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3-Trimethylsilylcycloalkylidenes. γ-Silyl vs γ-Hydrogen Migration to Carbene Centers

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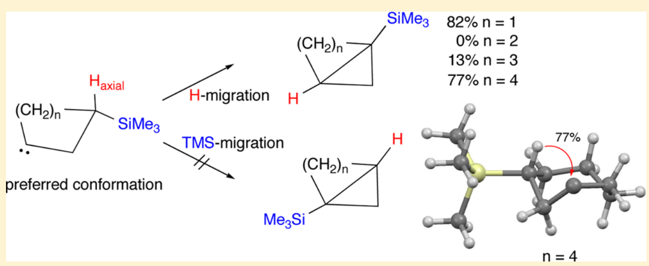
Supporting Information

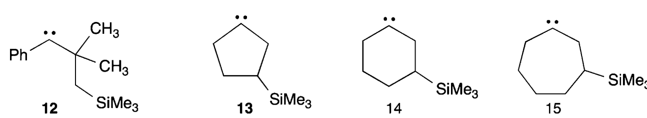
ABSTRACT: A series of γ-trimethylsilyl-substituted carbenes have been studied experimentally and by computational methods. In an acyclic system, 1,3-trimethylsilyl migration successfully competes with 1,3-hydrogen migration to the carbene center. The behavior of cyclic 3-trimethylsilyl-substituted carbenes contrasts with that of the acyclic system. Only 1,2-hydrogen migration processes are observed in the five-membered ring due to the high barrier to 1,3-hydrogen migration. In the cyclohexyl system, a small amount of a cyclopropane derived from 1,3-hydrogen migration occurs, as shown by a labeling study. In the cycloheptyl carbene system, a labeling study again showed that 1,3-hydrogen migration to the carbene center leads to the major product. Computational studies suggest that the cyclic carbenes all have lower energy conformations where the trimethylsilyl group is in a pseudo equatorial conformation where it cannot migrate to the carbene center. Computational studies also suggest that cyclohexyl and cycloheptyl carbene systems are slightly stabilized by a rear lobe interaction of the Si−C bond with the carbene center.



■ INTRODUCTION

A number of years ago, we became interested in the effect of the trimethylsilyl group on carbenes. This was an outgrowth of the remarkable stabilizing effect of β-silyl groups on isoelectronic carbocations.[1] β-silyl carbocations can form up to 10^{11} times faster than unsilylated analogs,[2] and they are calculated to be stabilized by up to 35 kcal/mol relative to β-H analogs.[3] The effect of β- and γ-silyl groups on carbenes has been studied in our laboratory.[4] The β-trimethylsilyl group migrates readily to the carbene center of **1**,[4a] while both the β-trimethylsilyl group and the β-hydrogen migrate to the carbene center in **3**.[4a] The bicyclic carbenes **6** and **8** reveal both the propensity for γ-trimethylsilyl groups to migrate to carbene centers as well as the ability of trimethylsilyl groups to enhance the migratory aptitude of adjacent hydrogen to carbenic centers.[4b] A labeling study shows that 1,3-hydrogen migration occurs in carbene **10** and not 1,3-silyl migration.[4f] These carbene reactions of **1**, **3**, and **6** suggest that trimethylsilyl groups migrate very efficiently to carbene centers. They also suggest that trimethylsilyl groups in **3**, **8**, and **10** increase the propensity for hydrogen to migrate to carbene centers.

In view of the reactions of the β-silyl carbenes **1** and **3** as well as the reactions of γ-silyl carbenes **6**, **8**, and **10** (Scheme 1), we were interested in the chemistry of other γ-trimethylsilyl-substituted carbenes. How will the behavior of less rigid carbenes compare with that of carbenes **6**, **8**, and **10**? What group(s) (TMS or H) will migrate to the carbene center in less rigid systems? Reported here are studies on γ-trimethylsilyl-substituted carbenes **12**−**15**.



■ RESULTS AND DISCUSSION

The first carbene to be generated was the acyclic system **12**, where the possibility of 1,2-hydrogen migration has been excluded by the presence of methyl groups, and 1,3-migration processes should dominate. The synthetic precursor to this carbene was the diazo compound **20**, which was prepared starting with isobutyronitrile, **16** (Scheme 2). Deprotonation of **16** followed by alkylation with chloromethyltrimethylsilane gave **17**, which was converted to ketone **18** by reaction with phenylmagnesium bromide. This relatively hindered ketone **18** was converted to the tosylhydrazone **19** by an acid-catalyzed reaction with tosylhydrazine. Deprotonation of **19** followed by vacuum pyrolysis of the dry salt[5] gave diazo compound **20** as a relatively stable distillable liquid.

Carbene **12** is generated by thermal decomposition of a solution of **20** in cyclohexane in a sealed tube at 100 °C. Thermal generation of this carbene and subsequent rearrangements likely proceed from the singlet state.[6] A complex product mixture is formed that includes five cyclopropane products (Scheme 3), whose structures were all confirmed by independent syntheses. The major product **21** (57%) and a minor product **22** (5%) are both derived from 1,3-hydrogen

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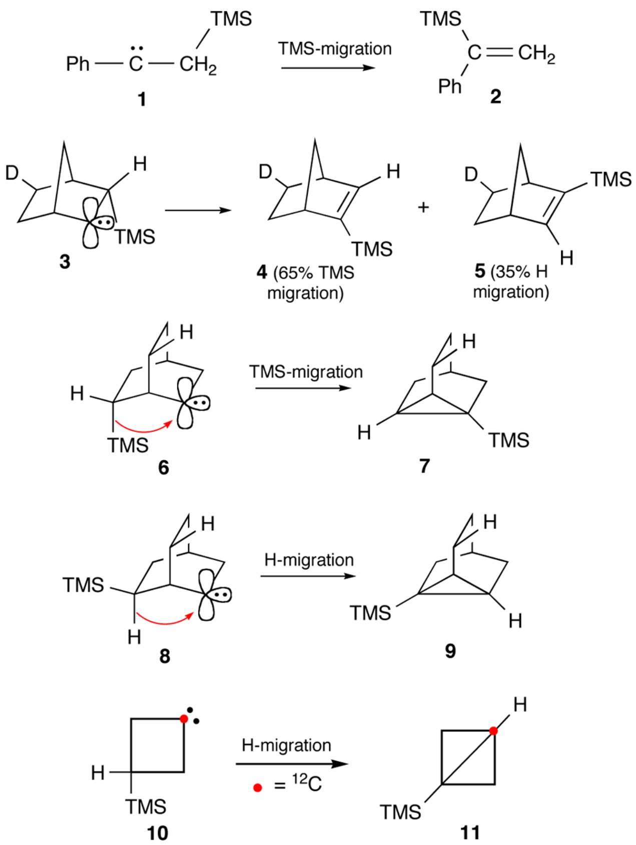
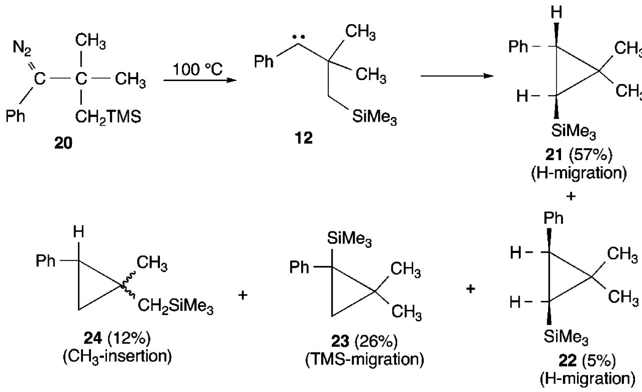
Scheme 1. Rearrangements of Trimethylsilyl-Substituted Carbenes



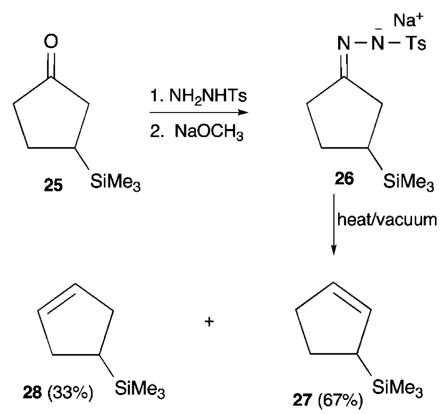
migration to the carbene center. The cyclopropane **23** (26%) is derived from trimethylsilyl migration. Also formed are small amounts (12%) of the isomeric cyclopropanes **24** derived from carbene insertion into the CH_3 groups of **12**. There are trace amounts of two minor alkene products that can be removed from the product mixture by ozonolysis, whose structures were not proven. This experimental study shows that in the unconstrained carbene **12**, although 1,3-hydrogen migration is preferred, 1,3-trimethylsilyl migration is still an important process. A computational study at the B3LYP/6-311+G** level also suggests that 1,3-hydrogen migration and 1,3-trimethylsilyl migration should be competitive.[7]

Attention was next turned to the more rigid cyclic carbene **13**. This carbene was generated by vacuum pyrolysis of the sodium salt of the tosylyhydrazone[5] derived from 3-trimethylsilylcyclopentanone, **26** (Scheme 4). The products formed are the alkenes **27** and **28** that are derived from 1,2-hydrogen migration to the carbene center. There is no trace of the bicyclopentane **30** that would be derived from 1,3-migration processes. This observation stands in contrast to the behavior of the analogous 3-trimethylsilylcyclobutylcarbene **10**, where 1,3-hydrogen migration predominates to give the bicyclobutane product **11**.

Scheme 3. Generation and Rearrangement of Carbene 12

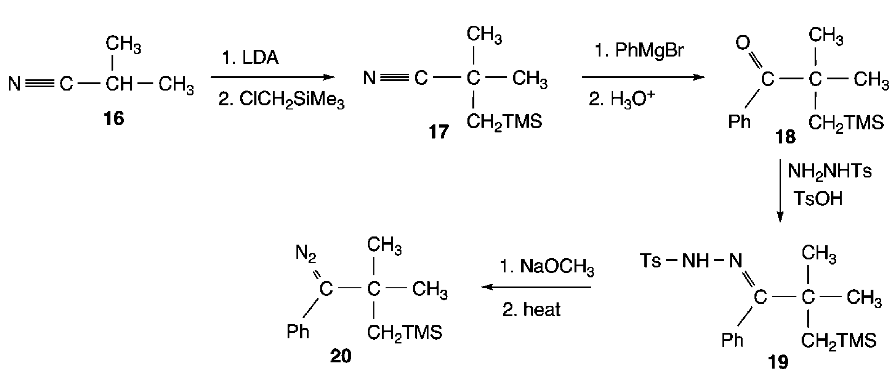


Scheme 4. Generation and Pyrolysis of Tosylhydrazone Salt 26



Computational studies[8] were used to better understand the lack of 1,3-migration processes in carbene **13**. Two conformations, **13a** and **13b**, were located at the M062X/6-311+G** computational level, with conformation **13a** being 0.7 kcal/mol lower than **13b**. Scheme 5 shows selected calculated

Scheme 2. Preparation of Diazo Compound 20



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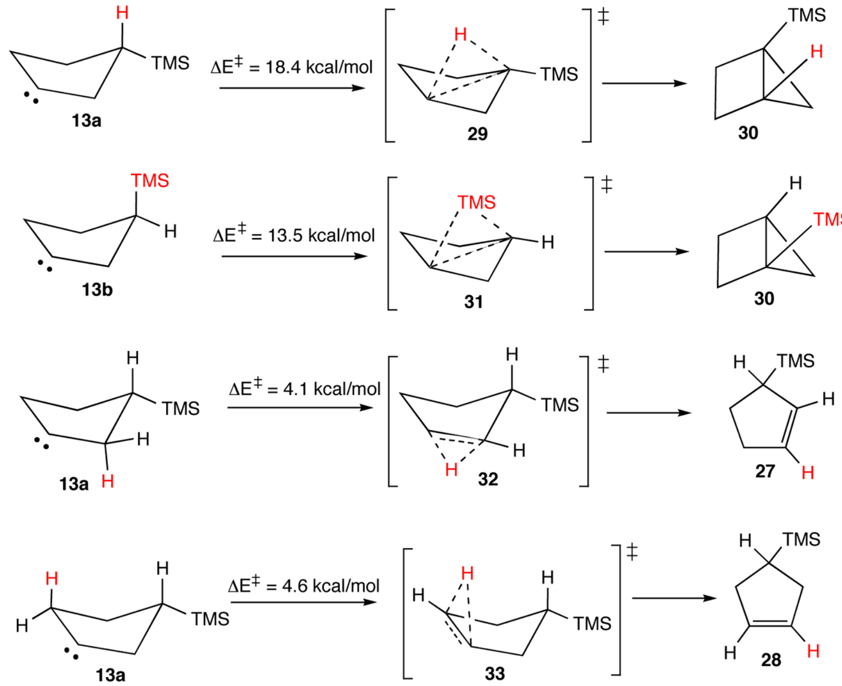
Scheme 5. M062X/6-311+G Calculated Barriers for Rearrangement of Carbene 13**



rearrangement barriers for these carbenes. The barrier to 1,3-hydrogen migration in **13a** is quite large (18.4 kcal/mol), and the corresponding 1,3-trimethylsilyl migration barrier in **13b** is also very large (13.5 kcal/mol). Two factors could contribute to the large barrier to 1,3-hydrogen migration. The first is the large ring stain in formation of the potential bicyclopentane product **30**, which has an estimated strain energy of 56 kcal/mol.[9] However, bicyclobutane **11** also has a large ring strain,[9] and, nonetheless, it is produced by a 1,3-hydrogen migration process ($\Delta E^{\ddagger}$ = 10.4 kcal/mol) from carbene **10**. Another factor is the geometry of carbenes **10** and **13b** as shown in Figure 1. The

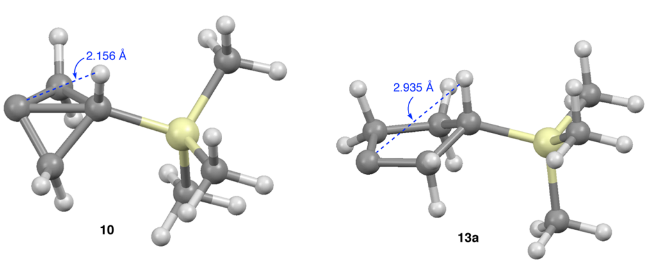
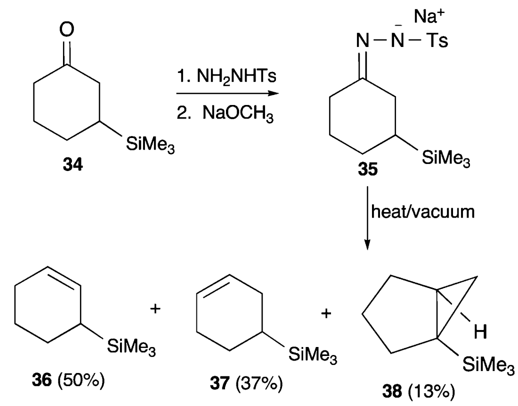


Figure 1. M062X/6-311+G** calculated structures of carbenes **10** and **13a**.

migrating hydrogen in **10** is only 2.156 Å from the carbene center, but 2.935 Å from the carbene center in **13a**. This greater distance could contribute to the significantly larger 1,3-hydrogen migration barrier in **13a**. On the other hand, the 1,2-hydrogen migration processes leading to the observed products **27** and **28** are calculated to be much more facile processes. 1,2-Hydrogen migration processes in the less stable carbene **13b** are also facile processes with comparable barriers. Also, the hydrogens *cis* and *trans* to the TMS group all migrate with comparable small barriers.

The approach to carbene **14** (Scheme 6) also utilized pyrolysis of a tosylhydrazone salt. In this case, vacuum pyrolysis of the sodium salt **35** gave three products **36**−**38**. Although the

Scheme 6. Generation and Pyrolysis of Tosylhydrazone Salt 35



major products are 1,2-hydrogen migration products **36** and **37**, the 13% of product **38** is derived from 1,3-migration to the carbene center. The behavior of carbene **14** therefore contrasts with that of the parent cyclohexylidene, which rearranges only to cyclohexene and gives no bicyclo[3.1.0]hexane.[10]

It was necessary to determine the origin of the 1,3-migration product **38**. Is this product derived from 1,3-hydrogen migration or from 1,3-trimethylsilyl migration to the carbene center? Previously a carbon-12 labeling experiment was used to determine which group migrated in carbene **10**.[4f] While an analogous approach would be feasible (but expensive) with carbene **14**, a different labeling approach was used. 3-Trimethylsilylcyclohexanone was deuterated by treatment with Na_2CO_3 in D_2O/CH_3OD. The 2,2,6,6-tetradeutero-3-trimethylsilylcyclohexanone was then converted to the tosylhydrazone salt **35-d$_4$** (Scheme 7), which was then subjected to vacuum pyrolysis. The cyclopropane product was isolated, and its structure was determined using ^{13}C NMR spectroscopy.

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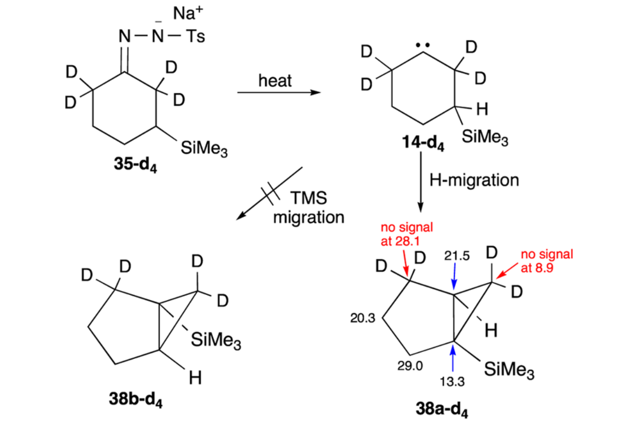
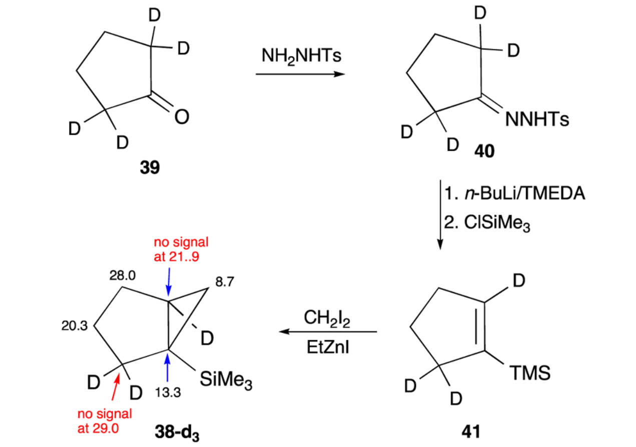
Scheme 7. Generation and Rearrangement of Labeled Carbene 14-d$_4$



Scheme 8. Synthesis of 2,2,5-Trideutero-1-trimethylsilylbicyclo[3.1.0]hexane, 38-d$_3$



The basis for the structural assignment was the lack of a signal at δ 28.1 and the presence of a signal at δ 29.0 in the cyclopropane product as seen in Figure 2. To aid in the ^{13}C NMR assignments, an authentic sample of deuterated cyclopropane **38-d$_3$** was prepared (Scheme 8). 2,2,5,5-Cyclopentanone-d$_4$, **39**, was converted to the tosylhydrazone **40**, and silylation of the vinyl anion derived from **40** gave the vinylsilane **41**. Cyclopropanation using a modified Simmons−Smith reaction gave cyclopropane **38-d$_3$**, which showed no ^{13}C NMR signal at δ 29.0 (C2) and a signal at δ 28.0 (C4). The signal at δ 29.0 in the pyrolysis product from **35-d$_4$** (Figure 2) is therefore due to C2, and the lack of a signal at δ 28.0 is due to the presence of deuterium at C4. The carbene rearrangement product was therefore **38a-d$_4$**, a product of hydrogen migration to the carbene center. The alternative product **38b-d$_4$**, derived from trimethylsilyl migration, was not observed.

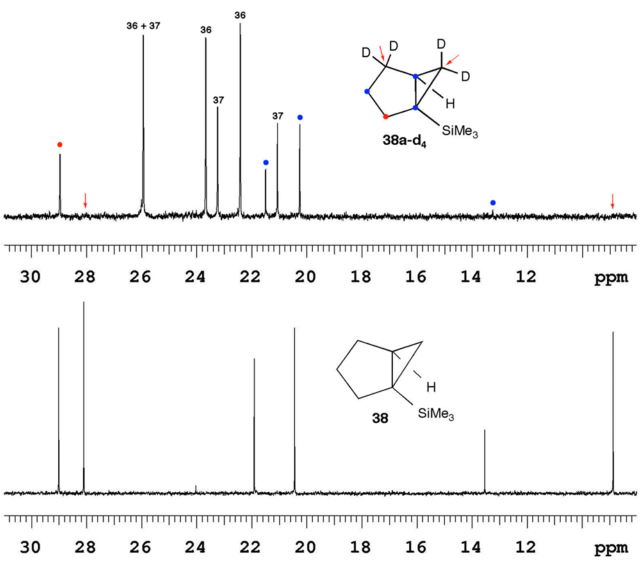


Figure 2. Partial ^{13}C NMR spectra of **38** and the products of pyrolysis of salt **35-d$_4$**.

Computational studies at the M062X/6-311+G** level were again used to gain insight into the preferential H-migration in carbene **14** (Figure3). There are two conformations of carbene **14**, with conformation **14a** being 1.1 kcal/mol lower in energy than conformation **14b**. Both the 1,3-hydrogen migration barrier in **14a** (2.0 kcal/mol) and the 1,3-trimethylsilyl migration barrier in **14b** (2.4 kcal/mol) are quite small. The transition state for interconversion of these two conformations via ring inversion could not be located computationally, but it is presumed to be significant.[11] This calculated energy diagram in Figure 3 accounts for H-migration as the predominant 1,3-migration process. However, it should be pointed out that calculated energy barriers for formation of alkenes **36** and **37** from carbene **14a** are 2.9 and 4.0 kcal/mol, respectively. These values are inconsistent with the fact that **38** is only the minor product formed in Scheme 6.

A question concerns potential stabilization of carbene **14a**. What is the stabilizing effect of the trimethylsilyl group? The isodesmic calculation in Scheme 9 suggests that carbene **14a** is more stable than cyclohexylidene, **44**, by 1.8 kcal/mol at M062X/6-311+G** level. While this stabilization energy is rather small, an analysis of the structure of carbene **14a** (Figure 4) offers some insight. There is a slight tilt of the carbene center toward C3 (relative to the parent carbene **44**). The C1−C3 bond distance shrinks from 2.369 Å in **44** to 2.324 Å in **14a**. At the same time, the C2−C3 bond length increases from 1.568 to 1.581 Å, while C1−C2 shrinks from 1.478 to1.471 Å. These trends all suggest a weak stabilizing interaction of the carbene center in **14a** with the C2−C3 bond and with the rear lobe of the C3−Si bond. This interaction is far less than in the corresponding 3-trimethylsilylcyclohexyl cation, where the calculated stabilization has a much more substantial value of 19.2 kcal/mol. However, the small stabilization in **14a** appears to be real and more significant than in carbene **13a**, where the calculated stabilization energy is an insignificant value of 0.4 kcal/mol.

The final carbene to be studied was 3-trimethylsilycycloheptylidene, **15**. The approach to this system was similar to the generation of carbene **14** (Scheme 10). Conjugate addition of trimethylsilyllithium to cycloheptenone gave **48**, which was converted to the corresponding tosylhydrazone salt **49** by standard methods. Pyrolysis of **49** in dry diglyme[12] gave the carbene derived products **50**−**52** in a 9:14:77 ratio.

An analogous deuterium labeling study was used to discern the origin of the major cyclopropane product **52**. Conversion of the labeled ketone **48-d$_4$** to the tosylhydrazone salt and pyrolysis of this salt generated the deuterium labeled carbene **15-d$_4$**. The structure of the cyclopropane rearrangement product was again determined by ^{13}C NMR spectroscopy

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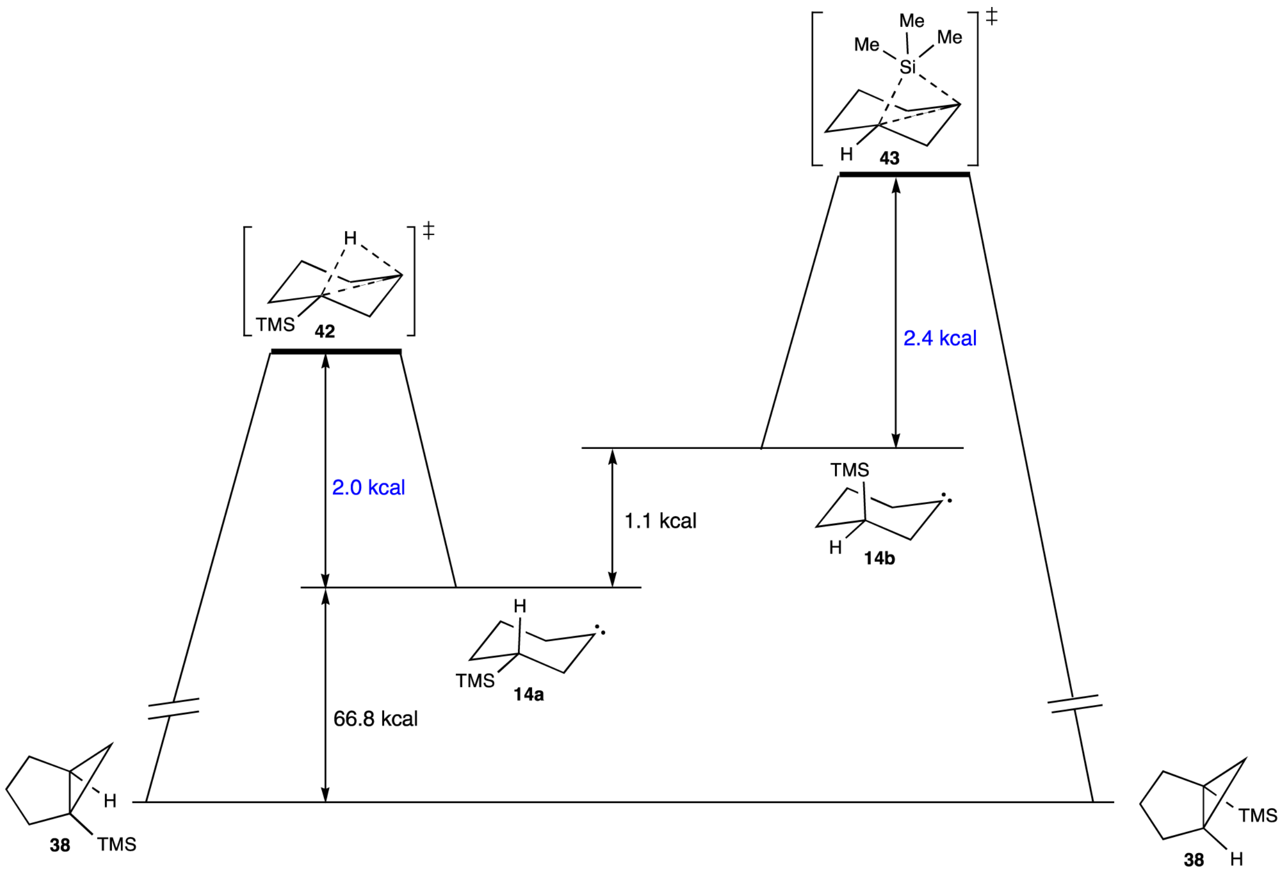
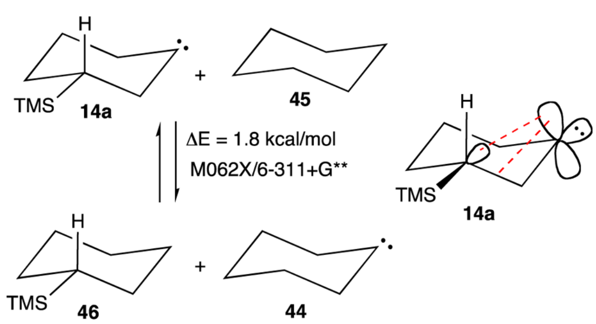


Figure 3. M062X/6-311+G** calculated energy diagram for conversion of carbenes **14a** and **14b** to **38**.

Scheme 9. Isodesmic Reaction of Carbene 14a with Cyclohexane



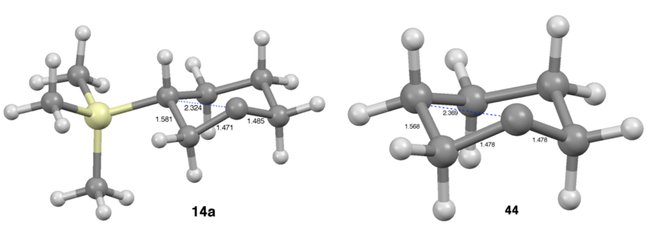
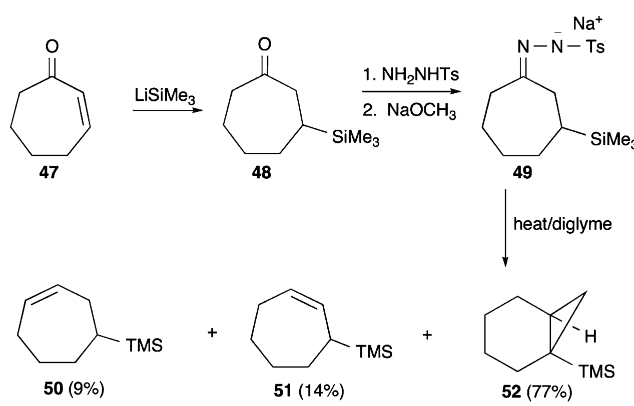


Figure 4. M062X/6-311+G** calculated structures of carbene **14a** and cyclohexylidene, **44**.

(Figure 5). But first it was necessary to unambiguously assign the ^{13}C signals in the unlabeled product **52**. This was accomplished by a combination of proton coupled ^{13}C NMR, COSY, HSQC, and HMBC methods. These assignments are shown in Scheme 11. As expected, C2 appears furthest downfield at δ 25.7 due to the silicon β-effect on chemical

Scheme 10. Generation and Pyrolysis of Tosylhydrazone Salt 49



shift, and C5 appears at δ 23.9. The structure of the pyrolysis product is assigned as **52-d$_4$** due to the lack of a ^{13}C signal at δ 23.9. Hence **52** arises from 1,3-hydrogen migration to the carbene center in **15**. Trimethylsilyl migration to the carbene center of **15-d$_4$** is not an important process.

Computational studies on carbene **15** are complicated by the existence of a number of conformational energy minima. Two pseudoequatorial energy minima have been located for carbene **15** at the M062X/6-311+G** level (Figure 6). The lowest energy is **15a**, which is 3.0 kcal/mol below **15b**. There is also one pseudoaxial energy minimum, **15c**, which is 3.2 kcal/mol above **15a**. The transition state for 1,3-hydrogen migration in **15a** is only 1.0 kcal/mol above **15a**. Barriers for 1,2-hydrogen migration in **15a** are much higher (7.1 and 6.9 kcal/mol). The

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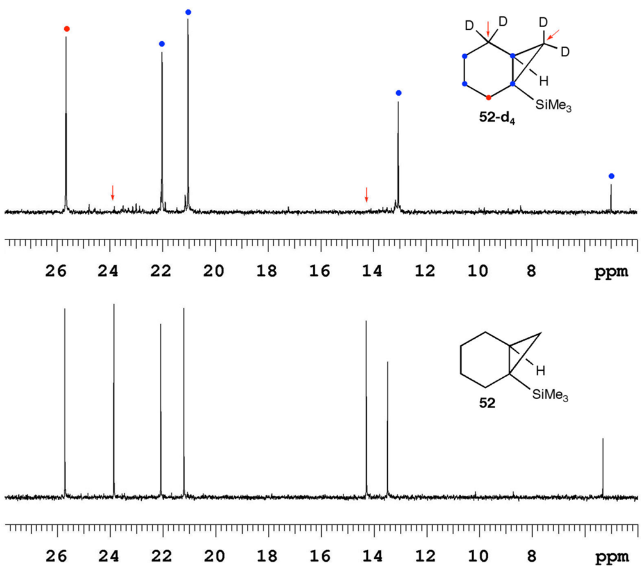


Figure 5. Partial ^{13}C NMR spectra of **52** and the pyrolysis product **52-d$_4$**.

transition state for 1,3-trimethylsilyl migration in **15c** has not been located at the M062X/6-311+G** level, although at the B3LYP/6-31G* level, the migration barrier is only 0.2 kcal/mol.

The computational behavior of carbene **15a** parallels that of **14a**. The analogous isodesmic reaction of **15a** with cycloheptane (Scheme 12) suggests stabilization of **15a** by the small value of 1.9 kcal/mol relative to cycloheptylidene, **53**. The carbene center of **15a** is closer to C3 (2.256 Å) than in the unsubstituted cycloheptylidene, **53** (2.354 Å). The C1−C2−C3 bond angle in **15a** is only 95°. The comparable angle in the parent carbene **53** is 101°. These features, as well as the C1−C2 and C2−C3 bond lengths, are consistent with a small stabilizing interaction between the carbene vacant orbital and the C2−C3 bond, as well as the rear lobe of the C3−Si bond.

■ CONCLUSIONS

The chemistry of the acyclic carbene **12** is dominated by 1,3 migration processes, with 1,3-H migration being slightly favored over 1,3-silyl migration. The behavior of the cyclic carbene **13** stands in contrast to the other carbenes studied.

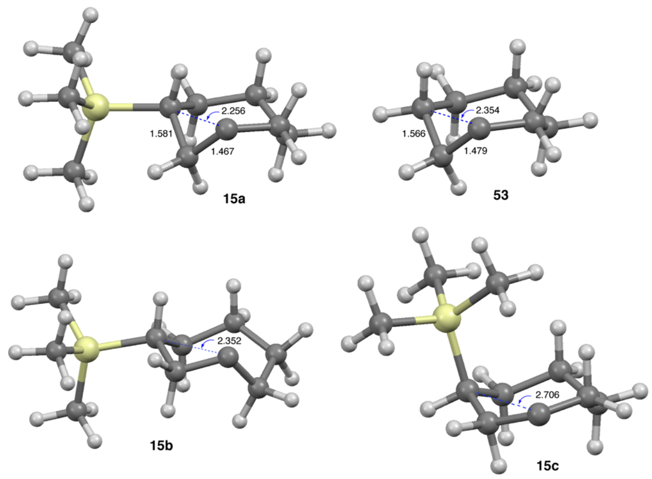
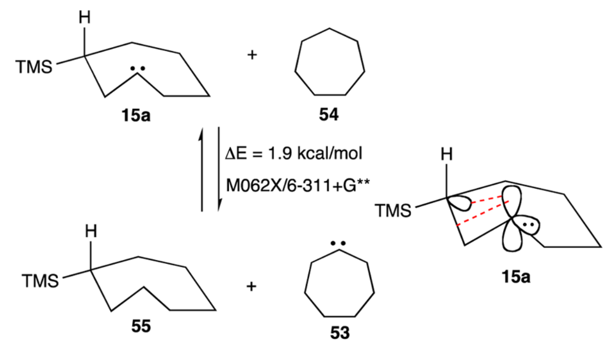


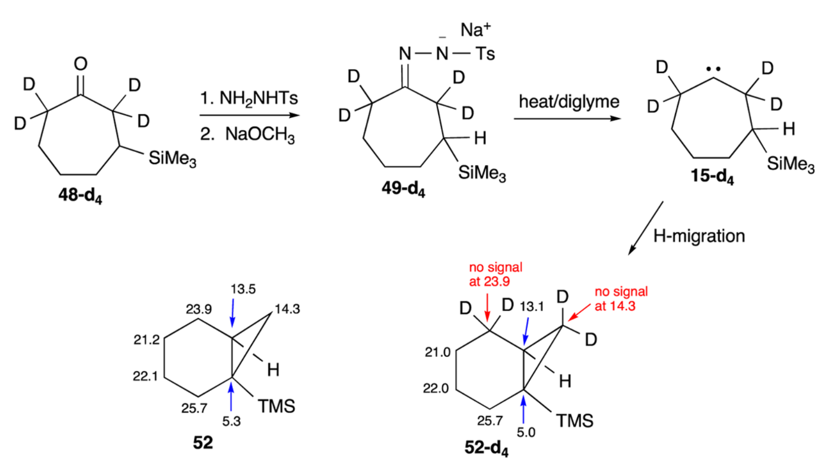
Figure 6. M062X/6-311+G** calculated structures of carbenes **15** and cycloheptylidene, **53**.

Scheme 12. Isodesmic Reaction of Carbene 15a with Cycloheptane



Only 1,2-H migration processes are observed. There are no 1,3-migration products, and this is consistent with computational studies that show relatively high barriers to 1,3-migration processes. The behavior of **13** therefore contrasts greatly with that of the cyclobutyl analog, **10**. While 1,2-H migration processes also predominate in the cyclohexyl system **14**, a small amount of 1,3-H migration occurs, as confirmed by a labeling study. In the cycloheptyl system **15**, the major product is the cyclopropane **52**, and a labeling study again showed that this product is derived from 1,3-H migration to the carbene center.

Scheme 11. Generation and Rearrangement of Labeled Carbene 15-d$_4$



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These experimental studies, as well as computational studies, suggest that, although trimethylsilyl migration processes are quite facile, they may not predominate due to conformational factors. The cyclic carbenes **10**, **13**, **14**, and **15** all have lower energy conformations where the trimethylsilyl group cannot migrate. Computational studies suggest that carbenes **14** and **15** are slightly stabilized by an interaction of the carbene center with the rear lobe of the Si−C bond.

■ EXPERIMENTAL SECTION

General. NMR spectra were recorded on a 600 MHz spectrometer. HRMS measurements were carried out using a spectrometer with an electrospray ionization source with time-of-flight mass analyzer.

Preparation of 1-Trimethylsilyl-2-cyano-2-methylpropane, 17. A solution of 3.76 g (37.3 mmol) of diisopropylamine in 30 mL of dry tetrahydrofuran under argon was cooled to −78 °C, and 22.5 mL of 1.6 M *n*-BuLi in hexanes (36.0 mmol) was added dropwise. The solution was warmed to 0 °C and then recooled to −78 °C. A solution of 2.37 g of isobutyronitrile (34.3 mmol) in 10 mL of THF was then added dropwise, and the solution was allowed to warm to −20 °C. The solution was then cooled to −78 °C, and 4.18 g of $ClCH_2SiMe_3$ (34.1 mmol) was added. The mixture was then warmed to room temperature and stirred for 8 h. The mixture was then quenched with water and transferred to a separatory funnel using ether. The ether extract was washed with water, saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator. The residue was distilled to give 4.69 g of **17** (89% yield), bp 80−83 °C (15 mm). ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6 H), 1.00 (s, 2 H), 0.14 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 126.3, 30.7, 30.25, 30.20, −0.06. IR (neat) 2233, 1252, 839 cm^{-1}. Exact mass (ESI)(M + Na$^+$) calcd for $C_8H_{17}NNaSi$: 178.1022. Found: 178.1026.

Preparation of 2,2-Dimethyl-1-phenyl-3-(trimethylsilyl)propan-1-one, 18. A solution of 30 mL of 0.90 M PhMgBr in ether (27 mmol) was stirred as 2.72 g of nitrile **17** (17.6 mmol) in 5 mL of ether was added dropwise. The solution was then refluxed for 3 h and then cooled in an ice bath. The solution was carefully quenched with aqueous NH_4Cl solution and transferred to a separatory funnel. The ether phase was washed with water, saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator, and the residue was distilled to give 3.08 g (75% yield) of ketone **18**, bp 104−106 °C (0.2 mm) which was contaminated with a small amount of biphenyl. A pure sample of ketone **18** was isolated by chromatography on silica gel using increasing amounts of ether in pentane. The biphenyl impurity eluted with pure pentane and ketone **18** eluted as an oil with 3−4% ether in pentane. ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 2 H), 7.45 (m, 1 H), 7.39 (m, 2 H), 1.38 (s, 6 H), 1.20 (s, 2 H), 0.00 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 209.0, 138.6, 130.8, 128.3, 128.0, 46.8, 30.3, 29.1, 0.6. IR (neat) 1672, 1248, 832 cm^{-1}. Exact mass (ESI)(M + Na$^+$) calcd for $C_{14}H_{22}NaOSi$: 257.1332. Found: 257.1315.

Preparation of Tosylhydrazone 19. A mixture of 302 mg of ketone **18** (1.313 mmol) and 262 mg of NH_2NHTs (1.409 mmol) in 3.0 mL of CH_3OH in a vial was stirred as 26 mg of $TsOH{\cdot}H_2O$ was added. The mixture was heated in an oil bath at 42−48 °C °C for 18 h. The methanol solvent was then removed using a rotary evaporator. The residue was taken up into 6 mL of $HCCl_3$ and filtered through a cotton plug in a pipet. The $HCCl_3$ was then removed using a rotary evaporator, and the residue was slurried with about 3 mL of pentane, cooled to 0 °C, and the pentane was decanted. After removal of the last traces of pentane under aspirator pressure, the solid tosylhydrazone, mp 84−86 °C was collected (483 mg; 93% yield). ^{1}H NMR ($CDCl_3$) δ 7.78 (m, 2 H), 7.45−7.40 (m, 3 H), 7.32 (m, 2 H), 6.85 (m, 3 H), 2.45 (s, 3 H), 1.09 (s, 6 H), 0.84 (s, 2 H), −0.04 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 165,6, 143.9, 135.6, 131.9, 129.40, 129.34, 129.21, 128.1, 127.7, 41.2, 29.7, 28.8, 21.6, 0.7. IR 1339, 1245, 1166, 833, 555 cm^{-1}. Exact mass (ESI)(M + H$^+$) calcd for $C_{21}H_{31}N_2O_2SSi$: 403.1870. Found: 403.1891.

Preparation of Diazo Compound 20. Tosylhydrazone **19** (334 mg; 0.830 mmol) was placed in a 10 mL flask and 1.92 mL of 0.478 M $NaOCH_3$ in methanol (0.917 mmol) was added via syringe. The mixture was stirred at room temperature until the tosylhydrazone dissolved, and the methanol was then removed using a rotary evaporator. The solid salt that formed was further evacuated at aspirator pressure for 2 h.

The solid salt was broken up with a spatula, and a short path distillation head with a receiver flask was attached. The pressure was reduced to <0.1 mm using a vacuum pump, and the salt was then heated using an oil bath. At about 85 °C a purple/red color began to appear, and the receiver flask was cooled in a dry ice bath. The temperature in the oil bath was slowly increased to 165 °C as the distillation head was warmed gently with a heat gun. No decomposition of the diazo compound was detected during the course of the pyrolysis. The diazo compound **20**, contaminated with a trace of methanol, collected in the cold receiver flask with the aid of a heat gun. The receiver flask was disconnected, and the deep red diazo compound was redistilled using a short path distillation head to give 179 mg of **20** (88% yield), bp ~70 °C (0.05 mm). Neat diazo compound **20**, which decomposes on standing at room temperature, gave no parent ion in the mass spectrometer. ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 2 H), 7.14 (m, 2 H), 7.05 (m, 1 H), 140 (s, 6 H), 1.24 (s, 2 H), −0.01 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 131.7, 128.7, 124.3, 123.6, 32.6, 31.7, 31.2, 0.2. IR (neat) 2027, 1248, 835 cm^{-1}.

Pyrolysis of Diazo Compound 20. Diazocompound **20** (26 mg) was dissolved in 3.6 mL of cyclohexane, and the solution was sealed in a pyrex tube under argon. The mixture was heated at 100 °C for 8.5 h. The color gradually disappeared with a half-life of approximately 1 h. The tube was opened, and the cyclohexane was removed using a rotary evaporator. The residue was chromatographed on 0.6 g of silica gel in a pipet and 19.4 mg of products (84% yield) eluted with pentane. NMR spectra of the product mixture are shown as Supporting Information. The products **21**−**24** were identified by NMR spectral comparison and gas chromatographic retention time comparison with authentic samples prepared as described below.

Preparation of Cyclopropanes 21 and 22. Phenyldiazomethane[5c] (53 mg) was dissolved in 1.73 g of 2-methyl-1-trimethylsilylpropene,[13] and the solution was sealed in a pyrex tube under argon. The solution was irradiated for 72 min with a Hanovia 450 W lamp. The tube was opened, and the excess 2-methyl-1-trimethylsilylpropene was removed by distillation using a short path distillation head at 15 mm pressure. The residue was chromatographed on 2.6 g of silica gel, and the fraction that eluted immediately with pentane was collected. After removal of the pentane, the residue (which contained **21** and **22** along with some alkene byproducts) was dissolved in 4 mL of methanol. The solution was cooled to −78 °C, and ozone was bubbled through the solution until the methanol solution became light blue in color. The mixture was warmed to about −30 °C, and a small amount of $NaBH_4$ was added. The mixture was then warmed to room temperature, and an aqueous workup followed using pentane extraction. The pentane extract was washed with water and then dried over Na_2SO_4. After removal of the pentane solvent using a rotary evaporator, the residue was chromatographed on 0.7 g of silica gel in a pipet using pentane to elute. A mixture of cyclopropanes **21** and **22** (37 mg; 38% yield) in a 63:37 ratio eluted as an oil with pure pentane. ^{1}H NMR of **21** ($CDCl_3$) δ 7.29−7.22 (m, 3 H), 7.19−7.14 (m, 2 H), 1.92 (d, J = 7.8 Hz, 1 H), 1.251 (s, 3 H), 0.829 (s, 3 H), 0.105 (s, 9 H), 0.027 (d, J = 7.8 Hz, 1 H). ^{13}C NMR of **21** ($CDCl_3$) δ 141.2, 129.0, 127.8, 125.5, 34.7, 25.2, 24.2, 23.7, 17.7, −0.10. Exact mass calcd for $C_{14}H_{22}Si$: 218.1491. Found: 218.1485. ^{1}H NMR of **22** ($CDCl_3$) δ 7.29−7.22 (m, 3 H), 7.19−7.14 (m, 2 H), 2.22 (d, J = 10.4 Hz, 1 H), 1.300 (s, 3 H), 1.104 (s, 3 H), −0.059 (d, J = 10.4 Hz, 1 H), −0.064 (s, 9 H). ^{13}C NMR of **22** ($CDCl_3$) δ 140.2, 130.8, 127.7, 125.8, 34.3, 31.1, 21.4, 20.4, 20.0, 0.9. IR (neat) 1247, 832 cm^{-1}. Exact mass calcd for $C_{14}H_{22}Si$: 218.1491. Found: 218.1503.

Preparation of Cyclopropane 23. A solution of 198 mg of 1-bromo-2,2-dimethyl-1-phenylcyclopropane[14] (0.880 mmol) in 2 mL of THF was cooled to −78 °C, and 1.2 mL of 1.5 M *t*-BuLi in pentane (1.800 mmol) was added via syringe. After 30 min at −78 °C, 200 mg of chlorotrimethylsilane (1.843 mmol) was added. The mixture was warmed to room temperature. After 3 h, water was added, and the

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mixture was transferred to a separatory funnel using ether. The organic phase was washed with water, saturated NaCl solution, and then dried over $MgSO_4$. After filtration, the solvents were removed using a rotary evaporator, and the residue was distilled using a short path distillation head. After a forerun containing 2,2-dimethyl-1-phenylcyclopropane, 127 mg of **23** (66% yield) was collected, bp 70−73 °C (2 mm). ^1H NMR of **23** ($CDCl_3$) δ 7.21 (m, 2 H), 7.14−7.07 (m, 2 H), 6.98 (m, 1 H), 1.31 (s, 3 H), 0.94 (d, *J* = 4 Hz, 1 H), 0.83 (d, *J* = 4 Hz, 1 H), 0.76 (s, 3 H), −0.06 (s, 9 H). ^{13}C NMR of **23** ($CDCl_3$) δ 145.3, 130.5, 129.6, 128.0, 127.3, 124.5, 26.9, 25.5, 24.9, 24.5, 22.0, −0.1. IR (neat) 1247, 832 cm^{-1}. Exact mass calcd for $C_{14}H_{22}Si$: 218.1491. Found: 218.1486.

*Preparation of Cyclopropanes **24**.* A solution of 25 mg of phenyldiazomethane in 4 mL of 2-methyl-3-trimethylsilylprop-1-ene[15] was sealed in a Pyrex tube under argon. The solution was irradiated for 45 min with a Hanovia 450 W lamp. The tube was opened, and the excess 2-methyl-3-trimethylsilylprop-1-ene was removed by distillation at aspirator pressure. The residue was passed through 0.6 g of silica gel in a pipet with pentane elution. The cyclopropanes **24** (20 mg; 43% yield) eluted as an oil in a 1.1:1 mixture of isomers with pure pentane. ^1H NMR of **24** ($CDCl_3$) δ 7.30−7.11 (m, 5 H), 1.86 (d of d, *J* = 8.5, 6.0 Hz, 0.52 H), 1.81 (d of d, *J* = 8.5, 6.0 Hz, 0.48 H), 1.24 (s, 1.5 H), 0.7−0.74 (m, 5 H), 0.49 (m, 0.48 H), 0.09 (s, 4.7 H), −0.03 (s, 4.3 H). ^{13}C NMR of **24** ($CDCl_3$) δ 140.44, 140.41, 129.0, 128.8, 127.84, 127.81, 125.384, 125.379, 30.86, 30.79, 27.9, 21.6, 21.2, 21.0, 20.3, 19.8, 18.6, 0.04, −0.05. IR (neat) 1247, 834 cm^{-1}. Exact mass calcd for $C_{14}H_{22}Si$: 218.1491. Found: 218.1498.

*Preparation and Pyrolysis of Tosylhydrazone Salt **26**.* Tosylhydrazine (247 mg; 1.328 mmol) was placed in a vial and stirred, and 2 mL was of methanol was added. 3-Trimethylsilylcyclopentanone[16] (204 mg; 1.308 mmol) was added, and the mixture was stirred for 4 h. The mixture was stored in the freezer overnight, and some tosylhydrazone crystallized. Most of the methanol was then removed using a rotary evaporator, and the crude residue was slurried with 2 mL of 20% ether in pentane. After cooling to −20 °C, the solvent was decanted from the solid product. The last traces of solvent were removed using a rotary evaporator. The yield of tosylhydrazone was 396 mg (93% yield). ^1H NMR and ^{13}C NMR spectra (Supporting Information) showed a mixture of two isomers.

The tosylhydrazone (299 mg; 0.923 mmol) prepared above was placed in a 15 mL flask, and 1.70 mL of 0.579 M $NaOCH_3$ (0.984 mmol) in methanol was added. The mixture was swirled for 10 min to dissolve the tosylhydrazone. The methanol was then removed using a rotary evaporator, and the residue was evacuated at 15 mm pressure for 5 h. The solid dry tosylhydrazone salt **26** was then broken up with a spatula, a short path distillation head with a receiver flask was attached, and the pressure was lowered to 0.2 mm. The flask was gradually heated to 130 °C as the receiver flask was cooled to −78 °C in a dry ice/acetone bath. At about 120 °C the pressure rose slightly, and there was a large pressure increase at about 130 °C. A liquid collected in the cooled receiver flask. At the end of the pyrolysis, the pressure dropped to about 0.2 mm. The distillate (60 mg) showed **27**[16] and **28**[16] in a 67:33 ratio as determined by NMR. See Supporting Information.

*Preparation and Pyrolysis of Tosylhydrazone Salt **35**.* Tosylhydrazine (386 mg; 2.075 mmol) was placed in a vial, and 2.5 mL was of methanol was added. 3-Trimethylsilylcyclohexanone[16,17] (344 mg; 2.024 mmol) was added, and the mixture was stirred. Tosylhydrazone product crystallized after a few hours, and about 80% of the methanol was removed using a rotary evaporator. The crude residue was slurried with 2 mL of 20% ether in pentane. After cooling to −20 °C, the solvent was decanted from the solid product. The last traces of solvent were removed using a rotary evaporator. The yield of tosylhydrazone product was 605 mg (88% yield). ^1H NMR and ^{13}C NMR spectra (Supporting Information) showed a mixture of two isomers.

The tosylhydrazone above (347 mg; 1.027 mmol) was placed in a 15 mL flask, and 1.88 mL of 0.579 M $NaOCH_3$ in methanol (1.089 mmol) was added. The mixture was swirled for 10 min to dissolve the tosylhydrazone. The methanol was then removed using a rotary evaporator, and the residue was evacuated at 15 mm for 5 h. The solid dry tosylhydrazone salt formed, and it was broken up with a spatula. A short path distillation head was attached, and the pressure was lowered to 0.2 mm. The flask was gradually heated to 140 °C as the receiver flask was cooled to −78 °C in a dry ice/acetone bath. A liquid (93 mg, 59% yield) collected in the receiver flask. NMR analysis (see Supporting Information) of the distillate showed a mixture of **36**,[16] **37**,[16] and **38** in a 50:37:13 ratio. ^1H NMR of **38** ($CDCl_3$) δ 1.81 (m, 1 H), 1.66−1.46 (m, 4 H), 1.24−1.09 (m, 2 H), 0.28−0.19 (m, 2 H), −0.06 (s, 9 H). ^{13}C NMR of **38** ($CDCl_3$) δ 29.0, 28.1, 21.9, 20.4, 13.5, 8.9, −2.9. IR (neat) 1247, 830 cm^{-1}. Exact mass calcd for $C_9H_{18}Si$: 154.1178. Found: 154.1181.

*Preparation and Pyrolysis of Tosylhydrazone Salt **35-d$_4$**.* 3-Trimethylsilylcyclohexanone, **34**, (440 mg) was placed in a flask, and 6.8 mL of D_2O was added along with 110 mg of K_2CO_3. The mixture was refluxed for 4 h and then extracted with 15 mL of pentane. The pentane extract was dried over Na_2SO_4, and the solvent was removed using a rotary evaporator. NMR analysis showed a high level of deuterium incorporation. The reaction product was recycled using an additional 6.8 mL of D_2O and 110 mg of Na_2CO_3. After refluxing for an additional 3 h and extraction with pentane, 411 mg (91% yield) of 2,2,6,6-tetradeutero-3-trimethylsilylcyclohexanone was recovered. NMR analysis (see Supporting Information) showed >96% deuterium incorporation.

Reaction of tosylhydrazine (453 mg) with 2,2,6,6-tetradeutero-3-trimethylsilylcyclohexanone (411 mg) in 2 mL of CH_3OD as solvent was completely analogous to reaction of undeuterated **34**. The tosylhydrazone salt **35-d$_4$** was prepared in an analogous fashion to the preparation of **35** using 445 mg of tosylhydrazone and 2.60 mL of 0.557 M $NaOCH_3$ in CH_3OD. The vacuum pyrolysis of **35-d$_4$** was also completely analogous to the pyrolysis of **35**.

*Preparation of 2,2,5-Trideutero-1-trimethylsilylbicyclo[3.1.0]-hexane, **38-d$_3$**.* Tosylhydrazine (2.191 g) was placed in a flask, and 6.0 mL of CH_3OD was added. A solution of 988 mg of 2,2,5,5-tetradeuterocyclopentanone in 2.5 mL of CH_3OD was added, and the mixture was warmed slightly to dissolve the tosylhydrazine. After 20 h, the flask was cooled in ice, and the product was collected in a Buchner funnel, washed with cold ether, and dried under vacuum. The yield of cyclopentanone-d$_4$ tosylhydrazone, **40**, was 2.762 g (96% yield). Conversion of tosylhydrazone **40** to **41** followed the same procedure as used to convert undeuterated cyclopentanone tosylhydrazone to 1-trimethylsilylcyclopentene.[18]

Ethylzinc iodide (2.0 mL of 1.0 M in ether) was placed in a flask under argon and 330 mg of CH_2I_2 was added. The mixture was refluxed for 5 min, and then a solution of about 58 mg of alkene **41** in a small amount of ether was added. The mixture was refluxed for 8 h. More ether was added to the mixture, which was then quenched with NaOH in water. Pentane was added, and the organic extract was separated and dried over $MgSO_4$. After filtration the solvent was removed using a rotary evaporator. The crude residue was distilled at 15 mm pressure using a short path distillation head, and a receiver flask cooled in an ice bath to prevent loss of the volatile **38-d$_3$**. ^1H NMR of **38-d$_3$** ($CDCl_3$) δ 1.80 (m, 1 H), 1.60 (m, 1 H), 1.49 (m, 1 H), 1.17 (m, 1 H), 0.25−0.19 (m, 2 H), −0.06 (s, 9 H). ^{13}C NMR of **38-d$_3$** ($CDCl_3$) δ 28.0, 20.2, 13.3, 8.7, −2.9.

*Preparation of 3-Trimethylsilycycloheptanone, **48**.* In order to prevent significant formation of 3-($SiMe_2SiMe_3$)cycloheptanone, the modified procedure for generation of TMSLi developed by Hudrlik[17b] was used. A magnetically stirred solution of 1.252 g of Me_3Si-$SiMe_3$ (8.575 mmol) in 3.5 mL of HMPA under argon was cooled to −78 °C. The mixture became solid and stirring stopped. Halide-free methyllithium (4.3 mL of 1.6 M, 6.880 mmol) in ether was added dropwise to the frozen mixture. On completion of the addition, 10 mL of dry THF was slowly added to the frozen mixture. The −78 °C bath was then replaced with an ice bath and stirring started after a few minutes as the mixture began to melt. The mixture was then stirred for 10 min in the ice bath, and the solution became dark red/orange. The mixture was recooled to −78 °C, and an additional 5 mL of THF was slowly added. A solution of 583 mg of cycloheptenone (5.300 mmol) in 2.5 mL of THF was next added dropwise at −78 °C. The mixture was warmed to about −40 °C and then quenched with water. The

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mixture was then transferred to a separatory funnel using 60 mL of pentane. The organic phase was washed with 3 portions of water. The aqueous extracts were collected for later destruction of the toxic HMPA. The pentane extract was dried over $MgSO_4$ and filtered, and the solvent was removed using a rotary evaporator. The residue was distilled to give 836 mg (86% yield) of **48**, bp 108−110 °C (15 mm). ^{1}H NMR of **48** ($CDCl_3$) δ 2.56 (m, 1 H), 2.49 (m, 1 H), 2.42 (m, 1 H), 2.35 (d of d, J = 14.6, 12 Hz, 1 H), 2.05 (m, 1 H), 2.00−1.86 (m, 2 H), 1.54 (m, 1 H), 1.31 (m, 1 H), 1.17 (m, 1 H), 0.82 (m, 1 H), −0.01 (s, 9 H). ^{13}C NMR of **48** ($CDCl_3$) δ 215.7, 44.5, 43.5, 31.9, 31.1, 24.4, 23.7, −3.5. IR (neat) 1698, 1247, 832 cm^{-1}. Exact mass calcd for $C_{10}H_{20}$ OSi: 184.1283. Found: 184.1280.

*Preparation and Pyrolysis of Tosylhydrazone Salt **49**.* Tosylhydrazine (90 mg; 0.484 mmol) was placed in a flask, and 0.5 mL of CH_3OH was added. 3-Trimethylsilylcycloheptanone, **48** (82 mg; 0.446 mmol) in 0.5 mL of CH_3OH was then added. The mixture was stirred at room temperature for 18 h, and then 1.10 mL of 0.478 M $NaOCH_3$ in methanol (0.526 mmol) was added. The methanol solvent was removed using a rotary evaporator, and the flask was then evacuated at 15 mm for 8 h. The solid was then dissolved in 7 mL of dry diglyme. A condenser was attached, and the solution (under argon) was slowly warmed in an oil bath from room temperature to 155 °C. The flask was then cooled to room temperature, and the mixture was transferred to a separatory funnel using 20 mL of pentane and 25 mL of water. The pentane extract was washed with 3 portions of water, and after drying over Na_2SO_4, the solvent was removed using a rotary evaporator. The crude residue was chromatographed on 0.6 g of silica gel in a pipet and eluted with pentane. The yield of chromatographed products was 31.0 mg (41% yield). NMR analysis (Supporting Information) showed **50**, **51**,[19] and **52**[20] in a 9:14:77 ratio.

*Preparation and Pyrolysis of Tosylhydrazone Salt **49-d₄***. 3-Trimethylsilylcycloheptanone, **48**, was converted to **48-d$_4$** by reaction in D_2O with Na_2CO_3 as a catalyst using a procedure analogous to the exchange reaction of 3-trimethylsilylcyclohexanone, **34**. The reflux time for each exchange was 24 h, and three exchanges were carried out. Procedures for conversion of **48-d$_4$** to the corresponding tosylhydrazone salt **49-d$_4$** (reaction with NH_2NHTs in CH_3OD followed by reaction with $NaOCH_3$ in CH_3OD) and solution pyrolysis of this salt in diglyme were completely analogous to the procedures used for the undeuterated **48**. NMR analysis (see Supporting Information) of the products after chromatography showed a mixture of **50-d$_4$**, **51-d$_4$**, and **52-d$_4$** in a 5:10:85 ratio.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 09 series of programs.[8] Structures were characterized as energy minima via frequency calculations that showed no negative frequencies or as transition states that showed one negative frequency.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01955.

Complete ref 8, the M062X/6-311+G** calculated structures, energies, and Cartesian coordinates of **13a**, **13b**, **14a**, **14b**, **15a**, **15b**, **15c**, **29**, **31**, **32**, **33**, **42**, **43**, **44**, **45**, **46**, **53**, **54**, and **55**, the B3LYP/6-311+G** calculated energy diagram for conversion of **12** to **21** and **23**, ^{1}H and ^{13}C NMR spectra of **17**, **18**, **19**, **20**, **21** and **22**, **23**, **24**, **38**, **38-d$_3$**, **48**, the tosylhydrazone mixtures derived from **25** and **34**, the pyrolysis products derived from **26**, **35**, **35-d$_4$**, **49** and **49d$_4$**, and 2,2,6,6-tetradeutero-3-trimethylsilylcyclohexanone as well as IR spectra for **17**, **18**, **19**, **20**, **21** and **22**, **23**, **24**, **38**, and **48** (PDF)

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Notes

The authors declare no competing financial interest.

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