **45**, 4984.
37 (a) H. Irngartinger and H. Rodewald, *Angew. Chem., Int. Ed.*, 1974, 13; (b) H. Kimling and A. Krebs, *Angew. Chem., Int. Ed.*, 1972, **11**, 932.
38 (a) J. Possart, A. Martens, M. Schleep, A. Ripp, H. Scherer, D. Kratzert and I. Krossing, *Chem.-Eur. J.*, 2017, **23**, 12305; (b) M. Rohde, L. O. Müller, D. Himmel, H. Scherer and I. Krossing, *Chem.-Eur. J.*, 2014, **20**, 1218.
39 (a) R. J. Wehmschulte and L. Wojtas, *Inorg. Chem.*, 2011, **50**, 11300; (b) M. Kira, T. Hino and H. Sakurai, *Chem. Lett.*, 1992, **21**, 555.