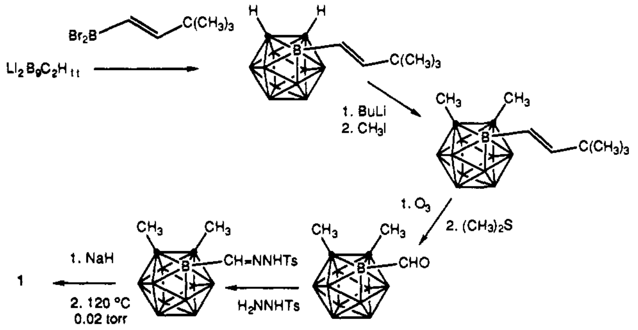
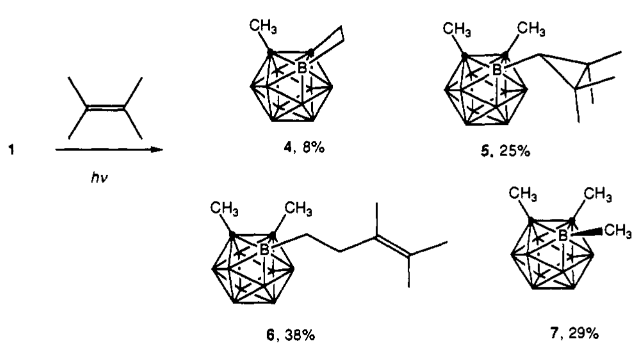
1 in 82% yield. Compound **1** appears stable, but should be treated with caution in view of the possible explosion hazard.



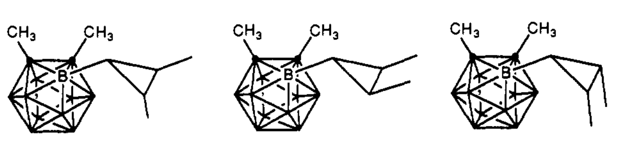
3

Irradiation of **1** in 2,3-dimethyl-2-butene through Pyrex with a 450-W Hanovia medium-pressure mercury arc led to four products in 60% yield. Intramolecular insertion gave **4**, which is the first compound reported that contains a two-carbon carbon-to-boron bridge.[8] Addition to the double bond gives **5**, and formal insertion into an allylic carbon–hydrogen bond produces **6**. Most unusual is the formation of 1,2,3-trimethyl-*o*-carborane (**7**), a major product and the apparent result of a double abstraction by carbene **2**.[9]

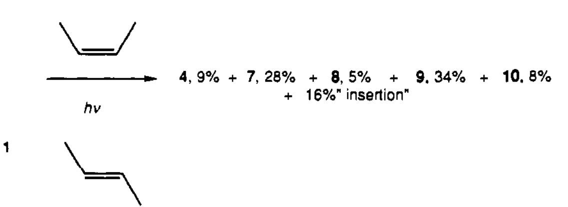


The substantial formation of **7** is unusual, and a likely origin is double abstraction of hydrogen by triplet **2**. Compound **4** does not give **7** either photochemically or on heating at the temperature of the photolysis of **1** (ca. 35 °C). As **7** is formed in solution, there is no reason to suspect rearrangements of "hot" molecules.

However, analysis of the products of reaction with *cis*- and *trans*-2-butene shows that the cycloaddition reaction is largely stereospecific. This indicates substantial singlet reactivity. In these reactions, **4** and products of carbon–hydrogen insertion are still formed, and compound **7** remains a major product.[10] The most economical explanation is that both spin states of carbene are present, with the singlet leading to most of the cyclopropanes and the triplet to most of the products of hydrogen abstraction as well as, presumably, the small amounts of cyclopropanes formed with loss of the stereochemistry present in the original olefins.



8 **9** **10**



This behavior contrasts both with reactions of 1-*o*-carboranylcarbene[11] and with those of the two-dimensionally aromatic phenylcarbene.[12] For neither of these carbenes are reactions of the triplet detectable, even though the triplet is the ground state in each case.[6,13] Thus, preliminary results bear out the expectation that carbene **2** should show enhanced triplet activity.

Supplementary Material Available: NMR, IR, and mass spectral data of compounds **1**, **4**, **5**, and **7–10** and experimental details for the synthesis and photolysis of **1** (3 pages). Ordering information is given on any current masthead page.

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(8) There is actually another, a carbon-to-boron-4 bridged "cyclobutanone" in the following: Wu, S.-h. Ph.D. Dissertation, Princeton University, 1989.

(9) All new compounds have been characterized by NMR and IR spectroscopy and analyzed by either combustion analysis or precise mass spectrometry.

(10) The cyclopropanes are stable to the reaction conditions, and the starting alkenes are not isomerized during the reaction. The products of intermolecular carbon–hydrogen insertion are not so stable, however, and do isomerize.

(11) Chari, S. L.; Chiang, S.-H.; Jones, M., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3138.

(12) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153. Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(13) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990.

A Single-Source Precursor to Titanium Nitride Thin Films. Evidence for the Intermediacy of Imido Complexes in the Chemical Vapor Deposition Process

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Monomeric titanium and zirconium complexes with multiple bonds to oxygen,[2] sulfur,[3] and nitrogen[4] have attracted considerable attention due to their novel structural features and interesting reactivity.[2-5] Recently, we have initiated a research program that is designed to prepare models for complexes involved in chemical

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(2) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *28*, 3602. Hiller, W.; Strähle, J.; Kobel, W.; Hanack, M. *Z. Kristallogr.* **1982**, *159*, 173. Guilard, R.; Latour, J.-M.; Lecomte, C.; Marchon, J.-C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228. Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782. Haase, W.; Hoppe, H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1968**, *B24*, 282.

(3) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426.

(4) (a) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985. (b) Profilet, R. D.; Zambrano, C. H.; Fanwick, P. E.; Nash, J. J.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 4364. (c) Hill, J. E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 664. (d) Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669. (e) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (f) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (g) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1991**, *30*, 1143.

(5) For leading references to the area, see: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. Chisolm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McLeverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 13.4.

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vapor deposition (CVD) processes of early transition metal materials.[6] Species containing metal–element multiple bonds have featured prominently in mechanistic conjecture about CVD reactions,[7] although little hard evidence is available to back up such speculation. One of us[8] has disclosed that excellent-quality thin films of titanium nitride can be prepared by the atmospheric pressure CVD reaction of titanium tetrachloride with alkylamines at temperatures between 350 and 600 °C. This process appeared ideal for detailed mechanistic scrutiny, since titanium tetrachloride is well-known to be highly reactive toward amines[9] and because titanium should be capable of stabilizing a variety of nitrogen ligand types. In this context, we report the synthesis and characterization of two complexes that are formed in the solution-phase reactions of titanium tetrachloride with *tert*-butylamine. To the best of our knowledge, the first of these, a chloride–amide–amine complex, comprises the first single-source CVD precursor to high-quality gold-colored films of titanium nitride. Additionally, a monomeric imido complex has been trapped with triphenylphosphine oxide and has been structurally characterized. Evidence is presented from mass spectrometry for the intermediacy of imido complexes in the CVD process.

Treatment of titanium tetrachloride with *tert*-butylamine (6–8 equiv) in dichloromethane at −78 °C, followed by warming to room temperature and workup, afforded the chloride amide $[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_2]_n$ (**1**) in 76% yield as bright orange crystals (eq 1).[10] The structure of **1** was based upon spectroscopic and microanalytical data. The NMR data show two different amide groups and two different coordinated amines, which is consistent either with a monomeric formulation with strong nonsymmetric hydrogen bonding or with a higher oligomeric constitution. Upon standing at 23 °C, **1** slowly lost the coordinated *tert*-butylamine to afford an orange powder of the variable composition $[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_{0-2}]_n$. This powder, although nonstoichiometric, possessed reactivity similar to that of **1**.

$$TiCl_4 + 6\,{}^tBuNH_2 \xrightarrow[-78\,°C \rightarrow RT]{CH_2Cl_2} \underset{\substack{\mathbf{1}\\76\%}}{[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_2]_n} + 2\,{}^tBuNH_3{}^+Cl^- \quad (1)$$

$$\Big\downarrow \text{-}NH_2{}^tBu \;\; 23\,°C$$

$$[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_{0-2}]_n$$

When complex **1** (or the nonstoichiometric orange powder) was treated with triphenylphosphine oxide (2 equiv) in dichloromethane at room temperature, an immediate color change from orange to lemon yellow occurred. Slow diffusion of hexane into this solution afforded yellow crystals of the imido complex $[TiCl_2(O{=}PPh_3)_2(N^tBu)]$ (**2**) in 15–20% yields (eq 2).[10] The structure of **2** was established by spectroscopic and analytical methods and from a crystal structure determination (vide infra). Improved yields (40–50%) of **2** were obtained by treatment of **1** with triphenylphosphine oxide (2 equiv) in dichloromethane, followed by removal of the volatiles, extraction of the yellow residue with benzene (to remove unreacted triphenylphosphine oxide), and vacuum drying. Complex **2** is formed from **1** by an amine elimination reaction. When **1** was reacted with triphenylphosphine oxide in chloroform-*d* at 23 °C, ^1H NMR analysis revealed the formation of **2** and 3 equiv of *tert*-butylamine. The reverse reaction (e.g., **2** + $3\,{}^tBuNH_2 \rightarrow$ **1**) was not observed, probably due to the strong ligating properties of triphenylphosphine oxide. Complex **2** was unaffected by 2 h of refluxing in benzene-d_6 and was unreactive toward diphenylacetylene, acetonitrile, and benzophenone at room temperature.

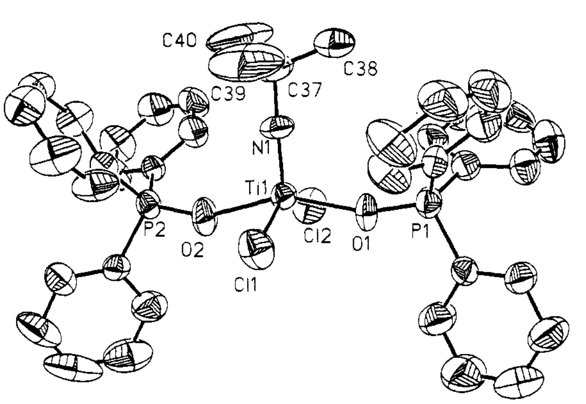

Figure 1. Perspective view of **2**. Selected bond lengths (Å) and angles (deg): Ti–N 1.672 (7), Ti–Cl(1) 2.372 (2), Ti–Cl(2) 2.383 (3), Ti–O(1) 2.008 (6), Ti–O(2) 2.047 (6); Ti–N–C(37) 174.0 (6), Ti–O(1)–P(1) 159.2 (4), Ti–O(2)–P(2) 154.6 (4), Cl(1)–Ti–Cl(2) 143.8 (1), Cl(1)–Ti–N 107.3 (2), Cl(1)–Ti–O(1) 86.6 (1), Cl(1)–Ti–O(2) 85.0 (2), Cl(2)–Ti–N 108.8 (2), Cl(2)–Ti–O(1) 87.7 (2), Cl(2)–Ti–O(2) 85.0 (2), N–Ti–O(1) 102.3 (3), N–Ti–O(2) 103.0 (3), O(1)–Ti–O(2) 154.6 (2).

$$\underset{\mathbf{1}}{[TiCl_2(NH^tBu)_2(NH_2{}^tBu)_2]_n} + 2\,Ph_3PO \xrightarrow[23\,°C]{CH_2Cl_2} \underset{\mathbf{2}}{[TiCl_2(N^tBu)(OPPh_3)_2]} + 3\,H_2N^tBu \quad (2)$$

Figure 1 shows a perspective view of **2** along with selected bond distances and angles. The complex is a monomeric imido complex of approximately square pyramidal geometry, with the titanium–imido linkage at the apex. The base of the pyramid comprises two trans chlorines and two trans phosphine oxide ligands. The observed geometry may arise from steric interactions of the phosphine oxide phenyl rings with the imido *tert*-butyl group, which would cause distortion from ideal trigonal-bipyramidal geometry. The titanium–nitrogen fragment is nearly linear (Ti–N–C(37) = 174.0 (6)°) with a titanium–nitrogen bond length of 1.672 (7) Å. To date, three other monomeric titanium imido complexes have been crystallographically characterized. Significantly, the titanium–nitrogen bond length in **2** is ~0.04 Å shorter than the corresponding distances in $[Ti(2,6\text{-}{}^iPr_2C_6H_3O)_2(py)_2(NPh)]$ (1.719 (3) Å),[4c] $[TiCl_2(py)_3(NP(S)Ph_2)]$ (1.720 (2) Å),[4d] and $[Ti(OAr)_2(NC_6H_4\text{-}C_6H_4N\text{-}C_6H_4NC_4Et_4)]$ (1.708 (5) Å).[4g]

When **1** (or the nonstoichiometric orange powder) was volatilized at 500 °C (0.05 mm) in an MOCVD reactor, the wall of the reactor was coated with a gold film. The material was identified as titanium nitride by its electron diffraction pattern and from the characteristic resistivity (600–900 μΩ-cm).[11,12] Thermolysis of **2** under identical conditions for depositions using **1** afforded an amorphous blue-black decomposition product instead of a gold film. Hence, **2** is not a precursor to titanium nitride films, which is reasonable, because of the phosphine oxide ligands.

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(6) For our previous efforts in the area, see: Winter, C. H.; Sheridan, P. H.; Heeg, M. J. *Inorg. Chem.* **1991**, *30*, 1962.

(7) For leading references, see: Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. Nandi, M.; Rhubright, D.; Sen, A. *Inorg. Chem.* **1990**, *29*, 3066.

(8) Williams, K.; Reck, G. P.; Proscia, J. W. *Abstracts of Papers*, Fourth Chemical Congress of North America, New York; American Chemical Society: Washington, D.C., 1991; INOR 309. Manuscript in preparation.

(9) Cowdell, R. T.; Fowles, G. W. A. *J. Chem. Soc.* **1960**, 2522 and references contained therein. See also: Jones, T. C.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1984**, 205. Bates, P. A.; Nielson, A. J.; Waters, J. M. *Polyhedron* **1985**, *4*, 1391.

(10) Complex **1**: mp 184–186 °C dec. Anal. Calcd for $C_{16}H_{42}Cl_2N_4Ti$: C, 46.95; H, 10.34. Found: C, 47.08; H, 10.70. Complex **2**: dec range 175–185 °C. Anal. Calcd for $C_{40}H_{39}Cl_2NO_2P_2Ti$: C, 64.36; H, 5.27; N, 1.88. Found: C, 63.97; H, 5.06; N, 1.72. Full spectral and analytical data are contained in the supplementary material.

(11) The titanium nitride characterization and mass spectral data are provided in the supplementary material. The elemental composition of all other significant peaks in the mass spectrum above mass 100 has been determined from their isotope patterns and will be described in a forthcoming full paper.

(12) Titanium(IV) dialkylamides have been claimed as single-source precursors to titanium nitride thin films: Sugiyama, K.; Pac, S.; Takahashi, Y.; Motojima, S. *J. Electrochem. Soc.* **1975**, *122*, 1545. However, later work has found that films produced by this method are contaminated with carbon and oxygen: Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1990**, *2*, 235.

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.

Acknowledgment. We thank Ford Motor Company, Glass Division, and the Institute for Manufacturing Research, Wayne State University, for financial support.

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]

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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]

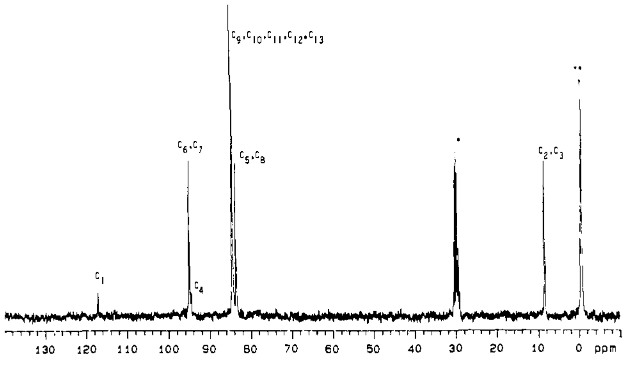
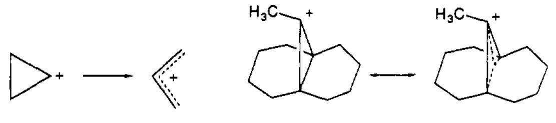


Figure 1. Proton-decoupled 75-MHz ^{13}C NMR spectrum of 1-ferrocenyl-1-cyclopropyl cation (**6**) in FSO_3H/SO_2ClF solution; * indicates peak due to lock solvent acetone-d_6, and ** indicates peak due to trimethylsilyl fluorosulfonate.



1 **2** **3**

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.

0002-7863/92/1514-1097$03.00/0