Experimental and Theoretical Investigations of Ring-Expansion in 1-Methylcyclopropylcarbene

Dasan M. Thamattoor,*[,†,§] John R. Snoonian,*[,‡,∥] Horst M. Sulzbach,[‡] and Christopher M. Hadad*[,‡]

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received February 25, 1999

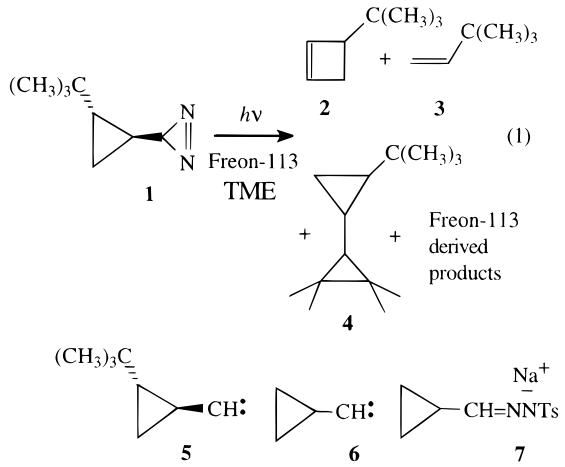
1-Methylcyclopropylcarbene, generated by photolysis of two isomeric hydrocarbon precursors, undergoes ring-expansion readily to give 1-methylcyclobutene. Experimentally, intramolecular carbon−hydrogen insertions are not observed. Trapping studies with TME demonstrates the formation of the expected cyclopropane adduct, and via a double-reciprocal analysis, the lifetime of 1-methylcyclopropylcarbene was determined to be 12 ns in 1,1,2-trichlorotrifluoroethane. Computational studies show that the barrier to ring-expansion is significantly smaller in 1-methylcyclopropylcarbene than in cyclopropylcarbene. The origin of the increased rate of ring-expansion is due to stabilization of the positive charge that occurs at the incipient tertiary carbon that is attached to the migrating carbon center.

Introduction

Carbenes can undergo rapid rearrangement processes, including hydrogen and carbon migrations. There are multiple means to generate carbenic intermediates in the gas phase and in solution, but some of these methods may be problematic due to possible rearrangements in the excited state of the chosen precursor.[1]

Substituents can often alter the rearrangement pathways available to carbenes. Methyl substitution alters the lifetime of H-migration in simple alkylchlorocarbenes as, for example, methylchlorocarbene has a lifetime of 330[2]−740[3] ns, while the lifetime of ethylchlorocarbene is less than 10 ns.[3,4] Cyclopropylcarbenes have been of interest to us, and they have been reported to undergo C-migration rearrangements.[5] For this system, in particular, we are interested in the effect of methyl substitution on the C-migration pathways. Computational studies on the cyclopropylcarbene system have also revealed that C-migration is a facile process, and furthermore, the different conformations of the carbene can lead to different products.[6] Bystander substituents have also been shown to accelerate carbene reactions, both experimentally[7] and theoretically.[8]

However, the choice of the appropriate carbene precursor is very important.[1,9] There has been substantial recent interest in the idea that conventional carbene precursors, such as diazirines and diazo compounds, can themselves give products identical to those expected from carbene intermediates.[10] For instance, it has been shown that the ring-expanded product 3-*tert*-butylcyclobutene (**2**) and the fragmentation product *tert*-butylethylene (**3**), which are among the decomposition products of diazirine **1** in $CF_2ClCFCl_2$ (Freon-113), are obtained from the precursor itself rather than the carbene **5** in solution at 0 °C.[11] The adduct **4**, on the other hand, was formed by the trapping of **5** by 2,3-dimethyl-2-butene (TME). It is also known that cyclobutene is the major product in the gas-phase pyrolysis of the tosylhydrazone salt (**7**).[5]



† Princeton University.

‡ The Ohio State University.

§ Current address: Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, IN 46556. Part of this work is taken from the Ph.D. Dissertation of Dasan M. Thamattoor, Princeton University, 1997.

∥ Current address: Vertex Pharmaceuticals, Inc., 130 Waverly Street, Cambridge, MA 02139.

(1) (a) Platz, M. S. *Adv. Carbene Chem.* **1998**, *2*, 133. (b) See also: Bonneau, R.; Liu, M. T. H. *Adv. Carbene Chem.* **1998**, *2*, 1.

(2) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873.

(3) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

(4) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973.

(5) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (b) Kirmse, W.; von Bülow, B. G.; Schepp, H. *Justus Liebigs Ann. Chem.* **1966**, *691*, 41.

(6) (a) Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519. (b) Chou, J.-H.; McKee, M. L.; De Felippis, J.; Squillacote, M.; Shevlin, P. B. *J. Org. Chem.* **1990**, *55*, 3291.

(7) (a) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (b) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

(8) (a) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Phys. Chem. A* **1998**, *102*, 8467. (b) Evanseck, J. D.; Houk, K. N. *J. Phys. Chem.* **1990**, *94*, 5518.

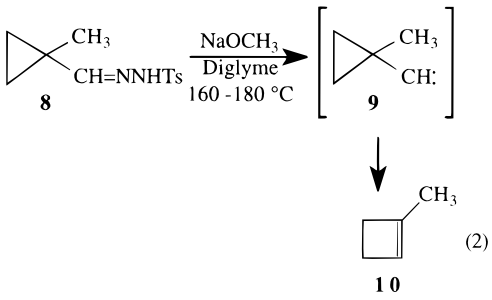
(9) Thamattoor, D. M.; Jones, M., Jr.; Pan, W.; Shevlin, P. B. *Tetrahedron Lett.* **1996**, *37*, 8333.

(10) Ruck, R. T.; Jones, M., Jr. *Tetrahedron Lett.* **1998**, *39*, 4433 and references therein.

(11) (a) Huang, H.; Platz, M. S. *Tetrahedron Lett.* **1996**, *37*, 8337. (b) Huang, H.; Platz, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 5990.

10.1021/jo9903454 CCC: $18.00 © 1999 American Chemical Society
Published on Web 07/23/1999

During the course of our investigation into other cyclopropylcarbenes, we became interested in the chemistry of 1-methylcyclopropylcarbene (**9**). Early work by Kirmse's group showed that the pyrolysis of tosylhydrazone salt (**8**) led predominanly to the ring-expanded product 1-methylcyclobutene (**10**).[12] It was suggested that **9** was an intermediate in this reaction (eq 2).



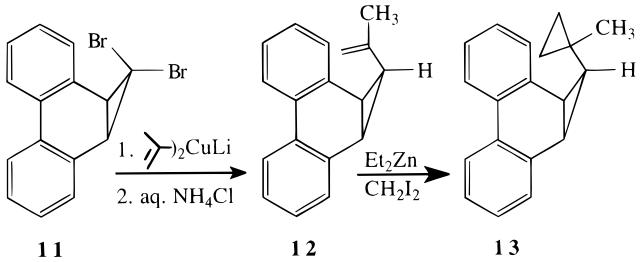
To avoid complications that could potentially be introduced by excited states of nitrogenous precursors,[1a] we decided to generate **9** by other means so as to estimate the lifetime of **9** and the role of methyl substitution on the rearrangement pathways.

Phenanthrene Precursor Route to 9. The hydrocarbons **13** and **17** were chosen as sources of **9** since similar compounds are known to produce alkylcarbenes upon photolysis.[13] The desired precursors were synthesized as shown in Scheme 1. Thus, the reaction of dibromide **11**[14] with lithium diisopropenylcuprate, followed by quenching with saturated aqueous ammonium chloride, led to the sterically more congested *endo* isomer **12**.[15] The *exo* isomer **16**, interestingly, was not observed in the reaction. (A detailed study of this unusual stereochemical effect will be reported elsewhere.) Subsequent cyclopropanation of **12** with diethylzinc and diiodomethane led to **13**.

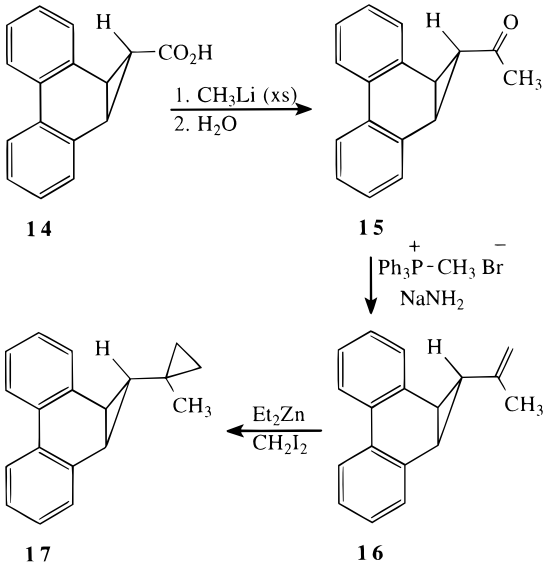
To prepare **17** (Scheme 2), the acid **14**[16] was converted into methyl ketone **15** with excess methyllithium.[17] A Wittig reaction using "instant ylid" led from **15** to the isopropenyl derivative **16**.[18] In the final step cyclopropanation of **16** was carried out to give **17**.

The photolyses of **13** and **17** in benzene-d_6 were carried out individually in Pyrex tubes. The *endo* isomer **13** produced 1-methylcyclobutene (**10**) and methylenecyclobutane (**18**) in a relative ratio of 72:28; whereas, the *exo* isomer **17** gave **10** and **18** in a relative ratio of 92:8 (Scheme 3). We have also determined that **10** and **18** do not interconvert under the reaction conditions. In other experiments, both **13** and **17** produced **10** and the expected adduct **25** when the photolyses were carried out in 2,3-dimethyl-2-butene (TME). An adduct between the carbene and solvent was not observed. Unfortunately, products due to fragmentation, such as ethene and propyne, could not be detected with our experimental setup.

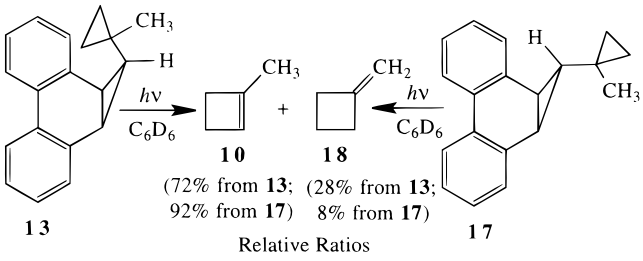
Scheme 1



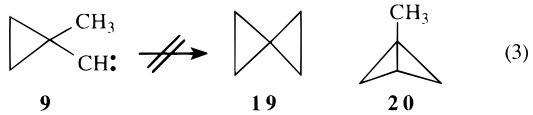
Scheme 2



Scheme 3



Thus, although the source of **18** is unclear at this time, it appears that **9** does undergo a facile C-migration rearrangement to yield ring-expanded **10**. Furthermore, the fact that neither spiropentane (**19**) nor 1-methylbicyclo-[1.1.0]butane (**20**) are produced in the photolyses suggests that **9** is not prone to undergo intramolecular carbon−hydrogen insertion reactions (eq 3).

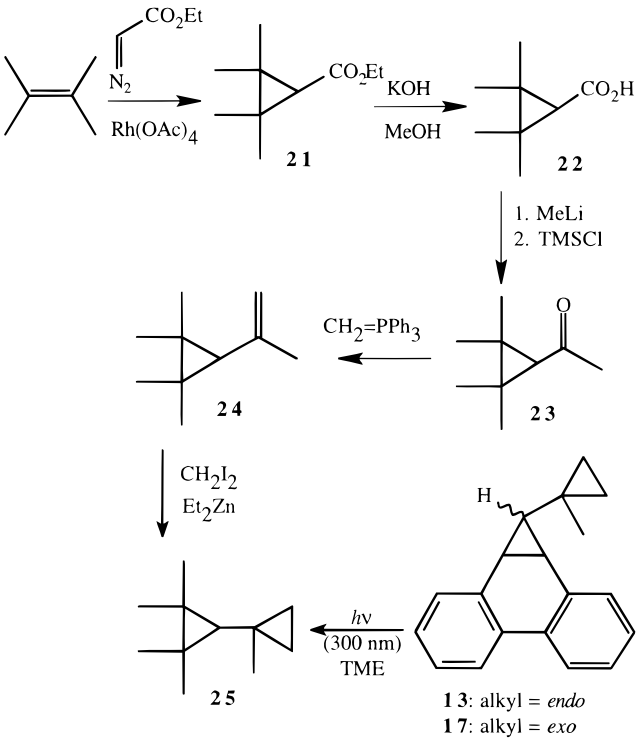


To ascertain some numerical estimates of the relative reactivity of **6** and **9**, we also explored trapping studies with 2,3-dimethyl-2-butene (TME). Once again, the phenanthrene precursors **13** (*endo*) and **17** (*exo*) were used, and to demonstrate clearly that TME could effectively trap the carbene **9**, we independently synthesized the cyclopropane adduct **25** (Scheme 4).

Cyclopropanation of TME with ethyl diazoacetate with rhodium acetate yielded **21**. Saponification of the ester

(12) Kirmse, W.; Bücking, H.-W.; *Justus Liebigs Ann. Chem.* **1968**, *711*, 31.
(13) (a) Ruck, R. T.; Jones, M., Jr. *Tetrahedron Lett.* **1998**, *39*, 2277. (b) Glick, H.; Likhotvorik, I. R.; Jones, M., Jr. *Tetrahedron Lett.* **1995**, *36*, 5715.
(14) Shaffler, J.; Retey, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *11*, 845.
(15) (a) Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1976**, *98*, 2362. (b) Kitatani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1600.
(16) Drake, N. L.; Sweeney, T. R. *J. Org. Chem.* **1946**, *11*, 67.
(17) Jorgensen, M. J. *Org. React.* **1970**, *18*, 1.
(18) Schlosser, M.; Schaub, B. *Chimia* **1982**, *36*, 396.

Scheme 4



yielded **22** which was converted to the methyl ketone **23** with MeLi and trimethylsilyl chloride. The ketone was converted to the corresponding alkene **24** using Wittig chemistry, and finally Simmons−Smith cyclopropanation yielded **25**. Compound **25** was fully characterized by NMR, GC/MS, and high-resolution MS. In particular, **25** would fragment readily under typical GC/MS conditions, but due to the independent synthesis, the fragmentation pattern could be readily discerned for the subsequent trapping studies of **9** with TME.

Indeed, direct photolysis of **13** in the presence of neat TME does generate phenanthrene and **25** in a 2:1 ratio. The photolysis of **17** under similar conditions also leads to a 2:1 ratio of those compounds. By varying the TME concentration in argon-purged 1,1,2-trichlorotrifluoroethane, it was possible to estimate the lifetime of **9** as generated by photolysis from **13** (Rayonet, 300 nm) at 5 °C for 12 h. Dicyclohexyl was used as an internal standard for the GC/MS characterization. Upon plotting 1/**25** vs 1/TME, we were able to obtain a ratio of k_o/k_{TME} of 0.0841, where k_o represents the rearrangement process for **9** (due to no reaction with solvent) and k_{TME} is the rate constant for adduct formation with TME (Figure 1).

Since the lifetime, τ, of **9** will be equal to $1/k_o$, it is possible to estimate the lifetime of singlet **9** by using the value of k_{TME} for (2-*tert*-butyl)-cyclopropylcarbene (**5**) in Freon-113 as determined by laser flash photolysis by Huang and Platz ($k_{TME} = 1.02 \times 10^9$ M^{-1} s^{-1}).[11] This analysis leads to a lifetime of **9** of only 12 ns. This lifetime compares to previously reported values for **5**,[11] **6**,[19] and **26**[19] (cyclopropyl methyl carbene) of 18, 24, and 21 ns, respectively, which are largely controlled by reactions with solvent. Thus, the parent cyclopropyl carbene (**6**) undergoes rearrangement more slowly than the methyl substituted **9**, and C-migration is a significant pathway.

(19) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 10440.

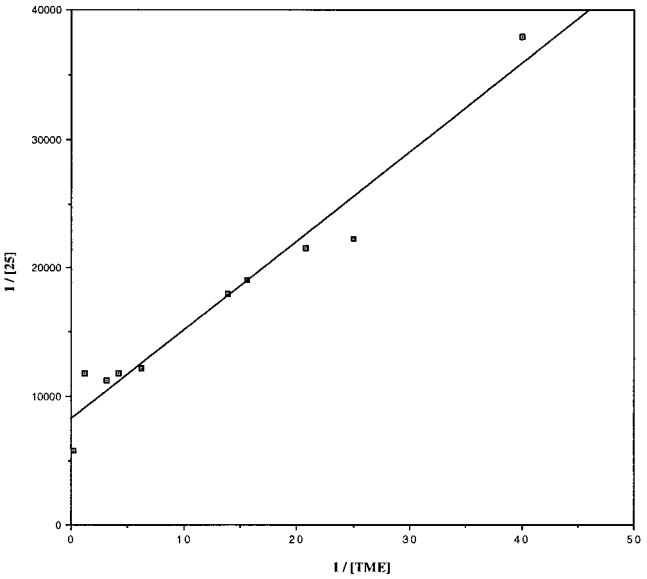
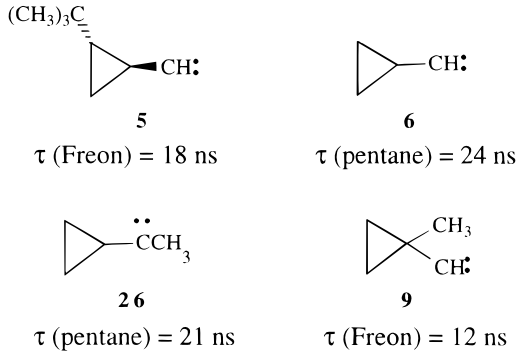


Figure 1. Double reciprocal plot of 1/[**25**] vs 1/[TME] concentration from direct photolysis of **13** under varying concentrations of TME in 1,1,2-trichlorofluoroethane solvent (5 °C for 12 h). The correlation coefficient (r^2) is 0.957.



To understand the effect of the methyl substituent in this C-migration process, we have also utilized computational methods.

Computational Results

As noted above, cyclopropylcarbene has been examined by Shevlin and McKee with ab initio molecular orbital theory.[6] In particular, they noted that there are two conformations of cyclopropylcarbene, and the *cis* isomer is more stable than *trans* by ~2 kcal/mol.[20] Furthermore, there is a significant activation barrier (~15 kcal/mol) for interconversion of the *cis* and *trans* isomers. The C-migration process is calculated to be the most favored pathway and the most favorable activation barrier (5.0 kcal/mol) is for C-migration in the *cis*-carbene isomer. Shevlin and McKee also noted that the *trans* conformer of **6** undergoes fragmentation to ethylene and acetylene in preference to C-migration. All of the C-migration pathway proceeds through the *cis* isomer.

We have previously shown that density functional theory[21] can provide accurate energies and geometries for the rearrangement processes in carbenes.[22] In par-

(20) It is perhaps more appropriate to use terms such as *syn* and *anti* to describe these conformations, but we have chosen to maintain the *cis* and *trans* nomenclature used in ref 6a. The *cis* and *trans* distinction refers to the relative location of the carbene C−H bond and either the ring C−H bond (**6**) or the ring C−CH_3 bond (**9**).

Table 1. Relative Energies (kcal/mol) of Intermediates and Stationary Points for Cyclopropylcarbene (6) and 1-Methylcyclopropylcarbene (9)[a]

	BH&HLYP/6-31G(d)			BH&HLYP/6-311++G(d,p)		
structure	ΔE_{BW}	ΔH^{298}	ΔG^{298}	ΔE_{BW}	ΔH^{298}	ΔG^{298}
6 *cis* C_s	0.0	0.0	0.0	0.0	0.0	0.0
6 *trans* C_s	1.8	1.8	1.1	1.5	1.6	0.9
6 *cis* TS−C	5.2	4.8	5.8	5.3	5.0	6.0
6 *trans* TS−C	22.3	21.4	22.3	22.2	21.3	22.1
cyclobutene	−65.4	−63.8	−62.4	−62.6	−61.0	−59.6
6 *cis* TS-frag	24.5	22.6	22.3	21.0	19.1	18.8
6 *trans* TS-frag	21.7	20.0	19.4	18.3	16.6	16.1
(ethene + ethyne)	−24.6	−27.7	−36.2	−30.6	−33.6	−42.1
9 *cis* C_1	0.0	0.0	0.0	0.0	0.0	0.0
9 *cis* C_s	0.1	−0.6	0.3	−0.1	−0.8	0.2
9 *trans* C_1	0.9	1.1	1.5	0.4	0.6	1.0
9 *trans* C_s	1.6	0.8	1.8	0.7	−0.1	0.9
9 *cis* TS−C	1.6	1.2	2.1	1.5	1.1	2.0
9 *trans* TS−C	15.3	14.4	15.2	14.5	13.5	14.3
1-methylcyclobutene	−70.2	−68.6	−67.9	−64.1	−62.5	−61.8
9 TS-spiro	20.0	18.4	19.8	19.1	17.5	18.9
spiropentane	−55.4	−53.7	−51.6	−52.2	−50.5	−48.3
9 *cis* TS-frag	24.3	22.7	21.7	20.8	19.2	18.2
9 *trans* TS-frag	21.4	19.9	18.3	17.8	16.3	14.7
(ethene + propyne)	−31.8	−33.6	−45.7	−37.2	−39.0	−51.1

[a] The energies of all **6** isomers are relative to the **6** *cis* C_s energy at the appropriate level. The energies of all **9** isomers are relative to the **9** *cis* C_1 energy at the appropriate level. The BH&HLYP/6-31G(d) energies are for fully optimized geometries at that level. The BH&HLYP/6-311++G(d,p) energies used the corresponding BH&HLYP/6-31G(d) geometry as well as the scaled ZPE corrections and thermal corrections to 298 K from the BH&HLYP/6-31G(d) vibrational frequency analysis. The ΔE_{BW} energies are at the bottom-of-the-well and do not include ZPE corrections. ΔH^{298} corresponds to relative enthalpies at 298 K. ΔG^{298} corresponds to relative free energies at 298 K.

ticular, in our previous study, we showed that the Becke half-and-half exchange functional[23] along with the Lee−Yang−Parr correlational functional[24] can yield results that are similar to coupled cluster theory.[25]

Therefore, for this project, we have utilized the BH&HLYP functional along with the standard 6-31G(d) basis set to explore the geometries of the relevant singlet carbenes (**6** and **9**) as well as the transition states for C-migration and fragmentation. In addition, we have obtained better relative energies with single point energy calculations at the BH&HLYP/6-311++G(d,p) level. For all of these calculations, we have included zero-point vibrational energy effects as well as thermal corrections to provide relative free energies at 298 K. The relative energies are presented in Table 1.

For the potential energy surface (Figure 2) of unsubstituted **6**, there are 2 minima for the singlet carbene and both are of C_s symmetry. The more stable structure (**6** *cis* C_s) has the *cis* relationship of the carbene H with the ring H. The **6** *trans* C_s isomer is only 0.9 kcal/mol higher in free energy. There are two transition states (both of C_1 symmetry) for the C-migration process, and they result from migration in the *cis* and *trans* conformations of the singlet carbenes. The *cis* C-migration transition state is the lower of the two structures and has a free energy of activation of 6.0 kcal/mol at 298 K. Both transition states lead to the same cyclobutene product, and both processes are very exoergic (∼ −60 kcal/mol). The larger free energy of activation for the *trans* transition state is due to the initial formation of a *trans* double bond, and as a result, the transition state is later and suffers from poor overlap in the transition state.

Fragmentation of the cyclopropyl carbene to ethene and ethyne has also been investigated. Shevlin and McKee previously noted that the *trans* conformer would preferentially fragment, while the *cis* conformer would preferentially undergo a C-migration process.[6] Figure 3 illustrates the structures involved in the fragmentation process for **6**, and as noted previously,[6] fragmentation, rather than C-migration, is energetically favored for the *trans* conformer.

The potential energy surface (PES) for **9** is presented in Figure 4. Qualitatively, the overall PES is similar to that of **6**; however, there are some differences. For instance, there are two minima for the singlet carbene (*cis* and *trans*), but both structures are of C_1 symmetry, rather than C_s. The **9** *cis* C_1 structure is favored by 1.0 kcal/mol.

The free energy of activation for the C-migration process is, once again, lower for the *cis* transition state, but both transition states have *decreased* free energies of activation when compared to unsubstituted **6**. In particular, the *cis* transition state has a free energy of activation of only 2.0 kcal/mol for C-migration, and this result is in agreement with the experimental determination that methyl substitution at the 1-position does lead to a shorter lifetime for **9** than for **6**. Both *cis* and *trans* transition structures lead to 1-methylcyclobutene, and once again, the *trans* transition state has a geometry that is later on the PES and, therefore, a higher free energy of activation. In addition, the transition state for C−H insertion to generate spiropentane has an even higher free energy of activation (18.9 kcal/mol), even though the formation of spiropentane is also very exoergic (−48.3 kcal/mol).

Fragmentation has also been considered (Figure 5) and there are two transition states for fragmentation, de-

(21) (a) Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991. (b) Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989.
(22) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III.; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 9787.
(23) (a) Becke, A. D. *J. Chem. Phys.* **1992**, *98*, 1372. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.
(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(25) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.* **1992**, *S26*, 879.

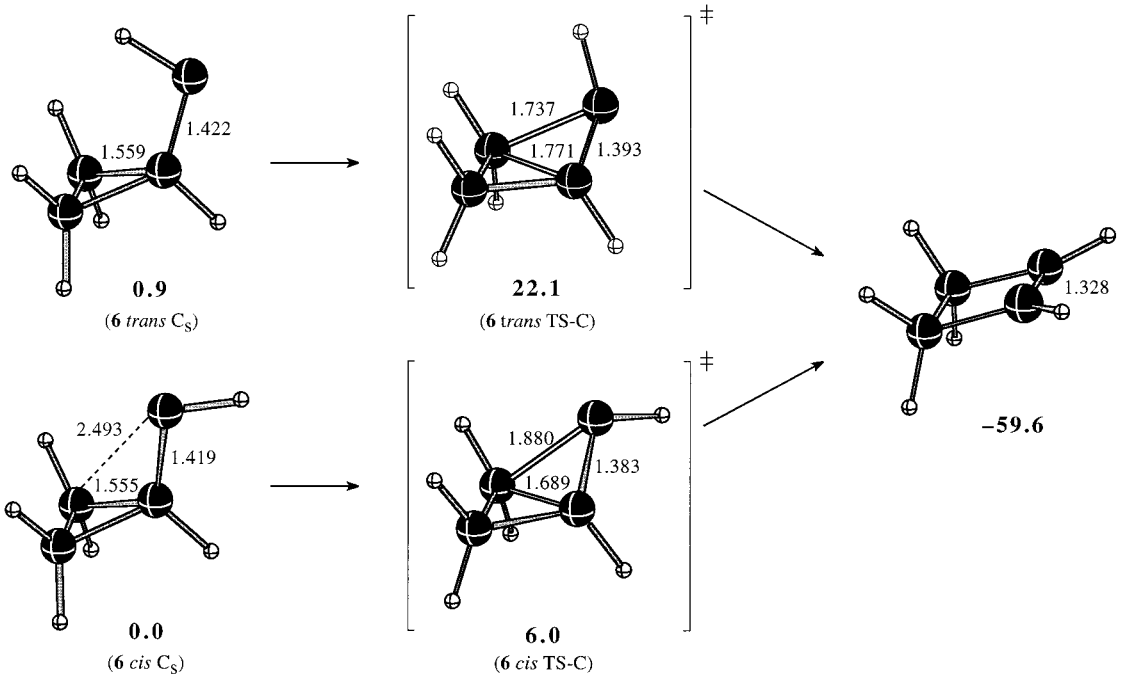


Figure 2. Intermediates and transition structures for C-migration in cyclopropylcarbene (**6**). The free energies at 298 K (relative to **6** *cis* C_s) are depicted in bold. Some bond distances are listed in Å.

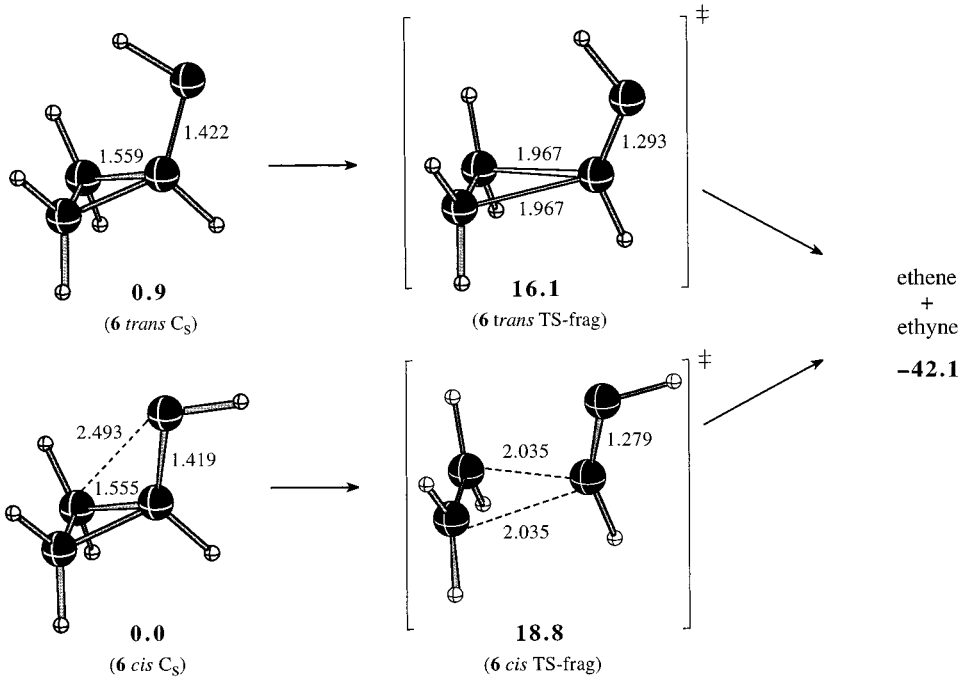


Figure 3. Intermediates and transition structures for fragmentation in cyclopropylcarbene (**6**). The free energies at 298 K (relative to **6** *cis* C_s) are depicted in bold. Some bond distances are listed in Å.

pending on the carbene conformer (*cis* or *trans*). Methyl substitution lowers the energy of the *trans* transition state for fragmentation, but affects the *cis* structure to a much smaller extent. Most importantly, unlike unsubstituted **6**, C-migration is the more favorable pathway for either the *cis* or *trans* conformers of 1-methylcyclopropylcarbene (**9**).

To rationalize the lower activation barrier to cyclobutene formation due to methyl substitution, we have investigated the charge distribution in the carbenes and the transition states for the different migration possibilities. We have chosen to evaluate the atomic charges in these systems via Bader's theory of atoms in molecules (AIM)[26] and Reed and Weinhold's Natural Population Analysis (NPA).[27,28] The AIM data are presented in Figures 4 (rearrangement of **6**) and 5 (rearrangement of **9**).

The preferred *cis* conformer of carbene **6** has a significant negative charge (−0.123 e) on the C atom adjacent to the carbene center (see the bold numbers in Figure 6). During the C-migration process, that C atom becomes

(26) (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (c) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory*; Clarendon Press: Oxford, 1990.

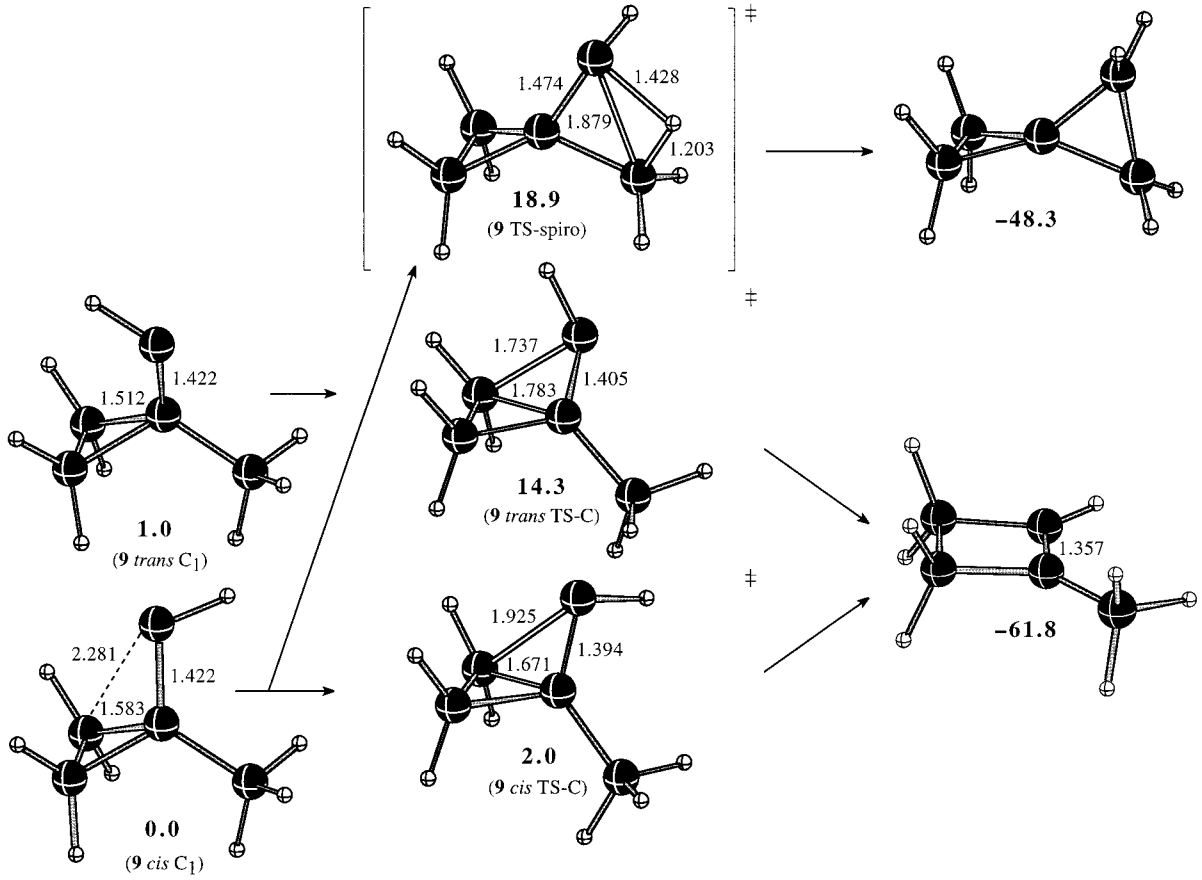


Figure 4. Intermediates and transition structures for C-migration and C−H insertion in 1-methylcyclopropylcarbene (**9**). The free energies at 298 K (relative to **9** *cis* C_1) are depicted in bold. Some bond distances are listed in Å.

more positively charged (increase of +0.147 e). (Unfortunately, we were unable to integrate the ring atoms for the lower energy *cis* transition state due to a numerical instability in the ring region where the bonds are being broken and formed.)

When the methyl group is present as for **9** (Figure 7), the C atom adjacent to the initial carbene center becomes more positively charged by only +0.121 e. The methyl group does act to transfer electron density to the atoms involved in the C-migration process and thereby stabilizes the transition state.

While these atomic charge differences were evaluated with the AIM method, similar (but larger magnitude) trends are noted with the NPA method (see the Supporting Information for similar figures as above). Numerically, the NPA charges tend to have the C atoms being more negative than the AIM method. As a result, the change in atomic charge that occurs for the C atom adjacent to the carbene center in the *cis* carbene **6** and the lower energy *cis* transition state is +0.276 e. With methyl substitution as in **9**, the change in atomic charge is +0.198 e.

Thus, both the AIM and NPA charges are in agreement that there is an increase of positive charge at the C atom adjacent to the carbene center during the C-migration process, and a methyl substituent serves to stabilize that increase of positive charge due to polarization/electron donation by the methyl group.

Conclusions

Experimentally, we have shown that 1-methylcyclopropyl carbene (**9**) preferentially undergoes C-migration to generate 1-methylcyclobutene. We have trapped the generated carbene with 2,3-dimethyl-2-butene (TME), and we have verified the generation of the cyclopropanated product via its independent synthesis. The lifetime of **9** has been determined (12 ns) via trapping studies with TME, and the lifetime is shorter than other cyclopropyl carbenes.

Computationally, we have calculated the potential energy surfaces for cyclopropylcarbene (**6**) and **9** with density functional theory. The lower energy transition state for C-migration has a free energy of activation of 6.0 kcal/mol for unsubstituted **6**, and the activation barrier decreases to 2.0 kcal/mol in **9** which has the methyl substituent. While fragmentation to ethene and ethyne is favorable for the *trans* conformer of **6**, C-migration is more favorable than fragmentation for all conformers of **9**.

The computational results reveal that there is an increase of positive charge in the transition state for C-migration and the adjacent methyl group serves to stabilize that increase. These results are consistent with the present experiments, previous studies which probed the effect of methyl groups on carbene rearrangements, and the effect of polar solvents on migration reactions.

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

(28) For a comparison of different methods for analyzing charge density distributions, see: Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

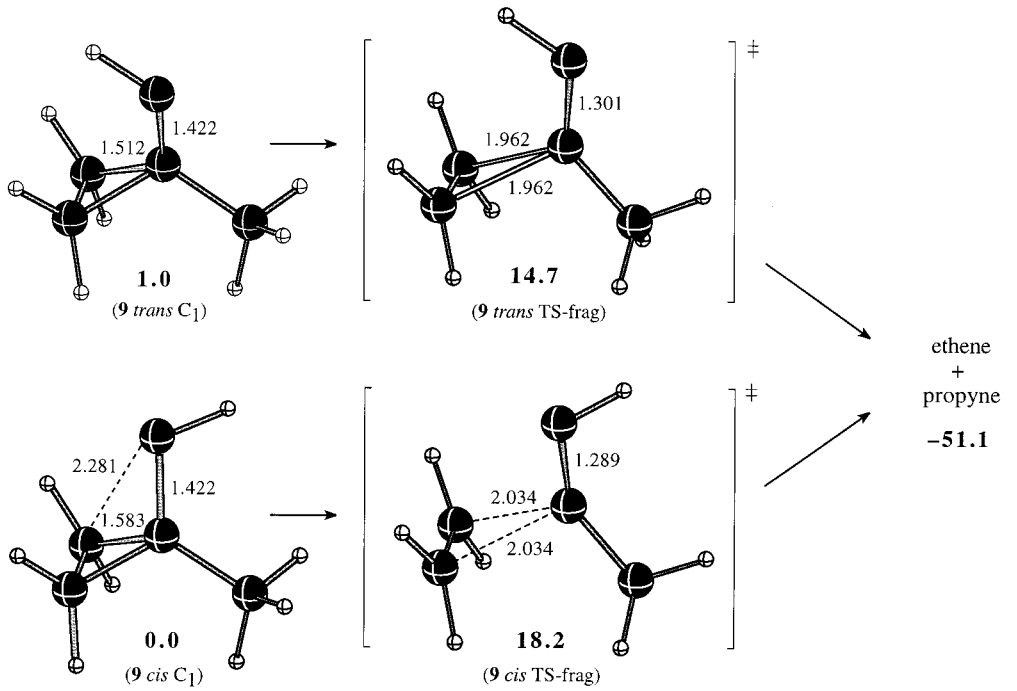


Figure 5. Intermediates and transition structures for fragmentation in 1-methylcyclopropylcarbene (**9**). The free energies at 298 K (relative to **9** *cis* C_1) are depicted in bold. Some bond distances are listed in Å.

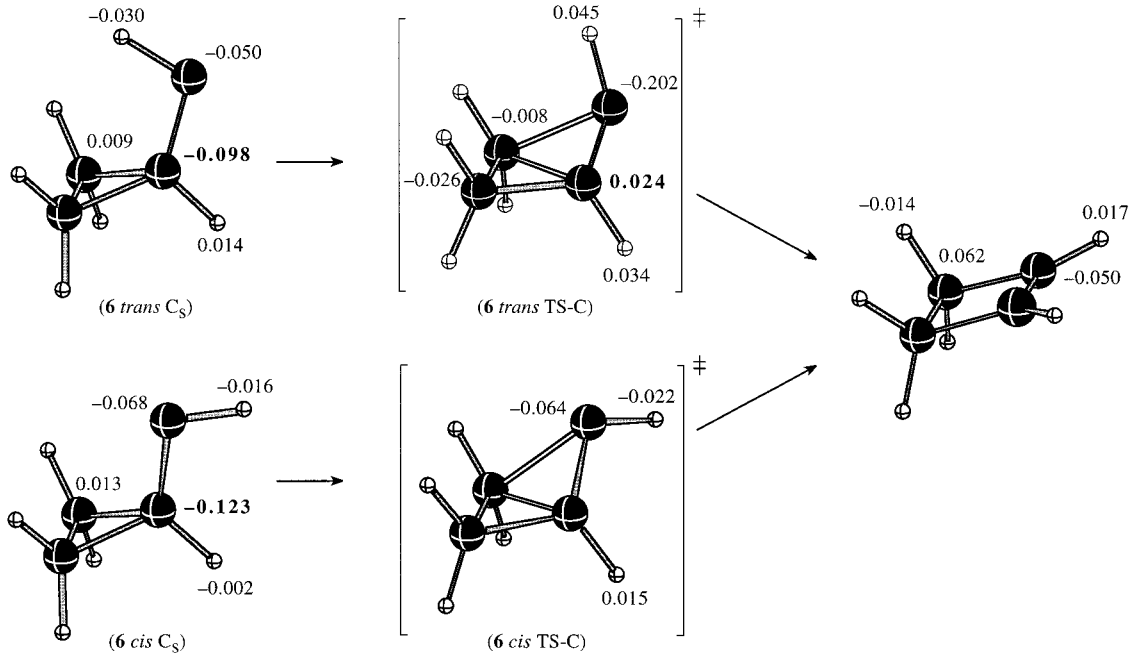


Figure 6. Atomic charges at the AIM level (in e) for the intermediates and transition structures for C-migration in cyclopropylcarbene (**6**). The wave functions are from BH&HLYP/6-311++G(d,p)//BH&HLYP/6-31G(d) calculations.

Experimental Methods

General Information. All reactions were conducted in flame-dried glassware under an argon atmosphere. For trapping experiments, 2,3-dimethyl-2-butene was distilled prior to use, and all other reagents were used without further purification. Air-sensitive solutions were transferred via oven-dried syringe needles or an oven-dried cannula under positive pressure of argon. Removal of volatiles by rotary evaporation was conducted using an ambient temperature water bath and water aspirator pressure. FT NMR spectra were taken in $CDCl_3$. Proton spectra were recorded at 250 MHz, and ^{13}C NMR spectra were recorded at 62.5 MHz. In both cases, residual $CHCl_3$ served as the internal standard with proton spectra referenced to δ 7.26 ppm and carbon spectra referenced to δ 77.0 ppm (center of triplet). Silica gel column chromatography was done using 230−400 mesh silica gel. Thin-layer chromatography analyses were done on glass plates coated with 250 μm of silica gel. Plates were visualized with vanillin stain, UV light, or iodine vapor. In cases where a product was purified by silica gel column chromatography, the R_f value given is that of the compound using the eluant employed for purification. Boiling and melting points are uncorrected. High-resolution mass spectra were obtained in EI mode. FT IR spectra were taken between NaCl plates as neat liquids (thin film), and for compound **22**, as a CCl_4 solution. GC/MS were taken at an ionizing voltage of 70 eV, and an HP-5MS column 5% in phenyl methyl siloxane with dimensions of 30 m × 250

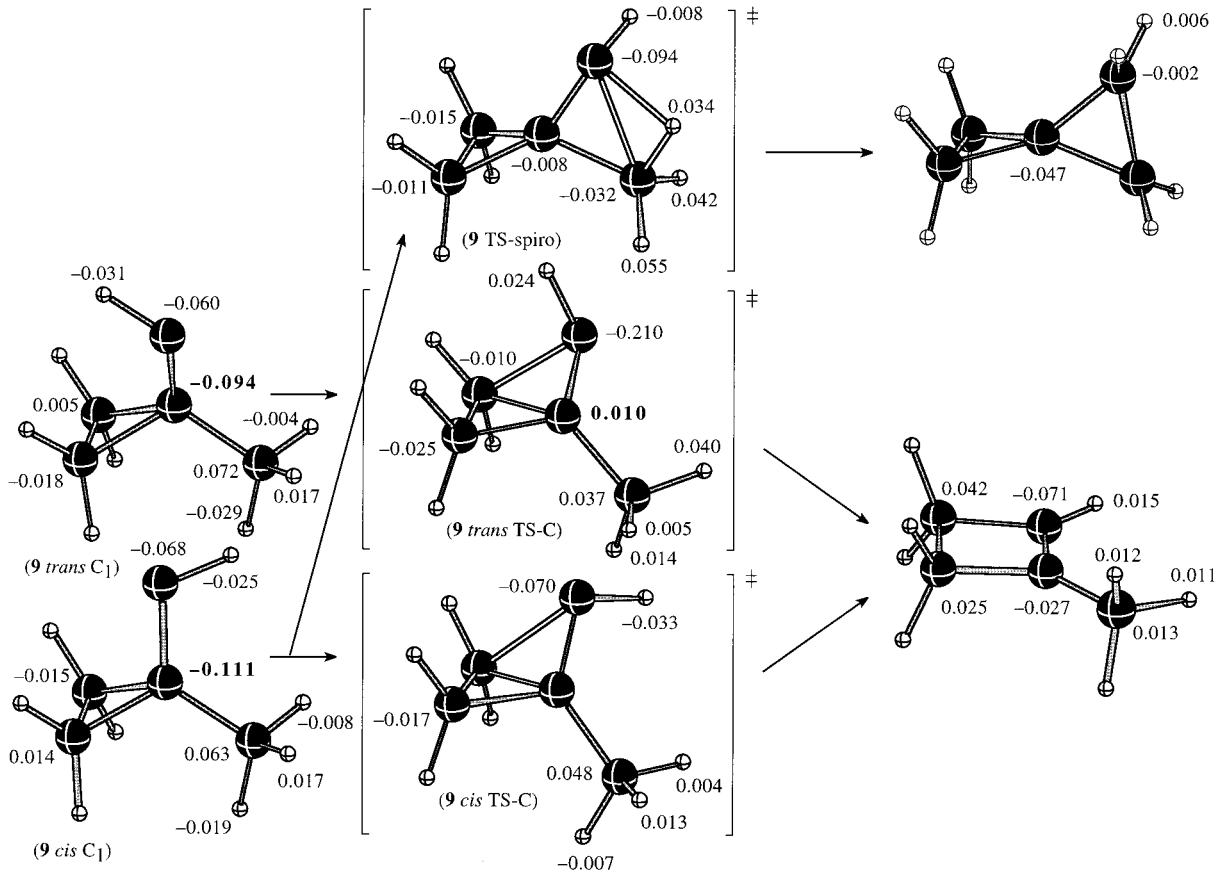


Figure 7. Atomic charges at the AIM level (in e) for the intermediates and transition structures for C-migration in 1-methylcyclopropylcarbene (**9**). The wave functions are from BH&HLYP/6-311++G(d,p)//BH&HLYP/6-31G(d) calculations.

μm × 0.25 μm was used. The following parameters were used: injector temperature, 250° C; initial temperature, 50° C; initial hold time, 3.00 min; rate, 15 °C/min; final temperature, 250 °C; detector temperature: 280 °C; total run time: 31.33 min. Where mass spectral data is given, the peak value is immediately followed by its relative abundance in parentheses.

***endo*-1-(2-Propenyl)-1a,9b-dihydrocyclopropa[*l*]phenanthrene (12).** A magnetically stirred solution of 2-bromopropene (7.6 g, 63 mmol) in ether (250 mL) was cooled in a dry ice/acetone bath, and treated with *tert*-butyllithium (75 mL, 1.7 M in pentane, 128 mmol). After the addition was complete, the solution was warmed to 0 °C over 30 min, cooled to −70 °C, and then transferred by cannula to a precooled slurry (−65 to −60 °C) of copper(I) iodide (6.1 g, 32 mmol) in ether (100 mL). After stirring for another 30 min at −65 °C, the cuprate reagent was treated with a solution of **11** (2.2 g, 6 mmol) in tetrahydrofuran (20 mL). The reaction mixture was then allowed to warm gradually to −20 °C, over 1 h, and quenched by careful addition of a saturated aqueous solution of ammonium chloride (40 mL). After stirring overnight, the two layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated ammonium hydroxide (until the washings were no longer blue), water, and brine. Removal of solvent followed by purification by column chromatography (silica gel/hexanes) gave **12** (243 mg, 17%): mp 141−142 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (m, 2 H), 7.42 (m, 2 H), 7.24 (m, 2 H), 4.46 (s, 1 H), 3.89 (s, 1 H), 2.81 (d, J = 9 Hz, 2 H), 2.02 (t, J = 9 Hz, 1 H), 1.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.1, 132.9, 131.7, 130.0, 127.2, 126.0, 122.4, 116.5, 24.4, 22.1, 21.6. HRMS (EI) *m*/*z* calculated for $C_{18}H_{16}$ (M^+) 232.1252, found 232.1238.

***endo*-1-(1-Methylcyclopropyl)-1a,9b-dihydrocyclopropa[*l*]phenanthrene (13).** To a magnetically stirred, ice-cold solution of **12** (0.31 g, 1.3 mmol) and diiodomethane (1.1 g, 4.1 mmol) in benzene (15 mL) was added, over 5 min, diethyl zinc (4 mL, 1 M in hexanes, 4 mmol). The cooling bath was removed 30 min after the addition was complete and the reaction mixture refluxed overnight. After quenching with saturated aqueous ammonium chloride, the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with saturated aqueous ammonium chloride and brine. The solvent was then evaporated and the residue purified by column chromatography (silica gel/hexanes) to afford **13** (0.19 g, 58%): mp 147−149 °C; IR (KBr) 3061, 3008, 2948, 1478, 1432, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8 Hz, 2 H), 7.37 (d, J = 7 Hz, 2 H), 7.28 to 7.21 (m, 4 H), 2.60 (d, J = 9 Hz, 2 H), 1.68 (t, J = 9 Hz, 1 H), 0.6 (s, 3 H), −0.13 (m, 2 H), −0.32 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 134.0, 132.6, 131.3, 128.1, 126.8, 123.3, 24.8, 24.6, 21.0, 13.4, 12.8. HRMS (EI) *m*/*z* calculated for $C_{19}H_{18}$ (M^+) 246.1408, found 246.1405.

***exo*-1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthrene-1-carboxylic Acid (14).** A magnetically stirred solution of the ethyl ester (1.9 g, 7 mmol) and potassium hydroxide (2.5 g of 85% purity, 38 mmol) in ethanol (25 mL) and water (5 mL) was refluxed overnight. After most of the ethanol was removed at the rotary evaporator, the residue was diluted with water and washed with dichloromethane. The aqueous layer was acidified with concentrated HCl and extracted with dichloromethane. The dichloromethane extracts were washed with water and brine and freed of solvent to obtain a crude solid. Recrystallization from 1,4-dioxane furnished the acid **14** (1.3 g, 76%): mp 261−262 °C (lit.[29] 257.5−258 °C); ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8 Hz, 2 H), 7.51 (d, J = 7 Hz, 2 H), 7.37 to 7. 30 (m, 4 H), 3.30 (d, J = 4 Hz, 2 H), 1.09 (t, J = 4 Hz, 1 H), presumably due to rapid exchange, the carboxylic acid

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P.

proton was not detected; ^{13}C NMR ($CDCl_3$) δ 179.8, 132.5, 129.8, 129.6, 128.0, 127.3, 123.3, 30.5, 26.2.

***exo*-1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthrene-1-ethanone (15).** To a magnetically stirred solution of **14** (1.0 g, 4 mmol) in tetrahydrofuran (25 mL) was added methyllithium (8 mL, 1.4 M in ether, 11 mmol) at room temperature. The reaction was stirred overnight and quenched carefully with water, and the two layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine. Drying over anhydrous sodium sulfate, followed by removal of solvent, gave a crude material that was chromatographed over silica gel with ethyl acetate/hexanes (1:4) as the eluent. Thus 378 mg (38% yield) of **15** were obtained: mp 185−186 °C; ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8 Hz, 2 H), 7.47 (d, J = 6 Hz, 2 H), 7.36 to 7.29 (m, 4 H), 3.28 (d, J = 4 Hz, 2 H), 2.29 (s, 3 H), 1.39 (t, J = 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 208.0, 133.3, 129.7, 129.6, 128.0, 127.1, 123.2, 34.2, 32.8, 31.4. HRMS (EI) *m*/*z* calculated for $C_{17}H_{14}O$ (M^+) 234.1045, found 234.1046.

***exo*-1-(2-Propenyl)-1a,9b-dihydrocyclopropa[*l*]phenanthrene (16).** To a mixture of methyltriphenylphosphonium bromide (772 mg, 2 mmol) and sodium amide (119 mg, 3 mmol) was added tetrahydrofuran (10 mL), and the resulting slurry was stirred for 45 min. Then, the ketone **15** (319 mg, 1 mmol) was added as a solid in one portion. Stirring was continued for another 7 h and the reaction mixture quenched with aqueous sodium hydroxide (7.5 mL). The two layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and brine, dried over sodium sulfate, and freed of solvent. Column chromatography of the residue (silica gel/hexanes) gave **16** (209 mg, 66%): mp 126−127 °C; ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 2 H), 7.41 (m, 2 H), 7.26 (m, 4 H), 4.78 (br s, 1 H), 4.73 (br s, 1 H), 2.71 (d, J = 4 Hz, 2 H), 1.79 (s, 3 H), 0.93 (t, J = 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 144.5, 135.2, 129.4, 129.1, 127.7, 126.2, 123.1, 108.5, 32.5, 27.5, 20.9. HRMS (EI) *m*/*z* calculated for $C_{18}H_{16}$ (M^+) 232.1252, found 232.1233.

***exo*-1-(1-Methylcyclopropyl)-1a,9b-dihydrocyclopropa[*l*]phenanthrene (17).** A solution of **16** (342 mg, 1.5 mmol) and diiodomethane (1.3 g, 5.0 mmol) in benzene (15 mL) was treated with diethylzinc (4.5 mL, 1.0 M in hexanes, 4.5 mmol). Quenching and work up afforded 224 mg (62%) of the product **17**: mp 126−127 °C; IR (KBr) 3055, 3015, 2988, 2948, 1591, 1478, 1000, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.94 (m, 2 H), 7.34 (m, 2 H), 7.22 (m, 4 H), 2.22 (d, J = 4 Hz, 2 H), 1.19 (s, 3 H), 0.52 (t, J = 4 Hz, 1 H), 0.42 (m, 2 H), 0.31 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 136.0, 129.4, 128.7, 127.6, 125.8, 123.1, 31.9, 24.4, 24.1, 15.9, 10.9. HRMS (EI) *m*/*z* calculated for $C_{19}H_{18}$ (M^+) 246.1408, found 246.1409.

Ethyl-2,2,3,3-tetramethyl Cyclopropanecarboxylate (21). To a mixture of 50.0 g (0.595 mol) 2,3-dimethyl-2-butene and 0.038 g of $Rh(OAc)_4$ was added dropwise over 2.5 h 9.7 g (0.085 mol) of ethyl diazoacetate. The mixture became slightly warm, and gas evolution was observed during the addition of the ethyl diazoacetate. After stirring for 12 h at ambient temperature, excess 2,3-dimethyl-2-butene was removed by distillation, and fractional vacuum distillation of the residue gave 7.7 g of **21** as a clear, colorless liquid. The sample contained about 3% diethyl fumarate and maleate, but was used in the next step without further purification: IR 2983, 2949, 1727, 1452, 1414, 1382, 1331, 1191, 1150, 1117, 1063 cm^{-1}; GC/MS 170 (1.1), 155 (62.6), 125 (37.9), 109 (22.2), 97 (100.0), 83 (22.8), 69 (17.5), 55 (54.5), 41 (18.2); H NMR δ 1.10 (s, 6H), 1.15 (s, 1H), 1.18 (t, 3H), 1.20 (s, 6H), 4.05 (q, 2H).

2,2,3,3-Tetramethyl Cyclopropanecarboxylic Acid (22). To 8.0 g of KOH in 40 mL of MeOH was added 5.0 g (29.4 mmol) of **21**. The solution was refluxed for 3 h after which time the mixture was cooled to ambient temperature, concentrated to a volume of approximately 20 mL by rotary evaporation, and poured into 200 mL of water. To this solution was carefully added concentrated HCl in small portions until the solution pH was ~1. The solution was filtered, and the filter cake was washed with two 30-mL portions of water. Recrystallization from 30% aqueous MeOH, gave 3.45 g of **22** (mp = 121−124 °C): IR 3538, 2952, 1741, 1688, 1455, 1397, 1381, 1326, 1231, 1185, 1165, 1112 cm^{-1}; GC/MS 142 (0.5), 127 (100.0), 109 (28.4), 97 (69.7), 81 (37.9), 69 (23.6), 55 (56.8), 41 (24.9); ^{1}H NMR δ 1.20 (s, 6H), 1.26 (s, 6H), the methine hydrogen could not be resolved because it overlaps the methyl group signals; ^{13}C NMR δ 16.60, 23.59, 31.38, 35.81, 178.87.

2,2,3,3-Tetramethylcyclopropyl Methyl Ketone (23). To a solution of 1.0 g (7.04 mmol) of **22** in 53 mL of THF cooled to −5° C was added over 1 min 15.0 mL of 1.4 M MeLi in Et_2O (21.0 mmol). After stirring for 2 h at −5° C, 21.0 g of TMSCl was added over 2 min. The solution was then warmed to ambient temperature, and 45 mL of 1.0 M HCl was added over 5 min (CAUTION-EXOTHERMIC). After stirring for 30 min, the solution was poured into 200 mL of water and extracted with three 80-mL portions of Et_2O. The total Et_2O solution was washed with 20 mL of water, dried over Na_2SO_4, and concentrated by rotary evaporation. Silica gel column chromatography using 9:1 pentane/Et_2O as the eluant yielded 0.702 g of **23** as a clear, colorless liquid (R_f = 0.62): IR 2974, 2874, 1694, 1456, 1375, 1310, 1261, 1216, 1099 cm^{-1}; GC/MS 125 (78.9 M^+ − C=O), 97 (100.0), 83 (9.8), 69 (26.5), 55 (85.9), 43 (43.3); ^{1}H NMR δ 1.18 (s, 6H), 1.22 (s, 6H), 1.51 (s, 1H), 2.18 (s, 3H).

1-Isopropenyl-2,2,3,3-tetramethylcyclopropane (24). To 1.36 g (3.81 mmol) of methyltriphenylphosphonium bromide suspended in 13.0 mL THF was added dropwise 2.4 mL of 1.6 M *n*-BuLi in hexanes (3.84 mmol) over 5 min. After 3 h at ambient temperature, 0.400 g (2.86 mmol) of **23** in 3.0 mL of THF was added over one minute. After 1 h at ambient temperature, the solution was stirred at 50 °C for 10 h. The solution was poured into 50 mL of water and extracted with three 40-mL portions of pentane. The total pentane solution was washed with 20 mL of water and dried over Na_2SO_4. Owing to the volatility of the product, the pentane was removed by fractional distillation at ambient pressure. Passage of the residue through a short column of silica gel using pentane as the eluant followed by removal of the pentane by fractional distillation at ambient pressure gave 0.180 g of **24** as a clear, colorless liquid. The compound **24** elutes on the solvent front: IR 3090, 2940, 1645, 1451, 1377, 1251, 1122, 1055; GC/MS 138 (1.1), 123 (100.0), 95 (14.3), 81 (62.7), 67 (20.3), 55 (18.4), 41 (19.9).

1-(1′-Methylcyclopropyl)-2,2,3,3-tetramethylcyclopropane (25). To a solution of 0.100 g (0.73 mmol) of **24** in 10.0 mL of Et_2O was added 3.6 mL of 1.0 M Et_2Zn in hexanes (3.63 mmol). After stirring for 5 min, 1.02 g (4.80 mmol) CH_2I_2 was added over 10 min (CAUTION-EXOTHERMIC). After 30 min at ambient temperature, the solution was stirred at 55 °C for 12 h and cooled to ambient temperature, and 20.0 mL of 1.0 M HCl was added over 20 min (CAUTION-EXOTHERMIC). The layers were separated, and the aqueous layer was extracted with two 20-mL portions of pentane. The total organic solution was washed with 10 mL of 1.0 M HCl and 10 mL of water, and dried over Na_2SO_4. The solution was concentrated by rotary evaporation at 0° C and at 200−300 Torr. Passage of the residue through a short column of silica gel using pentane as the eluant followed by removal of the pentane by rotary evaporation at 0° C and at 200−300 Torr gave 0.053 g of **25** as a clear, colorless liquid. The compound **25** elutes on the solvent front: IR 2957, 2925, 2870, 1457, 1377, 1012 cm^{-1}; GC/MS 152 (0.7), 137 (56.4), 123 (8.5), 109 (24.8), 95 (100.0), 81 (35.8), 67 (38.8), 55 (29.5), 41 (30.7); ^{1}H NMR δ 0.17−0.21 (2H), 0.52−0.58 (m, 3H), 1.03 (s, 6H), 1.06 (s, 9H). HRMS calculated 152.1565, found 152.1564(6).

Photolysis of the Precursor 13 in 2,3-Dimethyl-2-butene. In a quartz cuvette was placed 2.0 mg (0.008 mmol) of **13** dissolved in 2.0 mL of 2,3-dimethyl-2-butene. The cuvette was capped with a rubber septum, the edges of which were sealed with Parafilm, and the solution was purged by bubbling argon through the solution for 3 min. During the purge the cuvette was wrapped in foil. Following the purge the solution

Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

was irradiated with 300 nm light (Rayonet) for 24 h at 5° C. Analysis of the solution by GC/MS showed phenanthrene and **25** were present in ratio of approximately 2:1.

Photolysis of the Precursor 17 in 2,3-Dimethyl-2-butene. In a quartz cuvette was placed 2.0 mg (0.008 mmol) of **17** dissolved in 2.0 mL of 2,3-dimethyl-2-butene. The cuvette was capped with a rubber septum, the edges of which were sealed with Parafilm, and the solution was purged by bubbling argon through the solution for 3 min. During the purge the cuvette was wrapped in foil. Following the purge the solution was irradiated with 300 nm light (Rayonet) for 24 h at 10° C. Analysis of the solution by GC/MS showed phenanthrene and **25** were present in ratio of approximately 2:1.

Photolysis of the *exo* Precursor 17 to 1-Methylcyclopropylcarbene in Benzene-d_6. To an NMR tube was added approximately 0.5 mg (0.002 mmol) of **17** in 1.0 mL of benzene d6 (99.6% atom-*d*, Cambridge Isotope Laboratories). The solution was degassed by purging with argon for 3 min and then irradiated with 300 nm light (Rayonet) at 5 °C for 8 h. Following photolysis analysis by ^{1}H NMR showed that phenanthrene was present as evident by the presence of a new singlet at δ 7.5 ppm and that 1-methylcyclobutene and methylenecyclobutane were also present.

Computational Methods

All calculations were performed with Gaussian 94.[29] The 6-31G(d) and 6-311++G(d,p) basis sets were utilized with 6 D Cartesian functions.[30] All geometries were fully optimized at the Becke half-and-half exchange functional with the Lee−Yang−Parr correlational functional (BH&HLYP) as implemented in Gaussian 94. All minima and transition states were verified via vibrational frequency calculations and possessed the correct number of real and imaginary vibrational frequencies. All transition states were "connected" to their respective minima via careful optimization after displacement along the normal mode for the imaginary vibrational frequency.

The calculated zero-point vibrational energies were scaled by 0.9806.[31] Thermal corrections to 298 K (1 atm pressure) were utilized as generated by Gaussian 94 (but without any scaling of the vibrational frequencies). The NPA results were obtained with Gaussian 94, but the AIM charges were generated with AIMALL.[32]

Acknowledgment. We thank Professor Maitland Jones, Jr., for supporting portions of this work through a grant from the National Science Foundation (Princeton: NSF CHE-9322579). C.M.H. acknowledges support from the National Science Foundation (OSU: CHE-9733457), the Ohio Supercomputer Center, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J.R.S. acknowledges support from an Ohio State University Postdoctoral Fellowship. C.M.H. thanks Kenneth B. Wiberg (Yale University) for allowing us access to the AIMALL program on his computers, and Matthew S. Platz (The Ohio State University) for many helpful discussions.

Supporting Information Available: Analysis of the lifetime measurement for different concentrations of TME, figures for charge changes evaluated with the NPA method, and NMR, IR, and GC/MS spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO9903454

(30) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(31) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(32) Keith, T. A. *AIMALL*, Yale University, 1996.