

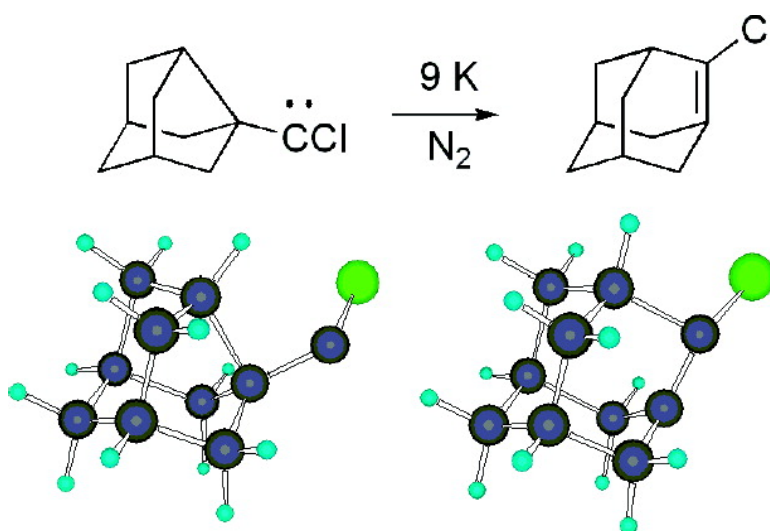
Communication

**Carbon Tunneling in the Ring Expansion of Noradamantylchlorocarbene**

Robert A. Moss, Ronald R. Sauers, Robert S. Sheridan, Jingzhi Tian, and Peter S. Zuev

*J. Am. Chem. Soc.*, **2004**, 126 (33), 10196-10197 • DOI: 10.1021/ja0488939 • Publication Date (Web): 31 July 2004

Downloaded from <http://pubs.acs.org> on April 1, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



**ACS Publications**  
 High quality. High impact.

## Carbon Tunneling in the Ring Expansion of Noradamantylchlorocarbene

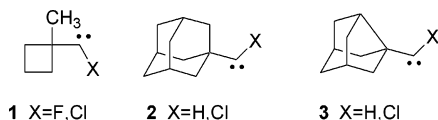
Robert A. Moss,<sup>\*,†</sup> Ronald R. Sauers,<sup>\*,†</sup> Robert S. Sheridan,<sup>\*,‡</sup> Jingzhi Tian,<sup>†</sup> and Peter S. Zuev<sup>†</sup>

*Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and Department of Chemistry, University of Nevada, Reno, Nevada 89557*

Received February 26, 2004; E-mail: rss@chem.unr.edu; moss@rutchem.rutgers.edu

Three themes of current interest converge in this report: direct observation of carbenic rearrangements, the chemistry of highly strained alkenes, and experimental detection of heavy-atom quantum mechanical tunneling (QMT).

Experimental demonstrations of heavy-atom tunneling are rare.<sup>1</sup> A well-established case is the automerization of cyclobutadiene.<sup>2</sup> One might anticipate that carbenic rearrangements, which feature many 1,2-C migrations,<sup>3</sup> would furnish other examples of heavy-atom tunneling. To observe carbon tunneling directly in a carbenic rearrangement we require a carbene reactive enough to rearrange in a cryogenic matrix, but not so reactive that its lifetime is too short for visualization. Carbon QMT was recently shown to be central to the ring expansion of 1-methylcyclobutylfluorocarbene (**1-F**) to 1-fluoro-2-methylcyclopentene.<sup>4,5</sup> At 8 K in Ar or N<sub>2</sub> matrices, **1-F** was observed to ring expand via C-tunneling 10<sup>152</sup> times faster than it could surmount the computed barrier of 6.45 kcal/mol.<sup>4</sup> Ring expansion of **1-Cl**, with a 3.1 kcal/mol barrier, was also computed to involve tunneling, but it rearranged too quickly (even at 8 K) to be observed.<sup>4</sup>



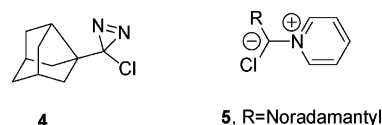
Neither adamantylcarbene (**2-H**) nor noradamantylcarbene (**3-H**) are observed upon photolysis of diazirine precursors in Ar matrices at 14 K.<sup>6</sup> Instead, one finds the ring-expanded product alkenes homoadamantene (from **2-H**) and adamantene (from **3-H**). In solution, **2-H** can be captured as the pyridinium ylide or (in low yields) by C–H or N–H insertion reactions.<sup>6a</sup> However, **3-H** cannot be intercepted by a variety of trapping agents;<sup>6</sup> only products derived from adamantene (or protoadamantene) are found. Either **3-H** rearranges too quickly to be trapped ( $\tau < 50$  ps), or adamantene is formed directly from excited diazirine. These results accord with B3LYP/6-31G\* computed activation energies for the ring expansions of **3-H** (0.35 kcal/mol) and **2-H** (6.06 kcal/mol).<sup>6</sup>

“Elusive carbenes” can be stabilized by halogen substitution.<sup>7</sup> Indeed the computed energy barriers to the ring expansions of **3-Cl** and **2-Cl** increase to 5.3 and 14.5 kcal/mol, respectively. These carbenes should therefore be persistent in cryogenic matrices. In contrast to **2-H**, **2-Cl** can be observed in an Ar matrix at 10 K, where it is stable for at least a week,<sup>8</sup> but readily yields 2-chloro-homoadamantene on irradiation.<sup>8</sup> We may now ask, if carbene **3-H** will be similarly “tamed” by Cl substitution, can **3-Cl** be observed? And will it decay by a normal activated process or via QMT?

Here, we report that noradamantylchlorocarbene (**3-Cl**) can be observed in low-temperature matrices, and we provide evidence for C-tunneling in its subsequent ring expansion. Carbene **3-Cl** is

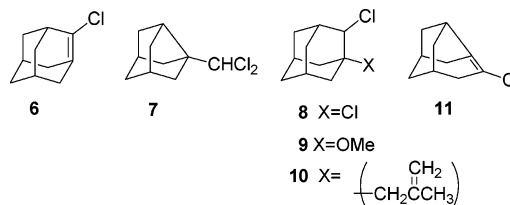
only the second carbene for which heavy-atom QMT has been observed directly and the first chlorocarbene example.

Noradamantylchlorodiazirine **4** was synthesized by conventional Graham oxidation of the corresponding amidine hydrochloride.<sup>9–11</sup> Laser flash photolysis (LFP)<sup>12</sup> at 351 nm of diazirine **4** ( $A_{347} = 2.5$ ) in 1,2-dichloroethane (DCE) containing 2–20 mM pyridine, gave ylide **5**,  $\lambda_{\max} \approx 372$  nm (see Figure S-1 in the Supporting Information). A correlation<sup>13</sup> of  $k_{\text{obs}}$  for the formation of **5** with



the concentration of pyridine was linear (Figure S-2), affording  $k_y = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the rate constant of ylide formation, and  $k_o = 5.1 \times 10^7 \text{ s}^{-1}$  for those processes that destroy carbene **3-Cl** at [pyr] = 0. We identify  $k_o$  with the ring expansion of **3-Cl** to 2-chloroadamantene (**6**); see below. The lifetime of **3-Cl** in DCE,  $(1/k_o) \approx 20$  ns, is at least 400 times greater than that of **3-H** (based on  $\tau < 50$  ps<sup>6a</sup>). The chlorine substitution that “converts” **3-H** to **3-Cl** greatly extends the carbene’s lifetime in solution.

Carbene **3-Cl** could also be trapped by a saturated solution of HCl in DCE, giving dichloride **7** accompanied by dichloride **8**, the addition product of HCl to chloroadamantene **6** (**7:8** = 1:1.9).<sup>14</sup> Attempted trapping of **3-Cl** in solution with MeOH or isobutene, however, led only to products derived from **6**, viz. **9** and **10**.<sup>14</sup> Formation of the apparent ene addition product **10** dramatically illustrates the high reactivity of anti-Bredt olefin **6**.<sup>15</sup>



Irradiation of diazirine **4** in a N<sub>2</sub> matrix (ca. 1:800) at 334 nm for 20 h at 8 K transformed its IR and UV/vis spectra to those of a new species with strongest absorptions at 1030 and 741 cm<sup>-1</sup> in the IR (Figure S-3) and a broad band in the UV/vis centered at 520 nm. This product was assigned to carbene **3-Cl** based on good congruence with spectra calculated at the B3LYP (Figure S-3) and TD-B3LYP (500 nm) 6-31+G\*\* levels. The experimental IR spectra fit best a carbene conformation with Cl aligned approximately 90° to the C–CH bond. Carbene **3-Cl** could be trapped by HCl in a HCl-doped matrix warmed to 30 K, affording dichloride **7**.

Subsequent irradiation of the matrix containing **3-Cl** at 546 nm for 6 h caused complete disappearance of the IR peaks of the carbene and the appearance of a new set of IR bands, with a

<sup>†</sup> Rutgers University.

<sup>‡</sup> University of Nevada, Reno.

particularly strong absorption at 584  $\text{cm}^{-1}$ . The UV/vis of **3-Cl** was similarly replaced by a strong absorption at 300–430 nm ( $\lambda_{\text{max}}$  350 nm). On the basis of the excellent fit with B3LYP (Figure S-3) and TD-B3LYP (350 nm) 6-31+G\*\* calculated spectra, this photoproduct is assigned as 2-chloroadamant-1-ene (**6**). Small amounts of alternative ring-expanded product **11** are impossible to rule out, however.<sup>16</sup> The highly strained bridgehead alkene was remarkably reactive; annealing in a  $\text{N}_2$  matrix doped with 2% HCl (32 K, 5 min) resulted in rapid disappearance of the IR bands of **6** and the appearance of bands of **8**, confirmed by comparison to authentic product from the solution reaction above.

Surprisingly, in the absence of light, matrix-isolated carbene **3-Cl** still slowly rearranged to **6**. Thus, over 3 days in the dark at 9 K in  $\text{N}_2$ , ca. 15% of **3-Cl** converted to **6**, as judged by the evolution of the IR spectra. As commonly observed in low-temperature matrices, first-order kinetics plots of the rearrangement of **3-Cl** to **6** were significantly curved; this has been attributed to distributions of diverse matrix sites with different reaction rates. However, it could be discerned that rates of formation of **6** were a bit faster in  $\text{N}_2$  at higher temperatures, e.g. 35% conversion of **3-Cl** in 3 d at 23 K. Rates were more rapid yet in Ar matrices, with ca. 50% rearrangement over 3 d at 23 K. (Figure S-4 shows kinetics plots at various temperatures.)<sup>17</sup>

As described above, heavy-atom QMT has been demonstrated in the low-temperature ring expansion of matrix-isolated 1-methylcyclobutylfluorocarbene (**1-F**).<sup>4</sup> Confirmed by calculations utilizing canonical variational theory with the small-curvature tunneling approximation (CVT/SCT), the tunneling process was signified by (1) measurable reaction rates at 8 K despite a calculated classical barrier of ca. 6 kcal/mol (exhibiting rates ca.  $10^{152}$  times faster than predicted classically); (2) relatively small nuclear displacements predicted for the tunneling event itself, where the maximum distance traveled by any of the carbons was 0.44 Å; (3) only relatively minor rate accelerations observed on warming samples to 25 K. On the basis of the close similarity to the carbene **1-F** ring expansion, we propose that rearrangement of **3-Cl** to **6** also proceeds via heavy-atom tunneling. The barrier for the rearrangement of **3-Cl** is predicted to be 5.3 kcal/mol at the B3LYP/6-31G\* level (vs 12.7 kcal/mol for rearrangement to **11**; computed transition-state geometries appear in Figure S-5). Assuming<sup>3</sup> that  $A \approx 10^{10} \text{ s}^{-1}$ , we estimate that  $k \approx 1.3 \times 10^{-118} \text{ s}^{-1}$  at 9 K for the classically activated ring expansion of **3-Cl**. From the first 10% of the carbene's observed decay in the  $\text{N}_2$  matrix at 9 K, we obtain  $k \approx 2.3 \times 10^{-7} \text{ s}^{-1}$ . Thus, we attribute this acceleration of  $\sim 10^{111}$  to QMT.

The nuclear displacements during the putative tunneling event can be approximated by comparison of the geometry of the starting carbene to that calculated for the product at the same energy along the intrinsic reaction pathway connecting **3-Cl** and **6**. The longest distance traversed by any of the carbons is only 0.44 Å for the carbenic center, relative to the molecular frame of reference (see Figure S-6). The other carbons in **3-Cl** move 0.08 to 0.43 Å (for the adjacent bridgehead atom), the hydrogens move 0.14 to 0.33 Å, and the Cl moves only 0.20 Å in the process. Finally, the small rate acceleration in the transformation of **3-Cl** to **6** when the absolute temperature was approximately tripled from 8 to 23 K is inconsistent with a classical thermally activated process. As was proposed for **1-F**,<sup>4</sup> we attribute these minor rate increases to matrix softening as temperature is raised.

Adamantylchlorocarbene **2-Cl** shows no evidence for tunneling at low temperature,<sup>8</sup> consistent with the calculated higher barrier

of 14.5 kcal/mol. Moreover, similar analysis of the geometric changes along the intrinsic reaction path suggests that somewhat larger nuclear displacement is required for rearrangement (e.g. 0.55 Å for the carbenic C). Both factors may contribute to the lack of low-temperature tunneling.

In summary, we believe that our results represent the first direct observation of heavy-atom quantum mechanical tunneling in a singlet chlorocarbene rearrangement. Our prior failure to detect 1-methylchlorocyclobutylcarbene (**1-Cl**) in low-temperature matrices was attributed to rapid tunneling-facilitated ring expansion; CVT/SCT calculations predicted a rearrangement rate constant of ca.  $10^4 \text{ s}^{-1}$ .<sup>4,18</sup> The lower exothermicity in **3-Cl** (20.5 vs 85.2 kcal/mol **1-Cl**), however, raises the barrier for the 1,2-carbon shift to an energy more comparable with that of the observable fluorocarbene **1-F**, thus slowing the tunneling rate to a measurable range. These results strengthen the case that heavy-atom tunneling may be more prevalent than previously appreciated, and provide valuable guidance for understanding these nonclassical reactions.

**Acknowledgment.** We are grateful to the National Science Foundation (Rutgers and Nevada) and to the donors of the Petroleum Research Fund administered by the American Chemical Society (Nevada) for financial support. We thank the National Computational Alliance (Grant CHE 030060) for partial support of this work on the IBM pSeries 690. This paper is dedicated to the memory of Orville L. Chapman.

**Supporting Information Available:** Experimental and computational details, Figures S-1–S-6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Brief review: McMahon, R. J. *Science* **2003**, *299*, 833.
- (2) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700. (b) Orendt, A. M.; Arnold, B. R.; Radziszewski, J. G.; Facelli, J. C.; Malsch, K. D.; Strub, H.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 2648. (c) Arnold, B. R.; Radziszewski, J. G.; Campion, A.; Perry, S. S.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 692.
- (3) Review: Merrer, D. C.; Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Amsterdam: Elsevier: 2001; Vol. 3, pp 53f.
- (4) Zuev, P. S.; Sheridan, R. S.; Albu, T. V.; Truhlar, D. G.; Hrovat, D. A.; Borden, W. T. *Science* **2003**, *299*, 867.
- (5) In contrast, calculations indicate that carbon tunneling is unimportant in ring expansions of cyclopropylhalocarbenes. See: Albu, T. V.; Lynch, B. J.; Truhlar, D. G.; Goren, A. C.; Hrovat, D. A.; Borden, W. T.; Moss, R. A. *J. Phys. Chem. A* **2002**, *106*, 5323.
- (6) (a) Tae, E. L.; Ventre, C.; Zhu, Z.; Likhovorik, I.; Ford, F.; Tippmann, E.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 10146. (b) Tae, E. L.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 3803.
- (7) Moss, R. A.; Fantina, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 6788.
- (8) Yao, G.; Rempala, P.; Bashore, C.; Sheridan, R. S. *Tetrahedron Lett.* **1999**, *40*, 17, and unpublished work.
- (9) Details of synthetic procedures and characterizations appear in the Supporting Information.
- (10) Gielen, H.; Alonso-Alija, C.; Hendrix, M.; Niewöhner, U.; Schauss, D. *Tetrahedron Lett.* **2002**, *43*, 419.
- (11) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.
- (12) For a description of the LFP installation, see: Moss, R. A.; Johnson, L. A.; Merrer, D. C.; Lee, G. E., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 5940.
- (13) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.
- (14) Products were characterized by GC–MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. All spectra are summarized in the Supporting Information.
- (15) Similar ene additions to strained alkenes have been observed previously: Ströter, T.; Jarosch, O.; Szeimies, G. *Chem. Eur. J.* **1999**, *5*, 1422.
- (16) Irradiations of matrices containing chloroadamantene **6** at 350 nm gave a new product tentatively identified as **11** based on analogy to the reported photochemistry of adamantene.<sup>6</sup>
- (17) Only traces of adamantene **6** are observed after irradiation of **4**. We estimate that only ca. 50–60% of carbene might react over a week under best conditions, due to matrix inhomogeneities.
- (18) It is possible that the failure to observe carbenes **1-H** and **2-H** in cryogenic matrices<sup>6</sup> is also due to rapid rearrangement via tunneling.

JA0488939