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γ-Trimethylsilylcyclobutyl Carbocation Stabilization

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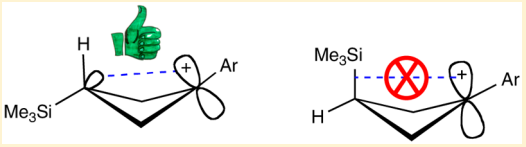
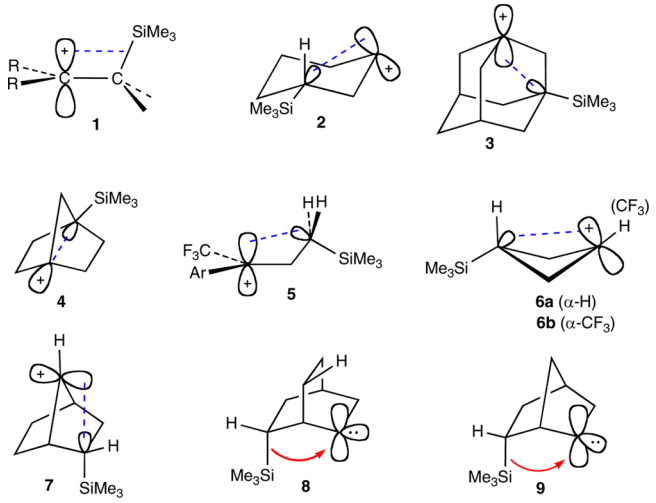
Supporting Information

ABSTRACT: A series of isomeric 3-trimethylsilyl-1-arylcyclobutyl carbocations, **10** and **11**, where the cross-ring 3-trimethylsilyl group has the potential to interact with the cationic center, have been generated under solvolytic conditions. When the cationic center can interact with the rear lobe of the carbon−silicon bond, rate enhancements become progressively larger as the substituent on the aryl group becomes more electron-withdrawing. When the potential interaction with the trimethylsilyl group is via a front lobe interaction, there is minimal rate enhancement over the range of substituents. Computational studies have also been carried out on these cations **10** and **11**. Calculated trimethylsilyl stabilization energies progressively increase with electron-withdrawing character of the aryl groups when the trimethylsilyl interaction is via the rear lobe. By way of contrast, there are minimal changes in stabilization energies when the potential trimethylsilyl interaction is via the front lobe of the carbon−silicon bond. These computational studies, along with the solvolytic studies, point to a significant rear lobe 3-trimethylsilyl stabilization of arylcyclobutyl cations. They also argue against any front lobe stabilization of the isomeric arylcyclobutyl cations.



INTRODUCTION

Carbocations directly adjacent to the trimethylsilyl group, as in **1**, are greatly stabilized by an interaction with the adjacent C−Si σ-bond. This β-silyl effect has been extensively studied.[1] We and others have been interested in the effect of silicon further removed from a cationic center and, in particular, the γ-silyl effect. Shiner and co-workers[2] have studied this γ-effect in solvolysis reactions that lead to carbocation **2**. This carbocation forms in solvolysis reactions at a moderately enhanced rate that is attributed to an interaction of the cationic center with the rear lobe of the carbon−silicon σ-bond. Additional studies by Grob and Sawlewicz[3] on cation **3** and Adcock et al.[4] on cation **4** support this suggestion. The rate enhancement in formation of cation **3** is a modest factor of 8.6, whereas the rate enhancement in formation of **4** is a more substantial value of 1300. In a recent synthetic application of this phenomenon, Tilley and co-workers[5] have observed the formation of trifluoromethyl substituted cyclopropanes by desilylation of carbocation **5** and analogues, with increased yields of cyclopropanes with electron-withdrawing aryl groups. In our laboratory, we have found remarkable rate-enhancing effects (factors of 10^5) in solvolysis reactions that form carbocations **6a**[6] and **7**.[7] A rate enhancement of over 10^6 has been observed in formation of **6b**.[5] Computational studies indicate that cation **6a** is more stable than the 2-trimethylsilylcyclobutyl cation; i.e., the γ-silyl effect in cation **6a** is even greater than the β-silyl effect.



We have also been interested in the effects of silicon on other electron-deficient reactive intermediates such as singlet carbenes.[8] Among such carbenes that have been studied in our laboratory are the carbenes **8** and **9**.[8b] These carbenes are characterized by their facile rearrangement via trimethylsilyl migration to the carbene center. This was suggestive of a long-range interaction of the γ-trimethylsilyl group with the carbene center. This γ-interaction of silicon with carbenes is quite different from the γ-stabilization of carbocations **2**−**7**. Whereas stabilization of these carbocations occurs via the "rear lobe" of the carbon−silicon σ-bond, our carbene studies suggested a "front lobe" interaction of carbenes analogous to the β-silyl effect seen in carbocations of type **1**. In light of these studies, it seemed reasonable to expect that γ-silyl carbocations could also be

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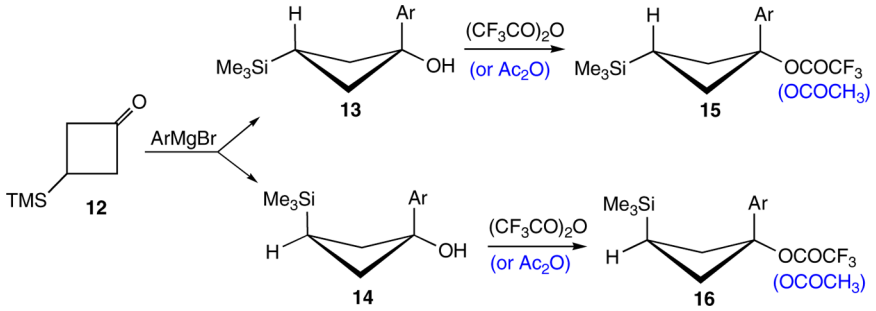
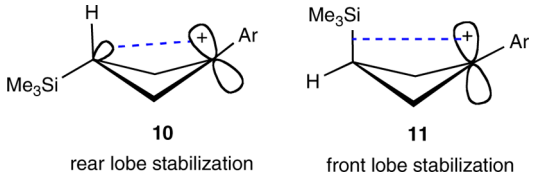
Scheme 1. Synthesis of Substrates for Solvolytic Studies



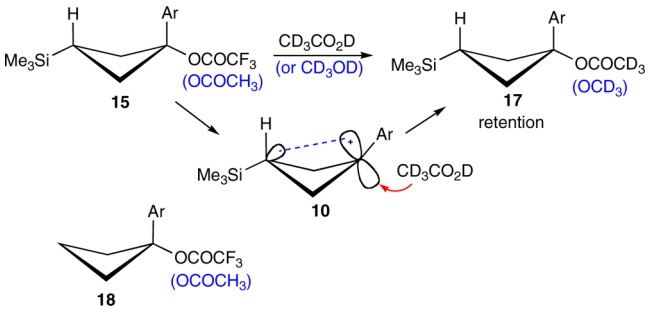
stabilized by a long-range "front lobe" interaction as shown in **11**. We, therefore, wanted to progressively destabilize cations **10** and **11** and to probe for the magnitude of long-range silicon stabilization of these carbocations.[9] We wanted to study such carbocations both experimentally and computationally. Reported here are our results comparing "rear lobe" silyl stabilized carbocations **10** with potential "front lobe" silyl stabilized carbocations **11**.



RESULTS AND DISCUSSION

The syntheses of precursors to cations **10** and **11** (Scheme 1) began with addition of a variety of Grignard reagents to 3-trimethylsilylcyclobutanone, which gave mixtures of alcohols **13** and **14**. These alcohols were, in turn, converted to trifluoroacetate or acetate derivatives **15** and **16** for solvolytic studies. We have previously reported[6] on the solvolytic behavior of **15** (Ar = C_6H_5), but we now have obtained data on substrates **15** with a range of aryl substituents. These substrates reacted in the solvents studied by first-order processes to give substitution products **17** with net retention of configuration (Scheme 2).

Scheme 2. Solvolyses of Substrates 15 in CD_3CO_2D and CD_3OD



The exception was **15** (Ar = C_6H_4-*p*-OCH_3), where solvolysis of the acetate derivative in CD_3OD gave 91% retention along with 9% of a product with inverted stereochemistry. Kinetic data for **15** and **16**, as well as data for the unsubstituted model cyclobutyl compounds **18**, are reported in Table 1.

The first thing that is apparent is that there are relatively small substituent effects in solvolyses of **15** as the aryl group is changed. The Hammett ρ+ value is only −2.40 for the five trifluoroacetate

Table 1. Solvolysis Rates for Substrates 15, 16, and 18 in Various Solvents

compound	solvent	T (°C)	k (s^{-1})
15 (Ar = C_6H_4-*p*-OCH_3)	CD_3OD	25.0	9.31×10^{-6}[a]
15 (Ar = C_6H_4-*p*-CH_3)	CF_3CH_2OH	25.0	5.87×10^{-4}[a]
15 (Ar = C_6H_5)	CD_3CO_2D	25.0	9.37×10^{-3}
15 (Ar = C_6H_4-*p*-Cl)	CD_3CO_2D	25.0	2.26×10^{-3}
15 (Ar = C_6H_4-*m*-Cl)	CD_3CO_2D	25.0	7.51×10^{-4}
15 (Ar = C_6H_4-*m*-CF_3)	CD_3CO_2D	25.0	4.16×10^{-4}
15 (Ar = C_6H_4-*p*-CF_3)	CD_3CO_2D	25.0	2.24×10^{-4}
16 (Ar = C_6H_4-*p*-OCH_3)	CD_3OD	25.0	6.26×10^{-6}[a]
16 (Ar = C_6H_4-*p*-CH_3)	CF_3CH_2OH	25.0	7.00×10^{-5}
16 (Ar = C_6H_5)	CD_3CO_2D	25.0	5.85×10^{-4}
16 (Ar = C_6H_4-*p*-Cl)	CD_3CO_2D	25.0	1.98×10^{-4}
16 (Ar = C_6H_4-*m*-Cl)	CD_3CO_2D	25.0	1.42×10^{-5}
16 (Ar = C_6H_4-*m*-CF_3)	CD_3CO_2D	25.0	4.69×10^{-6}
16 (Ar = C_6H_4-*p*-CF_3)	CD_3CO_2D	25.0	1.19×10^{-6}[b]
18 (Ar = C_6H_4-*p*-OCH_3)	CD_3OD	25.0	1.63×10^{-6}[a,b]
18 (Ar = C_6H_4-*p*-CH_3)	CF_3CH_2OH	25.0	9.46×10^{-6}[a]
18 (Ar = C_6H_5)	CD_3CO_2D	25.0	4.54×10^{-5}
18 (Ar = C_6H_4-*p*-Cl)	CD_3CO_2D	25.0	1.23×10^{-5}
18 (Ar = C_6H_4-*m*-Cl)	CD_3CO_2D	25.0	9.19×10^{-7}
18 (Ar = C_6H_4-*m*-CF_3)	CD_3CO_2D	25.0	2.77×10^{-7}[b]
18 (Ar = C_6H_4-*p*-CF_3)	CD_3CO_2D	25.0	8.08×10^{-8}[b]

[a]Rate of acetate derivative. [b]Extrapolated from data at higher temperatures.

derivatives. Introduction of a *p*-CF_3 substituent into **15** (Ar = C_6H_4-*p*-CF_3) slows the rate by only a factor of 42 relative to **15** (Ar = C_6H_5). A more "normal" value is seen for the model compounds **18** (ρ+ = −4.34), where introduction of a *p*-CF_3 group slows the rate by a factor of 562. Also apparent is the variable rate-enhancing effect of the trimethylsilyl group, which is summarized in Table 2. This table gives the **15**:**18** rate ratio as a function of substituent, and also includes our previously determined data for **19** and **20**. There is a steady increase in rate ratio as the substituent becomes more electron-withdrawing (less carbocation stabilizing). These rate effects are completely consistent with a rear lobe trimethylsilyl stabilized carbocation intermediate **10** in solvolyses of **15**. With increased demand for stabilization as the substituent becomes more electron-withdrawing, the γ-trimethylsilyl substituent in **10** interacts more strongly, resulting in a larger rate ratio.

The behavior of the *p*-OCH_3 derivative **15** (Ar = C_6H_4-*p*-OCH_3) begins to deviate from that of the other substrates **15**. The 9% inverted solvolysis product in CD_3OD indicates that the bridged ion **10** is not the sole intermediate in this reaction. It is suggested that the powerful cation stabilizing effect of the methoxy group is now beginning to offset the cross-ring silicon

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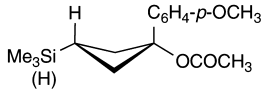
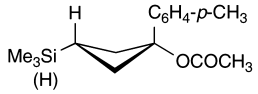
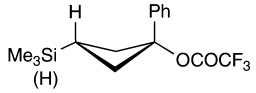
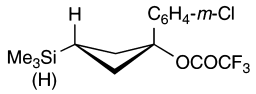
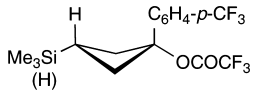
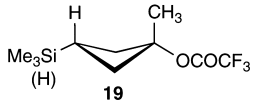
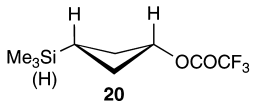
Table 2. Solvolysis Rate Ratios for 15:18 as a Function of Substituent

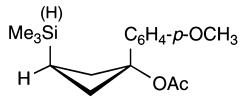
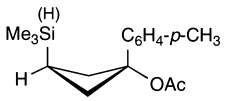
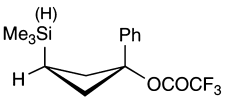
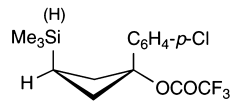
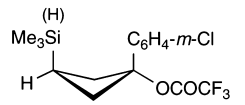
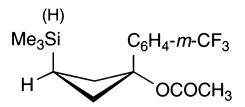
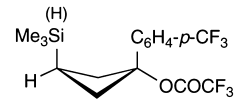
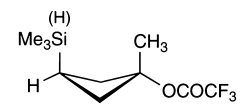
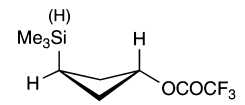
Substrates **15** and **18**	Rate Ratio **15/18**
	5.7
	62
	209
	817
	2775
 **19**	46,000
 **20**	10^5

stabilizing effect in the cation **10**. Substrate **15** (Ar = C_6H_4-*p*-OCH_3) appears to be reacting by a competing silicon assisted and an unassisted pathway, which results in some inverted product.

The substituent effects in the isomeric substrates **16** contrast with the behavior in **15**. Table 3 summarizes these substituent effects. While the silylated derivatives **16** all react slightly faster than the desilylated derivatives **18**, the effect is small in all cases. The Hammett ρ+ value for **16** is −4.25, which very similar to the value of −4.34 seen in the desilylated derivatives **18**. There is no systematic increase in the **16**:**18** rate ratio as the substituent becomes more electron-withdrawing. As the demand for cation stabilization increases, there is little response from the trimethylsilyl group. This implies very little interaction of the developing cationic center with the trimethylsilyl group, i.e., there is no kinetic evidence for stabilization of the cation **11** by an interaction with the front lobe of the carbon−silicon bond. It is suggested that substrates **16** react via cyclobutyl cations **11** that are stabilized by standard interactions with the bent bonds of the cyclobutane ring. The trimethylsilyl group may provide small inductive stabilization of these carbocations. The cyclobutyl bent bond stabilization in **11** is not sufficient to prevent subsequent ring inversion to give rear lobe silyl stabilized cation **10**, which results in acetates **17** as the major products of solvolyses of **16** in CD_3CO_2D (Scheme 3).[10]

Computational Studies. Density functional calculations[11] at the M062X/6-311+G** level were also used as a probe for trimethylsilyl stabilization of carbocations **10** and **11**. The value of ΔE for the isodesmic reaction in Scheme 4 was used to

Table 3. Solvolysis Rate Ratios for 16:18 as a Function of Substituent[a,b]

Substrates **16** and **18**	Rate Ratio **16/18**
	3.8[a]
	7.4[b]
	12.9
	16.2
	15.4
	16.9
	14.7
	4.4
	53

[a]Rates of acetate derivatives in CD_3OD. [b]Rates of acetate derivatives in CF_3CH_2OH.

compare the stability of cation **10** with that of the desilylated analogue, cation **24**. Table 4 gives a summary of ΔE values for this reaction, as well as the calculated C_1-C_3 and C_3-Si distances. As the group on the cation becomes more electron-withdrawing, there are large increases in the calculated stabilization of cation **10** by the trimethylsilyl group. The calculation suggests significant stabilization even in the *p*-OCH_3 substituted cation **10** (Ar = C_6H_4-*p*-OCH_3), where kinetic data indicate minimal cation stabilization in the solvolytic reaction. The stabilization of **10** (Ar = C_6H_4-*p*-OCH_3) amounts to 5.4 kcal/mol and increases to 16.5 kcal/mol in **10** (Ar = C_6H_4-*p*-NO_2). It is even larger when the aryl group is replaced with H (cation **6**) and with the electron-withdrawing cyano group (cation **25**).

The distance between the cationic carbon, C_1, and C_3 is indicative of a bonding interaction in all of these cations. There is a systematic shorting of the C_1-C_3 bond distance as the group

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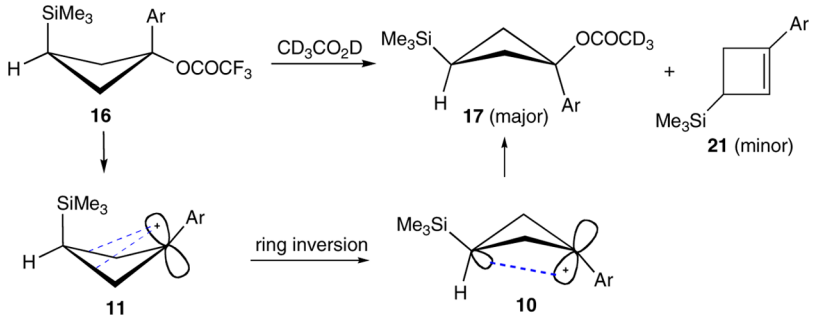
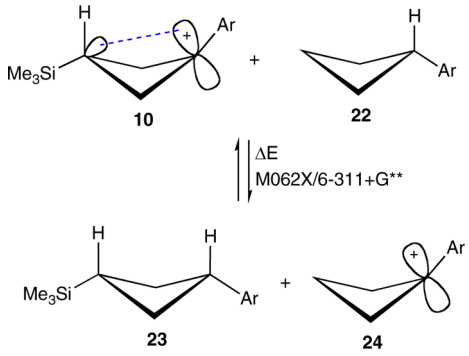
Scheme 3. Reaction of Substrates 16 in CD_3CO_2D



Scheme 4. Isodesmic Reactions of Cation 10



Scheme 5. Isodesmic Reactions of Cation 11

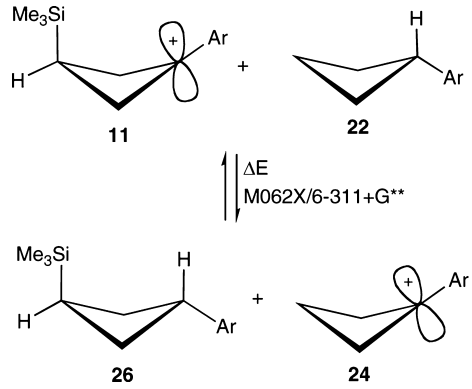
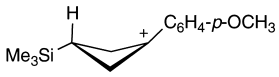
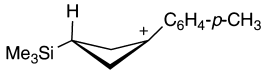
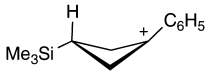
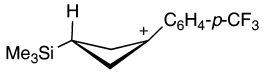
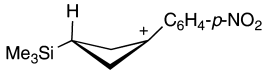
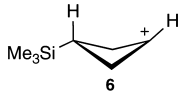
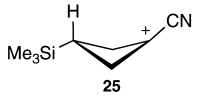
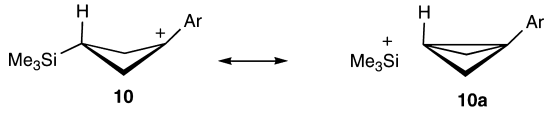


Table 4. M062X/6-311+G Calculated Stabilization Energies and Bond Lengths in Cations 10**

Cation	ΔE (kcal/mol)	C_1-C_3 ( )	C_3-Si ( )
	5.4	1.845	1.946
	9.1	1.766	1.961
	11.7	1.736	1.970
	13.3	1.721	1.975
	14.7	1.710	1.981
	16.5	1.697	1.987
 **6**	22.6	1.616	2.000
 **25**	26.2	1.623	2.031

becomes less cation stabilizing. This is illustrated in Figure 1, which shows the calculated structures of **10** (Ar = C_6H_4-*p*-OCH_3) and **10** (Ar = C_6H_4-*p*-CF_3). The respective bond distances of 1.845 and 1.710 Å in these structures compare to the value of 2.184 Å in the neutral molecule **23**. These structures imply a significant bonding interaction across C_1−C_3. There is a corresponding lengthening of the C_3−Si bond (from 1.946 to 2.032 Å) in **10** as the substituent becomes more electron-withdrawing. This compares to a C_3−Si bond length of about 1.88 Å in the neutral molecules **23**. These trends are all consistent with increasing rear lobe silyl stabilization of cations **10** as the substituent becomes less cation stabilizing. In valence bond terms, the importance of form **10a** increases as substituents on the aryl group become less cation stabilizing.



It is of interest to note that the *p*-methoxy stabilized cation **10** (R = C_6H_4-*p*-OCH_3) shows a shortened C_1−C_3 distance, as well as a lengthening of the C_3−Si bond, indicative of a significant rear lobe cation stabilizing interaction. This computational result contrasts with the kinetic study, which shows minimal rate enhancement in solvolysis of **10** (Ar = C_6H_4-*p*-OCH_3). As in our previous study,[12] gas phase computational studies appear to overestimate the importance of neighboring group participation as a carbocation stabilizing feature.

Attention was next focused on the isodesmic reactions of the isomeric cations **11** in Scheme 5. Results are summarized in Table 5, which gives the Δ*E* values as well as C_1−C_3 distances and C_3−Si bond lengths. In stark contrast to the behavior of cations **10**, cations **11** show minimal changes in calculated trimethylsilyl stabilization energies as substituents become electron-withdrawing. The increase from 3.2 to 4.8 kcal/mol as the substituent is changed from *p*-OCH_3 to *p*-CF_3 can hardly be

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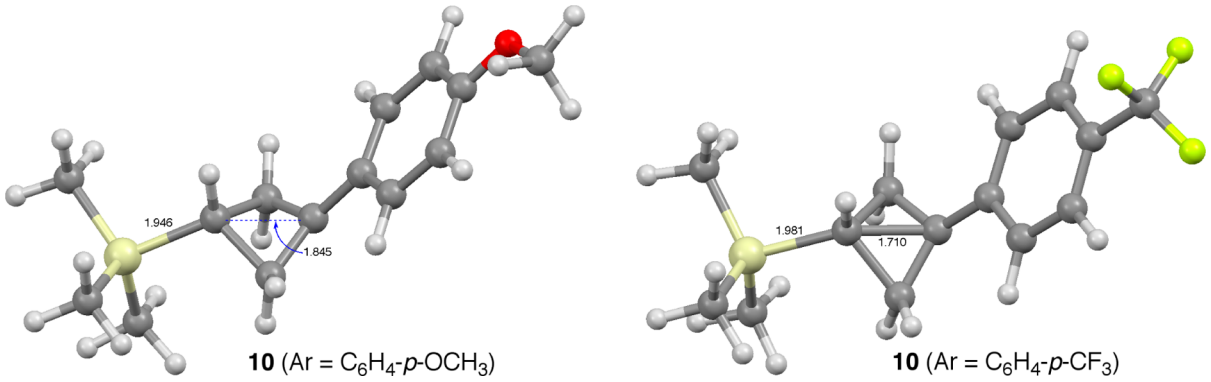
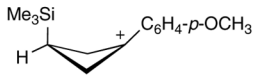
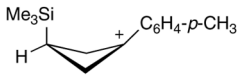
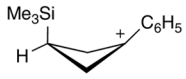
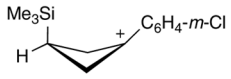
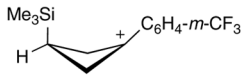
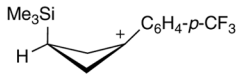


Figure 1. M062X/6-311+G** calculated structures of cations **10** (Ar = C_6H_4-*p*-OCH_3) and **10** (Ar = C_6H_4-*m*-CF_3).

Table 5. M062X/6-311+G Calculated Stabilization Energies and Bond Lengths in Cations 11[a]**

Cation	ΔE (kcal/mol)	C_1-C_3 ( )	C_3-Si ( )
	3.2	2.100 (2.098)[a]	1.907
	3.7	2.094 (2.092)[a]	1.910
	4.3	2.090 (2.087)[a]	1.911
	4.6	2.085 (2.079)[a]	1.914
	4.9	2.085 (2.080)[a]	1.914
	4.8	2.081 (2.081)[a]	1.914

[a] C_1–C_3 bond length in **24**.

taken as evidence for an interaction of the trimethylsilyl group with the cationic center of **11**.

The calculated structures of **11** (Ar = C_6H_4-*p*-OCH_3) and **11** (Ar = C_6H_4-*p*-CF_3) (Figure 2) are also informative. The C_1–C_3 distances show minimal changes as a function of substituent. Indeed, the slight changes in **11** parallel those seen in the desilylated cyclobutyl cations **24**. These C_1–C_3 bond distances give no indication of a significant C_1–C_3 bonding interaction. Finally, the C_3–Si bond lengths also show minimal changes as a function of substituent. There is no significant lengthening of the C_3–Si bond with electron-withdrawing groups as observed in cations **10**. There appears to be no response of the C_3–Si bond to increasing demand as cations **11** become more destabilized.

CONCLUSIONS

Solvolytic studies, as well as computational studies, provide convincing evidence for rear lobe silyl stabilization of carbocations of type **10**. By way of contrast, there is no compelling experimental or computational evidence for a cross-ring front lobe trimethylsilyl stabilizing interaction in cations **11**. Cations **11** appear to derive stabilization by the same mechanisms (bent bond interactions) that stabilize simple aryl substituted cyclobutyl cations. The trimethylsilyl group in **11** provides no significant additional stabilization. The validity of our previously suggested front lobe stabilization of carbenes **8** and **9** must await further scrutiny.

EXPERIMENTAL SECTION

General. NMR spectra were recorded on a 600 MHz spectrometer. HRMS measurements were carried out using either an electrospray ionization source with time-of-flight mass analyzer or a GC-mass spectrometer with an electron impact ionization source and time-of-flight mass analyzer. NMR analyses were carried out on an instrument operating at 600 MHz for ^{1}H NMR.

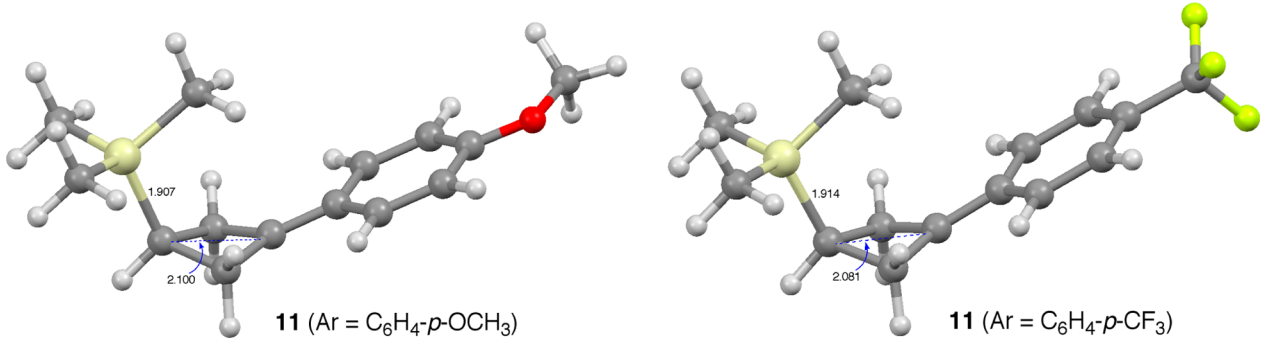


Figure 2. M062X/6-311+G** calculated structures of cations **11** (Ar = C_6H_4-*p*-OCH_3) and **11** (Ar = C_6H_4-*p*-CF_3).

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Preparation of Alcohols 13 and 14. Alcohols **13** and **14** were prepared by addition of aryl Grignard reagents[13] to 3-trimethylsilylcyclobutanone.[14] The following procedure is representative. A solution of 1.60 mL of 0.90 M 3-chlorophenylmagnesium bromide (1.44 mmol) in ether was cooled in an ice bath, and 170 mg (1.20 mmol) of 3-trimethylsilylcyclobutanone in 3 mL of ether was added dropwise. The mixture was then warmed to room temperature for 15 min and then quenched with approx 2.5 M aqueous NH_4Cl solution. The ether phase was separated, washed with water and saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator. ^{1}H NMR analysis of the crude reaction mixture showed alcohols **13** and **14** (Ar = C_6H_4-*m*-Cl) in a 40:60 ratio. The crude products were chromatographed on 8 g of silica gel and eluted with pentane, followed by increasing amounts of ether in pentane (1% ether increments). Alcohols **13** and **14** (254 mg; 94% yield) eluted with 6−10% ether in pentane. Early fractions were enriched with alcohol **13** (Ar = C_6H_4-*m*-Cl), while later fractions were enriched with alcohol **14** (Ar = C_6H_4-*m*-Cl). Pure samples of isomeric alcohols **13** and **14** could be isolated by the protocols described below.

Isolation of Alcohol 13 (Ar = C_6H_4-*m*-Cl). A mixture of alcohols **13** and **14** (199 mg of a 52:48 ratio; 0.783 mmol) was dissolved in 4 mL of ether, and 162 mg of 2,6-lutidine (1.514 mmol) was added. The solution was cooled to −10 °C, and 260 mg of trifluoroacetic anhydride (1.238 mmol) was added. After 10 min, the mixture was warmed to room temperature and then taken up into pentane. The solution was consecutively washed with cold water, cold dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give a mixture of trifluoroacetates **15** and **16** (243 mg, 89% yield) in a 52:48 ratio.

A solution of 72 mg (0.673 mmol) of 2,6-lutidine in 4.5 mL of acetic acid was added to the mixture of trifluoroacetates **15** and **16** prepared above. Trifluoroacetate **15** (Ar = C_6H_4-*m*-Cl) reacts in acetic acid with a half-life of about 16 min at 25 °C to form the acetate derivative. After stirring the solution for 21 h at 25−27 °C, the mixture was taken up into ether and 15 mL of water was added. The acetic acid was neutralized by addition of Na_2CO_3 with stirring. The mixture was transferred to a separatory funnel, and the ether extract was diluted with pentane and then washed with water and saturated NaCl solution. After drying over $MgSO_4$, the organic phase was filtered and the solvent was removed using a rotary evaporator. The residue was chromatographed on 6 g of silica gel. The column was eluted with increasing amounts of ether in pentane, and the product 1-(3-chlorophenyl)-3-(trimethylsilyl)-cyclobutyl acetate (154 mg) was eluted with 2−3% ether in pentane.

Methanol (4 mL) was added to 138 mg of the acetate (0.466 mmol) prepared above, and then 0.5 mL of 0.48 M $NaOCH_3$ in methanol (0.240 mmol) was added. The mixture was stirred for 8 h at room temperature, and the methanol was then removed using a rotary evaporator. The residue was taken up into ether, and the mixture was washed with a small amount of water, and saturated NaCl. The solution was dried over $MgSO_4$ and filtered, and the ether was removed using a rotary evaporator to give 116 mg (97% yield) of **13** (Ar = C_6H_4-*m*-Cl) as an oil. ^{1}H NMR of **13** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.57 (t, J = 1.9 Hz, 1 H), 7.47 (m, 1 H), 7.32 (t, J = 7.8 Hz, 1 H), 7.28 (m, 1 H), 2.56 (m, 2 H), 2.21 (m, 2 H), 2.03 (s, 1 H), 1.19 (t of t, J = 11.1, 8.8 Hz,) 1 H), 0.01 (s, 9 H). ^{13}C NMR of **13** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 148.0, 134.4, 129.8, 127.5, 125.7, 123.5, 75.5, 38.6, 11.5, −3.4. Exact mass (ESI)(M + Na^+) calcd for $C_{13}H_{19}ClNaOSi$: 277.0786. Found: 277.0800. Exact mass (EI)(M − H_2O) calcd for $C_{13}H_{17}ClSi$: 236.0788. Found: 236.0774.

Isolation of Alcohol 14 (Ar = C_6H_4-*m*-Cl). A mixture of alcohols **13** and **14** (197 mg of a 26:74 ratio; 0.774 mmol) was dissolved in 4 mL of ether, and 158 mg of 2,6-lutidine (1.477 mmol) was added. The solution was cooled to −10 °C, and 260 mg of trifluoroacetic anhydride (1.238 mmol) was added. After 10 min, the mixture was warmed to room temperature and then taken up into pentane. The solution was consecutively washed with cold water, cold dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give a mixture of trifluoroacetates **15** and **16** (265 mg, 97% yield) in a 25:75 ratio.

A solution of 51 mg of 2,6-lutidine (0.477 mmol) in 4 mL of methanol was added to the mixture of trifluoroacetates **15** and **16** prepared above. Trifluoroacetate **15** (Ar = C_6H_4-*m*-Cl) reacts in methanol with a half-life of about 8 min at 23 °C to form the methyl ether derivative. After stirring the solution for 70 min at 23 °C, 1.5 mL of 0.48 M $NaOCH_3$ in methanol was added. After 10 min at room temperature, the methanol was removed using a rotary evaporator and the residue was taken up into pentane and water. The pentane extract was dried over $MgSO_4$, and after solvent removal, the residue was chromatographed on 6 g of silica gel. The column was eluted with increasing amounts of ether in pentane. The methyl ether solvolysis product derived from **15** (50 mg) was eluted with 2−3% ether in pentane. The alcohol **14** (Ar = C_6H_4-*m*-Cl) (124 mg; 98% yield based on the amount of trifluoroacetate **16** in the starting mixture) was eluted with 5−8% ether in pentane, mp 59−60 °C. ^{1}H NMR of **14** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.37 (m, 1 H), 7.28 (m, 1 H), 7.25 (m, 1 H), 7.23 (m, 1 H), 2.40 (m, 2 H), 2.29 (m, 2 H), 2.08 (quin, J = 9.9 Hz, 1 H), 2.02 (s, 1 H), −0.03 (s, 9 H). ^{13}C NMR of **14** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 147.8, 134.3, 129.7, 127.3, 125.2, 123.0, 77.9, 36.9, 14.8, −3.5. Exact mass (ESI)(M + Na^+) calcd for $C_{13}H_{19}ClNaOSi$: 277.0786. Found: 277.0790. Exact mass (EI)(M − H_2O) calcd for $C_{13}H_{17}ClSi$: 236.0788. Found: 236.0780.

Preparation of Trifluoroacetates 15 and 16. Trifluoroacetates **15** and **16** were prepared by reaction of the corresponding alcohols **13** and **14** with trifluoroacetic anhydride (1.8 equiv) and 2,6-lutidine (2.0 equiv) in ether solvent. The following procedures are representative.

A solution of 40 mg of **13** (Ar = C_6H_4-*m*-Cl) (0.157 mmol) in 2 mL of ether and 35 mg of 2,6-lutidine (0.327 mmol) was cooled to 0 °C, and 62 mg of trifluoroacetic anhydride (0.295 mmol) in 0.5 mL of ether was added dropwise. The mixture was warmed to room temperature, and after 10 min, the mixture was taken up into pentane. The solution was consecutively washed with cold water, cold dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 51 mg (93% yield) of **15** (Ar = C_6H_4-*m*-Cl) as an oil. ^{1}H NMR of **15** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.55 (m, 1 H), 7.44 (m, 1 H), 7.37−7.32 (m, 2 H), 2.78 (m, 2 H), 2.46 (m, 2 H), 1.33 (t of t, J = 11.7, 8.4 Hz, 1 H), 0.02 (s, 9 H). ^{13}C NMR of **15** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 155.5 (q, J = 42 Hz), 141.5, 134.6, 130.0, 128.8, 126.5, 124.4, 114.1 (q, J = 286 Hz), 84.6, 35.8, 13.3, −3.6.

A solution of 56 mg of **14** (Ar = C_6H_4-*m*-Cl) (0.220 mmol) in 2 mL of ether and 48 mg of 2,6-lutidine (0.449 mmol) was cooled to 0 °C, and 84 mg of trifluoroacetic anhydride (0.400 mmol) in 0.5 mL of ether was added dropwise. The mixture was warmed to room temperature, and after 10 min, the mixture was taken up into pentane. The solution was consecutively washed with cold water, cold dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 74 mg (97% yield) of **16** (Ar = C_6H_4-*m*-Cl) as an oil. ^{1}H NMR of **16** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.35 (m, 1 H), 7.32−7.26 (m, 3 H), 2.78 (m, 2 H), 2.57 (m, 2 H), 2.03 (quin, J = 10 Hz, 1 H), −0.06 (s, 9 H). ^{13}C NMR of **16** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 156.1 (q, J = 42 Hz), 142.2, 134.4, 129.7, 128.7, 126.5, 124.3, 114.2 (q, J = 287 Hz), 89.5, 33.9, 15.4, −3.6. Neat trifluoroacetates **15** and **16** are prone to decomposition at room temperature and were, therefore, stored in pentane solution at 10 °C.

Preparation of Acetate 15 (Ar = C_6H_4-*p*-CH_3). A solution of 97 mg of a mixture of alcohols **13** and **14** (Ar = C_6H_4-*p*-CH_3) (0.415 mmol; 62% alcohol **13**, 38% alcohol **14**) and 81 mg of 2,6-lutidine (0.757 mmol) in 3 mL of ether was cooled to −10 °C, and 151 mg of trifluoroacetic anhydride (0.719 mmol) in a small amount of ether was added dropwise. The mixture was warmed to room temperature and recooled to −10 °C, and pentane was added. The mixture was then rapidly washed with cold water, cold dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give a mixture of trifluoroacetates **15** and **16**. A solution of 65 mg of 2,6-lutidine (0.607 mmol) in 3.64 g of acetic acid was immediately added to this trifluoroacetate mixture. After 17 h at room temperature, the solution was taken up into pentane (5 parts) and ether (1 part). The solution was washed with 2 portions of water and then with dilute Na_2CO_3 solution. After drying over $MgSO_4$, the solvents were removed using a rotary evaporator to give 105 mg (92% yield) of acetate **15** (Ar = C_6H_4-*p*-CH_3). ^{1}H NMR of

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15 (Ar = C_6H_4-*p*-CH_3) ($CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2 H), 7.18 (d, J = 8.1 Hz, 2 H), 2.70 (m, 2H), 2.34 (s, 3 H), 2.34 (m, 2 H), 1.94 (s, 3 H), 1.29 (t of t, J = 11.6, 8.5 Hz, 1 H), −0.01 (s, 9 H). ^{13}C NMR of **15** (Ar = C_6H_4-*p*-CH_3) ($CDCl_3$) δ 169.5, 139.3, 137.1, 128.9, 126.0, 81.0, 36.3, 21.7, 21.1, 13.7, −3.5. Exact mass (EI)(M − CH_3) calcd for $C_{15}H_{21}O_2Si$: 261.1311. Found: 261.1325.

Preparation of Acetate 15 (Ar = C_6H_4-*p*-OCH_3). A solution of 57.2 mg of alcohol **13** (Ar = C_6H_4-*p*-OCH_3) (0.229 mmol) in 1.0 mL of CH_2Cl_2 was stirred, and 47.5 mg of acetic anhydride (0.466 mmol) was added. Dimethylaminopyridine (35 mg; 0.287 mmol) was then added, and the mixture was stirred at room temperature for 6 h. The mixture was then taken up into 6 mL of pentane, and the solution was washed with cold water, dilute HCl solution, water, and $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 62.4 mg (93% yield) of **15** (Ar = C_6H_4-*p*-OCH_3). ^{1}H NMR of **15** (Ar = C_6H_4-*p*-OCH_3) ($CDCl_3$) δ 7.49 (d, J = 9 Hz, 2 H), 6.89 (d, J = 9 Hz, 2 H), 3.81 (s, 3 H), 2.70 (m, 2 H), 2.33 (m, 2 H), 1.93 (s, 3H), 1.26 (t of t, J = 11.6, 8.4 Hz, 1 H), −0.01 (s, 9 H). ^{13}C NMR of **15** (Ar = C_6H_4-*p*-OCH_3) ($CDCl_3$) δ 169.5, 158.8, 134.2, 127.7, 113.4, 80.9, 55.2, 36.3, 21.7, 13.8, −3.4. Exact mass (EI)(M − HOAc) calcd for $C_{14}H_{20}OSi$: 232.1283. Found: 232.1285.

Preparation of Trifluoroacetates 18. Trifluoroacetates **18** were prepared from the corresponding arylcyclobutanols[15] using the procedure described for preparation of **15** and **16**. The following procedure is representative. Reaction of 57 mg of 1-(3-chlorophenyl)-cyclobutanol (0.312 mmol) with 105 mg of trifluoroacetic anhydride (0.500 mmol) and 63 mg of 2,6-lutidine (0.589 mmol) in 2 mL of ether at 0 °C gave 79 mg (91% yield) of **18** (Ar = C_6H_4-*m*-Cl). ^{1}H NMR of **18** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.48 (m, 1 H), 7.38 (m, 1 H), 7.36−7.31 (m, 2 H), 2.79−2.67 (m, 4 H), 2.07 (m, 1 H), 1.79 (m, 1 H). ^{13}C NMR of **18** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 155.6 (q, J = 42 Hz), 141.8, 134.6, 130.0, 128.7, 126.3, 124.1, 114.2 (q, J = 286 Hz), 86.0, 34.3, 13.8.

Solvolyses of Trifluoroacetates 15 and 16 in CD_3CO_2D. The following procedure is representative. A solution of 4.5 mg of trifluoroacetate **15** (Ar = C_6H_4-*m*-Cl) and 2.5 mg of 2,6-lutidine in 475 mg of CD_3CO_2D was placed in an NMR tube at 25 °C for 3 h (10 half-lives). The tube was then analyzed by ^{1}H NMR spectroscopy that showed acetate **17** (Ar = C_6H_4-*m*-Cl) as the sole product. Acetate **17** (Ar = C_6H_4-*m*-Cl) was identified by ^{1}H NMR spectral comparison with an authentic sample of **17**-H_3 in CD_3CO_2D prepared by acetylation of alcohol **13** (Ar = C_6H_4-*m*-Cl) with acetic anhydride and dimethylaminopyridine. ^{1}H NMR of **17**-H_3 (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 7.50 (t, J = 1.9 Hz, 1 H), 7.42 (m, 1 H), 7.30 (t, J = 7.3 Hz, 1 H), 7.26 (m, 1 H), 2.66 (m, 2 H), 2.35 (m, 2 H), 1.97 (s, 3 H), 1.32 (t of t, J = 11.7, 8.6 Hz, 1 H), 0.00 (s, 9 H). ^{13}C NMR of **17** (Ar = C_6H_4-*m*-Cl) ($CDCl_3$) δ 169.4, 144.6, 134.2, 129.5, 127.6, 126.2, 124.0, 80.5, 36.2, 21.6, 13.6, −3.5. Exact mass (EI)(M − Cl) calcd for $C_{15}H_{21}O_2Si$: 261.1311. Found: 261.1318.

Solvolyses of Trifluoroacetates and Acetates. Kinetics Procedures. Rate constants reported in Table 1 were all determined using ^{1}H or ^{19}F NMR spectroscopy. Kinetic studies on **15** and **16** in CD_3CO_2D were carried out by dissolving approximately 4 mg of the appropriate substrate in 400 mg of CD_3CO_2D containing approximately 1.5 equiv of 2,6-lutidine. For runs at 25.0 °C, the sample was then placed in a 3 mm NMR tube and the tube was placed in a constant temperature bath at 25.0 °C. At appropriate time intervals, the sample was analyzed by ^{1}H NMR with the probe temperature set at 25.0 °C to determine relative amounts of starting trifluoroacetate. Rates of reaction of trifluoroacetates **18** were determined using ^{19}F NMR spectroscopy.[16] Kinetic studies on acetates in trifluoroethanol (0.05 M in 2,6-lutidine) were carried out using our previously described method[17] where the chemical shift of the added 2,6-lutidine was monitored as a function of time. First-order rate constants for disappearance of substrates were calculated by standard least-squares procedures. Correlation coefficients were all greater than 0.9998. Some typical data for **15**, **16**, and **18** are given as Supporting Information.

Computational Studies. *Ab initio* molecular orbital calculations were performed using the Gaussian 09 series of programs.[11] Structures were characterized as energy minima via frequency calculations that showed no negative frequencies.

■ ASSOCIATED CONTENT

Supporting Information

Complete ref 11, the M062X/6-311+G* calculated structures, energies, and Cartesian coordinates of cations **6**, **10**, **11**, **24**, and **25**, ^{1}H and ^{13}C NMR spectra of **13**, **14**, **15**, **16**, **17**, **18**, (Ar = C_6H_4-*m*-Cl), **15** (Ar = C_6H_4-*p*-CH_3), and **15** (Ar = C_6H_4-*p*-OCH_3), as well as kinetics studies on **15** (Ar = C_6H_4-*m*-Cl), **16** (Ar = C_6H_4-*p*-OCH_3), and **18** (Ar = C_6H_4-*m*-Cl). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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