The mass spectrum of **1** (electron impact, 70 eV, probe temperature 190–240 °C) provides evidence for monomeric and dimeric imido complexes in the CVD process. The highest observed mass envelope was centered at 365 (9.1% of 210 base peak), which is proposed to originate from loss of a methyl radical from the dimeric imido complex $[Cl_2Ti{=}N^tBu]_2$. Furthermore, peaks attributable to the monomeric imido complex $Cl_2Ti{=}N^tBu$ were centered at 190 ($Cl_2Ti{=}N^tBu$ + H, 26% of 210 base peak). The elemental composition of the 365 and 190 mass envelopes was confirmed by the close match of the observed isotope patterns and the calculated isotope patterns.[11] Hence, we propose that thermolysis of **1** affords the dimeric imido complex $[Cl_2Ti{=}N^tBu]_2$, which is in equilibrium with the monomeric imido complex $Cl_2Ti{=}N^tBu$.

The present results provide partial mechanistic insight into the sequence that leads from titanium tetrachloride and *tert*-butylamine to titanium nitride thin films. The system further implies that imido complexes should play important roles in other film-forming processes that rely upon the reaction of a metal species with ammonia or amines.[12,13] The results of this study should help to remove some of the "black box" nature of many CVD transformations. Further mechanistic work on titanium nitride and related material depositions is in progress and will be reported in due course.

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Supplementary Material Available: Details of the structure solution for **2**, tables listing positional parameters, thermal parameters, complete bond lengths and angles, and full experimental details for data collection and refinement for **2**, table of spectral and analytical data for **1** and **2**, table of mass spectral data for **1**, and characterization data for the titanium nitride film (11 pages); table listing calculated and observed structure factors for **2** (13 pages). Ordering information is given on any current masthead page.

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(13) For example, see: Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 7833. Kurtz, S. R.; Gordon, R. G. *Thin Solid Films* **1986**, *140*, 277. Sakei, Y.; Matsuzaki, R.; Yajima, A.; Akiyama, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3193.

1-Ferrocenyl-1-cyclopropyl Cation: The First Long-Lived Cyclopropyl Cation[1a]

G. K. Surya Prakash,*[1b] Herwig Buchholz,[1c]
V. Prakash Reddy,[1b] Armin de Meijere,[1d] and
George A. Olah*[1b]

Loker Hydrocarbon Research Institute and
Department of Chemistry
University of Southern California
Los Angeles, California 90089-1661
Institut für Organishe Chemie
Georg-August Universität, Tammannstrasse 2
D-3400, Göttingen, Germany

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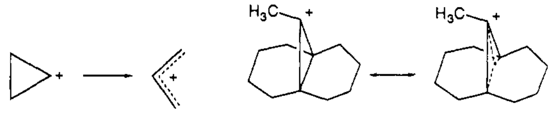
Observation of a stable unencumbered cyclopropyl cation, **1**, has not yet been achieved[2] due to facile ring opening to the energetically more stable allyl cation **2**. Such a rearrangement is a low-barrier Woodward–Hoffmann allowed process.[3] The only evidence for a cyclopropyl type cation built into a rigid framework under long-lived stable-ion conditions has been our earlier work[4a] relating to the geometrically constrained 11-methyl-11-tricyclo-[4.4.1.0^{1,6}]undecyl cation (**3**), which shows significant β C–C bond interaction reflecting a half-opened cyclopropyl cation. Support for such a "half-opening" comes also from ab initio calculations.[4b] There were also some reports of NMR spectroscopic detection of 1-(methylthio)-2,2,3,3-tetramethylcyclopropyl cation from the corresponding chloride.[4c] However, the results are not clear. The constrained propellane systems in which the cyclopropyl group is "locked in" and related cyclopropyl derivatives have also been investigated under solvolytic conditions.[5,6] In the solvolytic reactions, unrearranged cyclopropyl products were obtained with retention of configuration.[5,6]



1 2 3

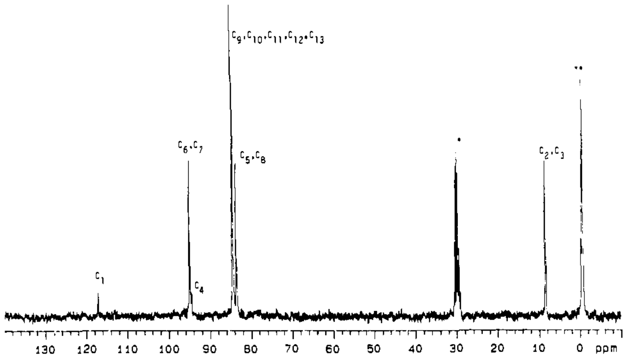


Figure 1. Proton-decoupled 75-MHz ^{13}C NMR spectrum of 1-ferrocenyl-1-cyclopropyl cation (**6**) in FSO_3H/SO_2ClF solution; * indicates peak due to lock solvent acetone-d_6, and ** indicates peak due to trimethylsilyl fluorosulfonate.

We report now the preparation and NMR spectroscopic characterization of the 1-ferrocenyl-1-cyclopropyl cation (**6**) under superacidic conditions, wherein the carbocationic center derives its stabilization through the adjacent ferrocenyl group.[7] The cyclopropyl group remains intact with no half-opened nature.

Dissolution of 1-ferrocenyl-1-cyclopropyl trimethylsilyl ether (**4**)[8a,9] in FSO_3H/SO_2ClF[8b] at −78 °C (using a dry ice/acetone

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(1) (a) Stable Carbocations. 285. For Part 284, see: Prakash, G. K. S.; Rasul, G.; Bausch, J.; Olah, G. A. *J. Org. Chem.*, submitted for publication. (b) University of Southern California. (c) University of Hamburg. (d) Georg-August Universität, Göttingen, Germany.

(2) Friedrich, E. C. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; see reviews cited therein.

(3) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531–6544 and references therein. (b) Buss, V.; Schleyer, P. v. R.; Allen, L. C. *Top. Stereochem.* **1973**, *7*, 253–293. (c) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8193–8195. (d) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *Ibid.* **1976**, *98*, 6700–6702. (e) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649–5657. (f) Taylor, C. A.; Zerner, M. C.; Ramsey, B. *J. Organomet. Chem.* **1986**, *317*, 1–10.

(4) (a) Olah, G. A.; Liang, G.; Ledlie, D. B.; Costopoulos, M. G. *J. Am. Chem. Soc.* **1977**, *99*, 4196–4198. (b) Schleyer, P. v. R.; Bremer, M. *J. Org. Chem.* **1988**, *53*, 2362–2364. (c) Riefling, B. Ph.D. Thesis, University of Göttingen, Germany, 1975.

(5) (a) Schöllkopf, U.; Fellenberger, K.; Patsch, M.; Schleyer, P. v. R.; Su, T.; Van Dine, G. W. *Tetrahedron Lett.* **1967**, 3639–3644. (b) Kutzelnigg, W. *Ibid.* **1967**, 4965. (c) Schöllkopf, U. *Angew Chem., Int. Ed. Engl.* **1968**, *7*, 588–598.

(6) (a) Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608–6613. (b) Ledlie, D. B.; Swan, T.; Pile, J.; Bowers, L. *Ibid.* **1976**, *41*, 419–424. (c) Warner, P.; Lu, S. L. *J. Am. Chem. Soc.* **1976**, *98*, 6752–6753 and references therein. (d) Groves, J. T.; Ma, K. W. *Tetrahedron Lett.* **1974**, 909–912. (e) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946–7953. (f) Banert, K. *Chem. Ber.* **1985**, *118*, 1564–1574. (g) Seebach, D.; Braun, M.; du Preez, N. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 49. *Tetrahedron Lett.* **1973**, 3509–3512. (h) Wasserman, H. H. *Angew. Chem.* **1972**, *84*, 312–313. (i) Salaün, J. *J. Org. Chem.* **1978**, *43*, 2809–2815.

(7) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; Chapter 9.

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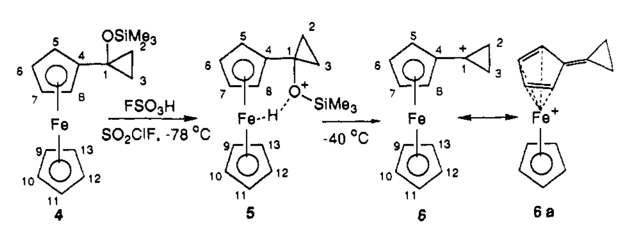

4 **5** **6** **6a**

bath) resulted in a dark green solution. The 300-MHz[8c] ^{1}H NMR spectrum at −85 °C indicated the formation of protonated ether **5** with the following absorptions: δ (^{1}H) 4.48 (s, H_6, H_7), 4.16 (s, H_9, H_{10}, H_{11}, H_{12}, H_{13}), 4.04 (s, H_5, H_8), 0.78 and 0.35 (s, H_2, H_3), −0.03 (s, $Si(CH_3)_3$), −3.21 (s, OH). The 75-MHz ^{13}C NMR spectrum showed the following peaks: δ(^{13}C) 97.9 (s, C_4), 77.9 (d, J_{CH} = 181.7 Hz, C_6, C_7), 77.3 (d, J_{CH} = 185.6 Hz, C_9, C_{10}, C_{11}, C_{12}, C_{13}), 75.5 (d, J_{CH} = 182.7 Hz, C_5, C_8) 60.4 (s, C_1), 17.4 (t, J_{CH} = 166.0 Hz, C_2, C_3), −1.6 (q, J_{CH} = 122.1 Hz, $Si(CH_3)_3$). Comparison of the ^{13}C NMR data with those of the pregenitor **4**[8a] shows no drastic change, in accordance with the structure of **5**. Indicative of **5** is also the observation of the highly shielded acidic proton on the ether oxygen at δ(^{1}H) −3.21, indicating strong agostic[10] interaction with the iron atom.

Allowing the solution to reach −40 °C in the NMR probe for 8 min followed by obtaining the spectrum by recooling to −60 °C showed irreversible changes, indicating the formation of 1-ferrocenyl-1-cyclopropyl cation **6**. The ^{13}C NMR spectrum (Figure 1) consists of the following absorptions: δ(^{13}C) 117.1 (s, C_1), 94.8 (d, J_{CH} = 184.6, C_6, C_7), 94.3 (s, C_4), 84.3 (d, J_{CH} = 183.6 Hz, C_9, C_{10}, C_{11}, C_{12}, C_{13}), 83.5 (d, J_{CH} = 190.4 Hz, C_5, C_8), 7.6 (t, J_{CH} = 166.0 Hz, C_2, C_3). The trimethylsilyl group absorption at δ(^{13}C) 1.6 is assigned to trimethylsilyl fluorosulfate. The observation of the cyclopropyl group methylene carbon signals at δ(^{13}C) 7.6 supports the formation of a free cyclopropyl cation with extensive charge delocalization into the ferrocenyl moiety as expressed in the resonance structure **6a**. Such delocalization is also supported by the observation of a signal for the carbocationic center at δ(^{13}C) 117.1. The C6 and C7 cyclopentadienyl carbons are extensively deshielded (δ(^{13}C) 94.8) compared to the C5 and C8 carbons. The assignments are also in accord with previously studied ferrocenyl-substituted carbocations.[11] The ^{1}H NMR data [δ(^{1}H) 5.76 (s, H_6, H_7), 4.3 (s, H_9, H_{10}, H_{11}, H_{12}, H_{13}), 4.3 (s, H_5, H_8), 1.59 and 1.25 (s, H_2, H_3)] are also in accord with structure **6**. Support for **6** comes from the nonequivalence of H_2 and H_3 cyclopropyl protons as well. Attempts to quench **6** to an intact cyclopropyl product were, however, unsuccessful.[12]

The large shielding of the cyclopropyl methylene carbons in **6** compared to **4** (by ca. 9.5 ppm) can be rationalized in terms of significant double bond character of the C1–C4 bond in the former. In fact, in going from methylcyclopropane to methylenecyclopropane, a shielding (3.2 ppm) of the ^{13}C NMR chemical shifts of the cyclopropyl methylene carbons is observed.[13]

In conclusion, we have been successful in the generation and observation of the first persistent tertiary cyclopropyl cation under long-lived stable-ion conditions. The cyclopropyl group in **6** remains intact due to substantial positive charge delocalization into the adjacent ferrocenyl moiety.

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[8] (a) Compound **4** was obtained in 63% yield, as a yellow solid, by the cyclopropanation[9a] of [1-[(trimethylsilyl)oxy]ethenyl]ferrocene,[9b] which was readily available from acetylferrocene by Duboudin's procedure.[9c] NMR data for **4**: δ(^{1}H) ($CDCl_3$) 4.08 (s, H_6,H_7), 4.01 (s, H_9,H_{10},H_{11},H_{12},H_{13}), 3.92 (s, H_5,H_8), 1.11 and 0.92 (m, H_2,H_3); δ(^{13}C) ($CDCl_3$) 94.4 (s, C_4), 69.0 (d, C_9,C_{10},C_{11},C_{12},C_{13}), 67.5 (d, C_6,C_7), 67.2 (d, C_5,C_8), 55.2 (s, C_1), 17.1 (t, C_2,C_3), 1.3 (q, $Si(CH_3)_3$). (b) Freshly distilled materials were used; FSO_3H was used in 10-fold excess. (c) The NMR studies were carried out on a Varian Associates Model Unity 300 Superconducting NMR spectrometer equipped with a variable-temperature ^{1}H, ^{19}F broad band probe using capillary acetone-d_6 lock. The chemical shifts are referenced from capillary TMS.

[9] (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* **1968**, 3495–3498. (b) Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864–4870. (c) Cazlau, P.; Moulines, F.; Laporte, O.; Duboudin, F. *J. Organomet. Chem.* **1980**, *201*, C9–C13.

[10] Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1987.

[11] Olah, G. A.; Liang, G. *J. Org. Chem.* **1975**, *40*, 1849–1850 and references therein. Also see: Braun, S.; Abram, T. S.; Watts, E. *J. Organomet. Chem.* **1975**, *97*, 429–441.

[12] Quenching the solution with excess methanol/K_2CO_3 at −78 °C gave decomposed products.

[13] Crawford, R. J.; Tokunaga, H.; Schrijver, L. M. H. C.; Goddard, J. C.; Nakashima, T. *Can. J. Chem.* **1978**, *56*, 992–997. Monti, J. P.; Faure, R.; Vincent, E. J. *Org. Magn. Reson.* **1976**, *8*, 611–617.

Structure and Bonding Nature of 2,4,5-Triselena-1,3-disilabicyclo[1.1.1]pentane: A Novel [1.1.1]Propellane-Type Molecule[1]

Hitoaki Yoshida,[2a] Yoichi Takahara,[2b] Tomoki Erata,[2c] and Wataru Ando*,[2a]

Department of Chemistry and Institute
of Applied Physics, University of Tsukuba
Tsukuba, Ibaraki 305, Japan
Production Engineering Research Laboratory
Hitachi Ltd. 292, Yoshida, Totsuka
Yokohama 244, Japan

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The nature of the bridgehead bond of propellanes has been of considerable recent interest;[3,4] however, only a few isolable group 14 [1.1.1]propellanes and bicyclo[1.1.1]pentanes are known experimentally.[4] Here, we wish to report the preparation of a novel [1.1.1]propellane-type molecule **1-Se3** (2,4,5-triselena-1,3-disilabicyclo[1.1.1]pentane) and discuss the nature of the bridgehead bond.

A benzene solution of **1-Se4**[5] in a sealed tube was irradiated with a low-pressure Hg lamp for 18 h to give **1-Se3**, liberating Se as a reddish brown precipitate.[6] The title compound **1-Se3**

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[1] Yoshida, H.; Ando, W. Presented in part at the 6th Conference on the Chemistry of Selenium and Tellurium, Osaka, Japan, July 8–13, 1991. Chalcanes. 2. For Part 1, see ref 5.

[2] (a) Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan. (b) Production Engineering Research Laboratory, Hitachi Ltd. 292, Yoshida, Totsuka, Yokohama 244, Japan. (c) Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan.

[3] (a) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679. (b) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233. (c) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. (d) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. (e) Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247. Schmidt, M. W.; Nguyen, K. A.; Gordon, M. S.; Montgomery, J. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5998. Nguyen, K. A.; Carroll, M. T.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 7924. (f) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408. (g) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878. Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591. (h) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456. Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063. Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. Nagase, S. *Polyhedron* **1991**, *10*, 1299. (i) Streitwieser, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1261. (j) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267. (k) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. (l) O'Keeffe, M.; Gibbs, G. V. *J. Chem. Phys.* **1984**, *81*, 876. Note that the IUPAC name for [1.1.1]propellane is tricyclo[1.1.1.$0^{1,3}$]pentane.

[4] (a) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. (b) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454. Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839. (c) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794.

[5] Yoshida, H.; Ando, W. *Organometallics* **1991**, *10*, 27.

[6] Irradiation with a halogen lamp yielded the same product, **1-Se3**, but the rate was very slow. The UV maximum of **1-Se4** (450 nm) is explained by the lone pair–lone pair interaction of two neighboring Se atoms.[5,7] This four-electron interaction served to destabilize the molecule; therefore, we expected the photolytic cleavage of the selenium–selenium bond. However, the corresponding sulfur analogue **1-S4** did not show such photochemical reactivity.

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