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Recent advances in the experimental and computational characterization of carbocations: Silyl effects in bicyclobutonium ions

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Abstract: Two trialkylsilyl substituted bicyclobutonium ion were investigated by NMR spectroscopy in superacid solution and by quantum chemical ab initio calculations. The 1-(trimethylsilyl)bicyclobutonium ion undergoes a threefold degenerate methylene rearrangement. The 3-*endo*-(*tert*-butyldimethylsilyl)bicyclobutonium ion is the first static bicyclobutonium ion. The NMR-spectra of this carbocation are a direct proof for the hypercoordinated and puckered structure of bicyclobutonium ions.

INTRODUCTION

Cyclobutyl cations (1) are intermediates in solvolysis reactions of cyclopropylmethyl and cyclobutyl halides. Experimental investigations, in particular NMR spectroscopic investigations, of persistent carbocations in solution show that the cyclobutyl ring of the unsubstituted cyclobutyl cation $[C_4H_7]^+$ **1** is puckered and bridged between C_α and C_γ. The puckering and bridging can be explained by the stabilizing interaction of the back lobe of the *endo*-C_γ-H σ-bond orbital with the vacant p-orbital at C_α (Fig. 1). Bridged cyclobutyl cations have a pentacoordinated γ-carbon and are called bicyclobutonium ions.

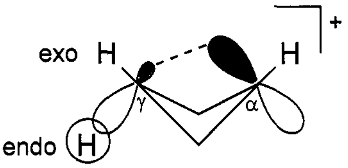

Fig. 1. Interaction of the *endo*-C_γ-H σ-bond orbital of the bicyclobutonium ion **1** with the vacant p-orbital at C_α.

The averaged ^{1}H- and ^{13}C-NMR methylene signals observed for the parent bicyclobutonium ion **1** (Fig. 2, **I**, R=H) are in accord with a fast methylene rearrangement.

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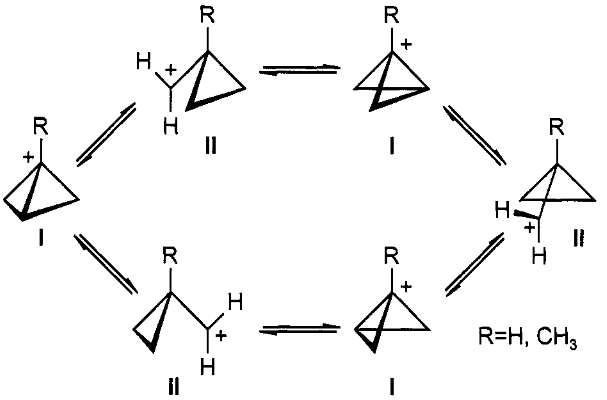
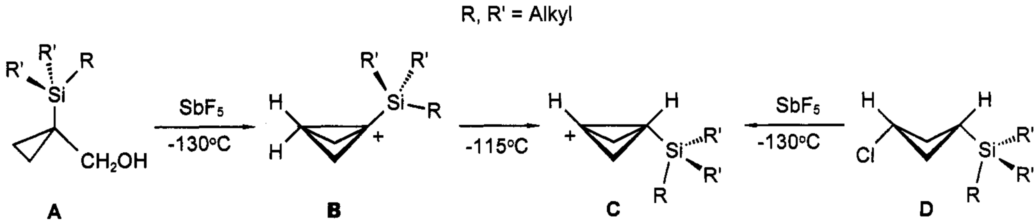


Fig. 2. Threefold degenerate rearrangement of bicyclobutonium ions via cyclopropylmethyl cation structures.

The temperature dependence of the ^{13}C-NMR chemical shifts of the parent $C_4H_7^+$ cation system indicates that besides **1** smaller amounts of isomeric cyclopropylmethyl cation structures **2** (Fig. 2, **II**, R=H) are involved in the rearrangement process (Fig. 2) which contribute to the observed averaged chemical shifts. The cyclopropylmethyl cation structure **2** is a local minimum (MP2/6-31G(d)) only marginally higher in energy compared to **1**. The 1-methylbicyclobutonium ion $[1\text{-}CH_3\text{-}C_4H_6]^+$ **3** also undergoes a fast methylene rearrangement (Fig. 2, **I**, R=CH_3). Contrary to the parent cation system $C_4H_7^+$ the (1'-methylcyclopropyl)methyl cation **4** (Fig. 2, **II**, R=CH_3) is a transition state (MP2/6-31G(d)). Thus (1'-methylcyclopropyl)methyl cation structures **4** do not contribute to the averaged chemical shifts observed for the threefold degenerate methylene rearrangement of 1-methylbicyclobutonium ions **3**.

RESULTS

We anticipated from our investigations of silyl effects in other types of carbocations (2) that trialkylsilyl substituted cyclobutyl/bicyclobutonium cations will have different energy surfaces as compared to the parent $C_4H_7^+$ (**1** / **2**) or the methyl substituted cation structures $[C_4H_6CH_3]^+$ (**3** / **4**),(3). We have experimentally investigated the route from alcohol **A** to cation **B** for **A** (R = R' = Me) which yields the 1-trimethylsilyl bicyclobutonium ion **5** (Scheme 1).



Scheme 1. Pathways for the generation of for trialkylsilyl (SiRR'$_2$) substituted bicyclobutonium cations.

Two possible reaction routes for the generation of 3-trialkylsilyl substituted bicyclobutonium ions **C** were also investigated: **A** → **B** → **C**, for **A** (R = *tert*-Butyl; R' = Me), which involves a 1,3-hydride shift from the initially formed cation **8** to the 3-(*tert*-butyldimethylsilyl)bicyclobutonium ion **9** and route (**D** → **C**) which leads from the cyclobutyl chloride **D** (R = R' = Me) directly to the 3-trimethylsilyl bicyclobutonium ion **12** (Scheme 1).

1-Silyl substituted bicyclobutonium ions (3, 4)

Experimental results

Matrix-co-condensation of (1'-(trimethylsilyl)cyclopropyl)methanol (Scheme 1, **A** (R = R' = Me)) with SbF_5 onto a surface of SO_2ClF / SO_2F_2 at –196 °C yields after homogenization at –130 °C a yellow solution. The ^{1}H-NMR spectrum at –128 °C (Fig. 3) shows two signals at 3.24 ppm (3H) and 4.05 ppm (3H) for the averaged CH_2 groups in addition to the $Si(CH_3)_3$ methyl signal at 0.38 ppm (9H). The ^{13}C-NMR spectrum at –128 °C (Fig. 4) shows a singlet at 137.4 ppm and a doublet of doublets which appears as a pseudo triplet at 48.9 ppm ($^1J_{CH}$ = 177 Hz) in addition to the quartet of the trimethylsilyl group at -5.2 ppm ($^1J_{CH}$ = 119 Hz). Selective decoupling of either proton resonance at 3.24 ppm or 4.05 ppm causes the pseudo triplet of the ^{13}C signal at 48.9 ppm to collapse to a doublet. No temperature dependence of the ^{1}H- and ^{13}C-NMR chemical shifts was observed in the accessible range from -120 °C to -145 °C.

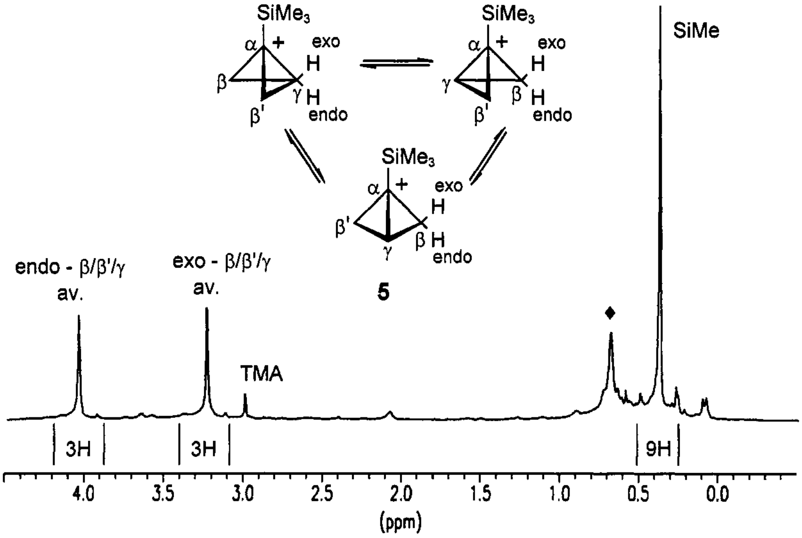


Fig. 3. 400 MHz ^{1}H-NMR spectrum of the 1-(trimethylsilyl)bicyclobutonium ion **5** (◆: $FSiMe_3$) at –128 °C (internal standard TMA $\delta(NMe_4^+)$ = 3.00 ppm).

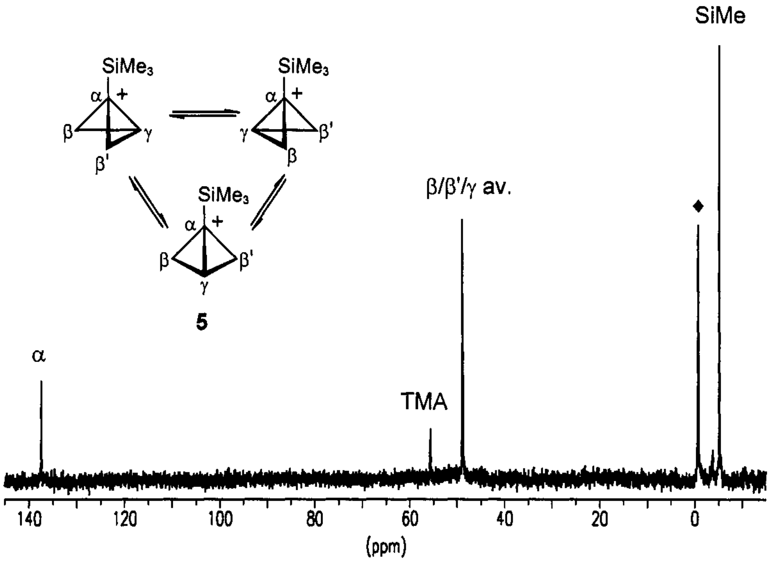
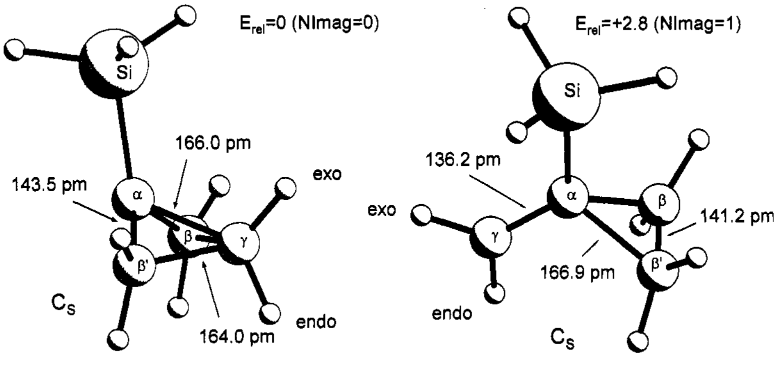


Fig. 4. 100 MHz ^{13}C-NMR spectrum of the 1-(trimethylsilyl)bicyclobutonium ion **5** (◆: $FSiMe_3$) at −128 °C (internal standard TMA $\delta(NMe_4^+) = 55.65$ ppm).

Computational results (5)

At the MP2/6-31G(d) level of theory the 1-silylcyclobutyl cation $[1\text{-}SiH_3\text{-}C_4H_6]^+$ (Fig. 5) which serves as a model compound for $[1\text{-}Si(CH_3)_3\text{-}C_4H_6]^+$ **5** is an energy minimum (Imaginary Frequencies, NImag =0) and has a hypercoordinated puckered 1-silylbicyclobutonium structure **6** (C_α-C_γ distance: 166.0 pm). Cation **6** is about 2.8 kcal mol^{-1} lower in energy than the isomeric (1'-silylcyclopropyl)methyl cation 7 (Fig. 5) which is characterized as a transition state (NImag=1). The ^{13}C-NMR chemical shifts calculated (GIAO-MP2/tzpdz) for the optimized (MP2/6-31G(d)) geometry of the 1-silylbicyclobutonium model cation **6** ($C_{\beta/\beta}$ 79.6 ppm; C_γ: -14.5 ppm; $C_\beta/C_{\beta'}/C_\gamma$ av.: 48.2 ppm; C_α: 133.9 ppm) agree with the experimental values for the 1-trimethylsilyl substituted bicyclobutonium ion **5** ($C_\beta/C_{\beta'}/C_\gamma$ av.: 48.9 ppm; C_α: 137.4 ppm), while this is not the case for the chemical shifts calculated for the (1'-silylcyclopropyl)methyl cation 7.



6 **7**

Fig. 5. Ab-initio calculated (MP2/6-31G(d)) geometries of the 1-silylbicyclobutonium ion **6** and the (1'-silylcyclopropyl)methyl cation 7; selected bond lengths and relative energies in kcal/mol (ZPE included).

3-Silyl substituted bicyclobutonium ions

Experimental results

Matrix-co-condensation of (1'-(*tert*-butyldimethylsilyl)cyclopropyl)methanol (scheme 1, **A** (R = *tert*-Butyl; R' = Me)) with SbF_5 onto a surface of SO_2ClF/SO_2F_2 at –196 °C yields after homogenization at –130 °C a yellow solution. The initial ^{13}C-NMR spectrum obtained at –130 °C shows two sets of signals, one set corresponding to the 1-(*tert*-butyldimethylsilyl)bicyclobutonium ion **8** and another set of signals (99.6 ppm ($^1J_{CH}$=184 Hz); 66.3 ppm ($^1J_{CH}$=171 Hz); -21.0 ppm ($^1J_{CH}$=156 Hz) and signals for the Me, *tert*-Butyl groups) corresponding to the 3-endo-(*tert*-butyldimethylsilyl)bicyclobutonium ion **9**. At –115 °C the first set of signals disappears within 10 minutes and only the peaks for cation **9** remain (Fig. 6). Structural assignment for cation **9** was confirmed by HC-COSY- and COSY45-NMR spectra shown in Fig. 7 and Fig. 8 respectively. NMR spectra of cations generated from β-CD_2-labeled progenitors and quantum chemical model calculations of transition states for 1,3-hydride shifts indicate that the rearrangement of the 1-silylsubstituted bicyclobutonium ion **8** to the 3-silylsubstituted bicyclobutonium ion **9** occurs most likely by a 1,3-hydride shift from C_γ to C_α across the bridging bond. 3-silyl-substituted bicyclobutonium ions are also accessible from direct ionization of 3-silyl-substituted cyclobutyl chlorides. Matrix-co-condensation of *cis/trans*-3-(trimethylsilyl)cyclobutyl chloride (Scheme 1, **D** (R = R' = Me)) with SbF_5 onto a surface of SO_2ClF / SO_2F_2 at -196 °C yields after homogenization at -130 °C a yellow solution of carbocations **12**. The ^{13}C-NMR spectrum obtained for cation **12**, except for the alkyl groups at silicon, is very similar to the ^{13}C-NMR spectrum of carbocation **9**, $\Delta\delta$ for C_α-, $C_\beta/C_{\beta'}$ < 1 ppm.

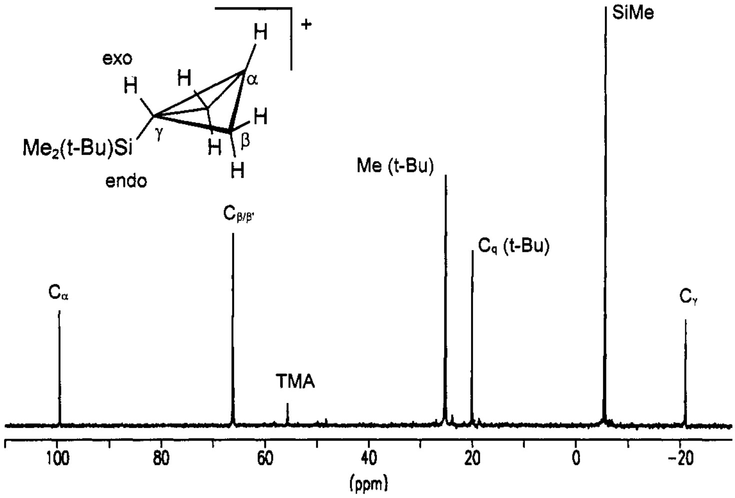


Fig. 6. ^{13}C-NMR spectra; rearrangement of the 1-(*tert*-butyldimethylsilyl)bicyclobutonium ion **8** to the 3-*endo*-(*tert*-butyldimethylsilyl)bicyclobutonium ion **9** at -115 °C (internal standard TMA $\delta(NMe_4^+)$ = 55.65 ppm).

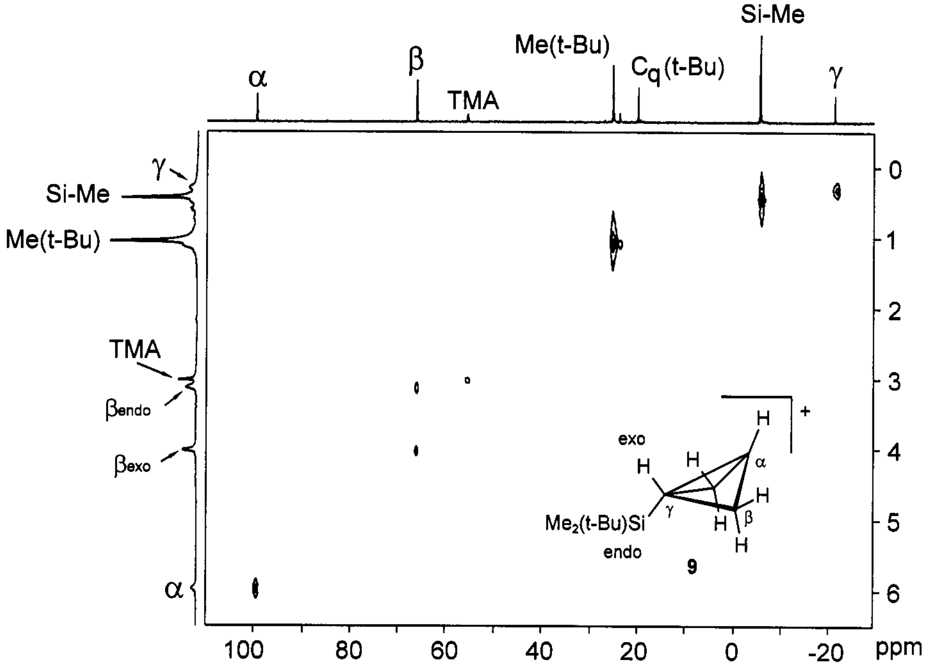


Fig. 7. HC-COSY-NMR spectrum of 9 at -115 °C; internal standard TMA δ(NMe_4^+) = 55.65 ppm (^{13}C) and 3.00 ppm (^1H).

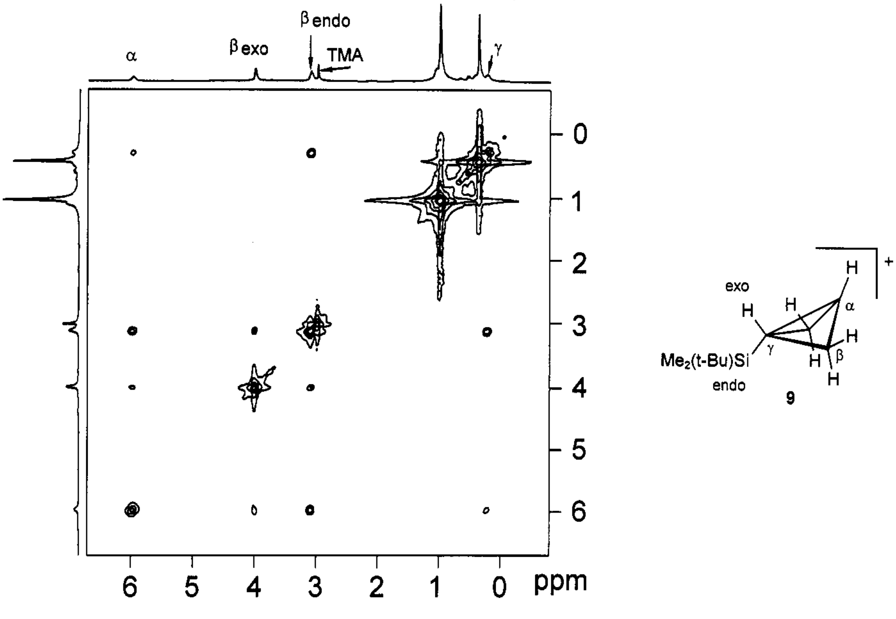
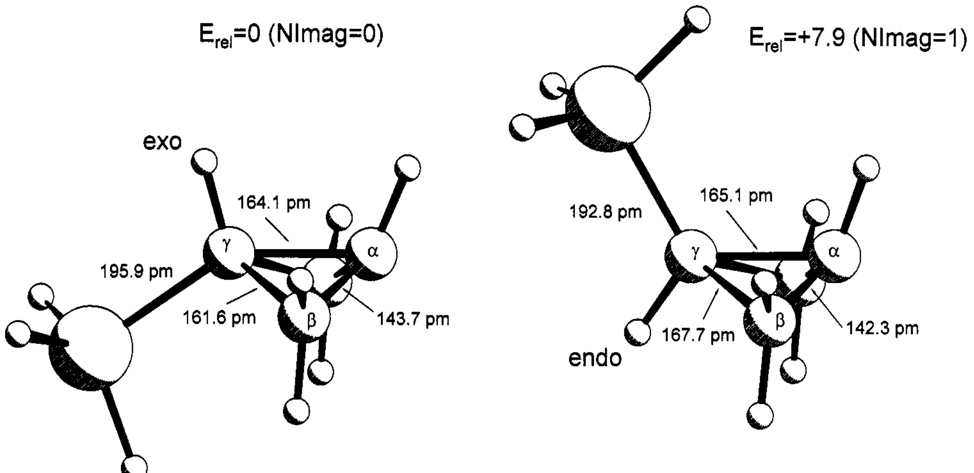


Fig. 8. COSY45-NMR spectrum of 9 at -115 °C (internal standard TMA δ(NMe_4^+) = 3.00 ppm).

Computational results (5)

The geometries of the model structures 3-*endo*-silylbicyclobutonium ion [3-endo-SiH_3-C_4H_6]$^+$ **10** and the 3-*exo*-silylbicyclobutonium ion [3-*exo*-SiH_3-C_4H_6]$^+$ **11** were optimized at the MP2/6-31G(d) level of theory (Fig. 9). The 3-*endo*-silylbicyclobutonium ion **10** is an energy minimum (NImag=0) and is calculated to be

7.9 kcal/mol lower in energy than the 3-*exo*-silylbicyclobutonium ion **11** which is characterized by a frequency calculation as a transition state (NImag=1). The C_α-C_γ distance in cation **10** (164.1 pm) is shorter than the C_α-C_γ distance calculated for the unsubstituted bicyclobutonium ion **1** (165.4 pm). This indicates a stronger bonding interaction between C_α and C_γ for the silylbicyclobutonium ion **10** which is due to the stabilizing interaction of the *endo*-silyl group at C_γ with the formally positively charged carbon C_α. The ^{13}C-NMR chemical shifts calculated (GIAO-MP2/tzpdz) for the 3-*endo*-silylbicyclobutonium ion **10** are in good agreement with the experimental values for the 3-*endo*-(*tert*-butyldimethylsilyl)bicyclobutonium ion **9** and the 3-*endo*-(trimethylsilyl)bicyclobutonium ion **12**. The calculated chemical shifts for C_α and $C_\beta/C_{\beta'}$ of the γ-*endo*-silyl isomer **10** are in better agreement with the experimental data than those calculated for the γ-*exo*-silyl isomer **11**. The assignment is also confirmed by SOS-DFT (Perdew/IGLO-III) calculation of the cross ring $^3J_{H\alpha H\gamma}$ spin spin coupling constant which is 5.5 Hz measured experimentally and 5.9 Hz calculated for the *endo*-silyl isomer **10** but is only 1.2 Hz calculated for the *exo*-silyl isomer **11**.



10 **11**

Fig. 9. Ab-initio calculated geometries (MP2/6-31G(d)) and relative energies [kcal/mol] (ZPE included) of the 3-*endo*-silylbicyclobutonium ion **10** and the 3-*exo*-silylbicyclobutonium ion **11**.

CONCLUSIONS

The 1-(trimethylsilyl)cyclobutyl cation **5** is obtained by reaction of (1'-(trimethylsilyl)cyclopropyl)methanol with SbF_5 at −130 °C. It has a hypercoordinated puckered 1-(trimethylsilyl)-bicyclobutonium structure and undergoes a fast threefold degenerate methylene rearrangement leading to averaged NMR signals for the *exo*-methylene protons (*exo* $H_\beta/H_{\beta'}/H_\gamma$), for the *endo*-methylene protons (*endo* $H_\beta/H_{\beta'}/H_\gamma$), and for the methylene carbon atoms ($C_\beta/C_{\beta'}/C_\gamma$) respectively. The isomeric (1'-(trimethylsilyl)cyclopropyl)methyl cation does not contribute to the NMR chemical shifts. The reaction of (1'-(*tert*-butyldimethylsilyl)cyclopropyl)methanol with SbF_5 at −130 °C leads to the 1-(*tert*-butyldimethylsilyl)bicyclobutonium ion **8**. Like **5**, cation **8** undergoes a fast methylene rearrangement leading to ^{13}C- and ^1H-NMR spectra with averaged methylene signals. At -115 °C cation **8** rearranges to the 3-*endo*-(*tert*-butyldimethylsilyl)bicyclobutonium ion **9**. Cation **9** is the first bicyclobutonium ion that is static on the NMR time scale. This is due to the efficient stabilization of the positive charge by the γ-*endo*-trialkylsilyl substituent. The corresponding 3-*endo*-(trimethylsilyl)bicyclobutonium ion **12** is generated from *cis/trans*-3-(trimethylsilyl)cyclobutyl chloride. Structural and stereochemical assignment was confirmed by CH-COSY- and HH-COSY-NMR spectra. The quantum chemical calculations of chemical shifts and spin spin coupling constants fully support the interpretation of the experimental results.

ACKNOWLEDGMENT

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