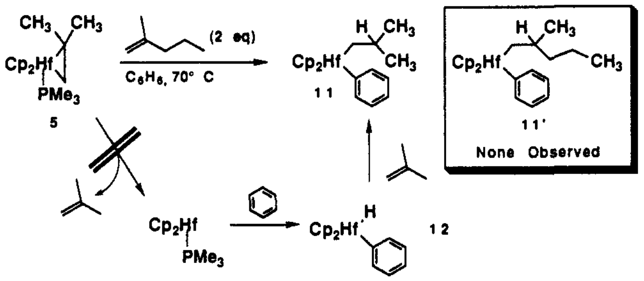
Scheme IV



centration dependent. We are continuing efforts to deduce the structure of **6**.[11]

As depicted in Scheme III, **5** participates in several interesting reactions. Treatment of **5** with 1 equiv of diphenylacetylene produces the alkyne complex **7** in good yield. Similarly, excess diphenylacetylene gives the known metallacycle **8**.[4b] Use of alkynes without aromatic groups gives slightly different results. Thus, **5**, upon exposure to a slight excess of 2-butyne, gives a ca. 3:1 ratio of the trimethylphosphine adduct of the hafnocene complex of 2-butyne and tetramethylhafnacyclopentadiene.[13] Complex **5** can be protonated[14] and participates in C–H bond activation reactions.[15] If **5** is allowed to react with a slight excess of benzyl alcohol, alkoxide **9** is produced. Of interest is that only the regioisomer shown is produced. That **9** is not formed by isomerization of its isomer **10** was shown by exposing **10**, independently prepared, to the reaction conditions used to convert **5** to **9**. When this protocol was used, no **9** was observed. This regiochemical outcome is consistent with the incoming alcohol approaching from the side of **5** away from the trimethylphosphine moiety (i.e., protonation presumably occurs faster than phosphine dissociation and probably requires coordination of the alcohol prior to proton transfer, or with protonation of the weakest and most electron rich Hf–C bond).

Unexpectedly, heating **5** at 70 °C in benzene causes C–H activation and produces complex **11** in good yield.[15] If this reaction is performed in neat C_6D_6, the deuterium ends up solely at the methine position. In order to probe whether the reaction of **5** with alcohols and with benzene involves a free (or PMe_3-bound) hafnocene intermediate,[16] the following experiments were performed. If **5** is heated in C_6H_6 in the presence of 2 equiv of 2-methyl-1-pentene, no incorporation of this olefin is seen in the product **11** (Scheme IV). Likewise, treatment of **5** with benzyl alcohol in the presence of 2 equiv of 2-methyl-1-pentene gives only regular product **9**, with no incorporation of the added olefin. In the reaction with benzene, if hydride **12** were an intermediate, it would be expected to hydrometalate the excess 2-methyl-1-pentene to produce **11'**. What these experiments show is that isobutylene is not lost to provide a free (or PMe_3-bound) hafnocene intermediate which reacts with benzene or benzyl alcohol to give the observed product. These experiments, as can be seen from the reactions with alkynes depicted above, however, do not indicate that the isobutylene cannot be displaced under the appropriate conditions. It should be noted that a similar C–H activation is not seen with zirconocene olefin complexes; heating **1a** results only in the loss of the olefin, with formation of I as the major product.[10b]

Work is ongoing in our laboratory to further delineate the structure of **6**[11] and to probe the reactivity of **5** and other related hafnocene complexes.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the National Institutes of Health (GM-34917) and Firmenich SA for their generous financial assistance.

Supplementary Material Available: Experimental section containing the preparation and spectroscopic and analytical characterization of compounds **3–5**, **7**, and **9–11** along with crystallographic data and procedures, an ORTEP diagram of **5**, tables of bond distances and angles for **5**, and table of final positional and thermal parameters for **5** (19 pages); table of structure factors for **5** (22 pages). Ordering information is given on any current masthead page.

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[11] We believe that **6** may be an unstable allyl hydride complex. ^1H NMR (500 MHz, C_6D_6, 60 °C): δ 5.12 (s, 10 H), 3.56 (br, 1 H), 2.32 (d, J = 2.0 Hz, 4 H), 1.43 (d, J = 1.5 Hz, 3 H), free PMe_3 is observed at δ 0.87 (d, J = 2.4 Hz). ^{13}C NMR (125 MHz, C_6D_6, 60 °C): δ 99.79, 50.59. No other ^{13}C signals that were not attributed to either **5**, **11**, or PMe_3 were observed in the sample. Allyl hydride complexes have been observed and studied in the bis(pentamethylcyclopentadienyl) zirconocene system.[12]

[12] (a) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, 1984. (b) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

[13] Sabade, M. B.; Farona, M. F. *J. Organomet. Chem.* **1986**, *310*, 311.

[14] Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

[15] For examples of C–H activation by Zr(IV) complexes, cf.: Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731 and ref 13.

[16] For a description of the generation and trapping of the analogous hydridophenylzirconocene, cf.: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

Cationic TBP Silicon: A Stable Intermediate in the Proton-Assisted Departure of an Equatorial Substituent

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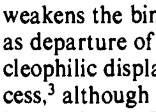
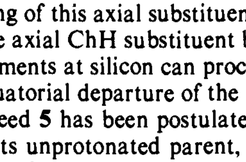
Received November 16, 1989

Organophosphorus chemistry is replete with examples of nucleophilic displacements involving a TBP phosphorus intermediate. In acidic media, this process normally occurs via the proton-assisted cleavage of an axially oriented group, often following a Berry pseudorotation.[1] A few years ago, we presented NMR evidence for the existence of **1–4**,[2] which are representatives of five-coordinate intermediates wherein protonation of the chalcogen (Ch) weakens the binding of this axial substituent to the central atom as departure of the axial ChH substituent begins to occur. Nucleophilic displacements at silicon can proceed by a similar process,[3] although equatorial departure of the leaving group cannot be ruled out. Indeed **5** has been postulated to form in a rapid equilibrium with its unprotonated parent, prior to the rate-determining cleavage of the Si–O_{eq} bond in an acid-catalyzed hydrolysis reaction.[4] Here we report the synthesis of **6**, the first stable representative of incipient proton-assisted equatorial bond cleavage of a five-coordinate intermediate to be isolated, and its structure determination.

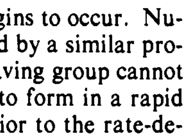


	Ch	Z	n
1	O	lp	0
2	O	H	+1
3	S	lp	0
4	S	lp	+1



5

R = Me, Ph, *p*-tolyl



6

When weakly electrophilic Me_3SiN_3 is added to a solution of azasilatrane **7**, the novel, mixed crystalline compound **8** is obtained

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[1] Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976.

[2] (a) Carpenter, L. E., II; De Ruiter, B.; Van Aken, D.; Buck, H. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 4918. (b) Carpenter, L. E., II; Verkade, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 7084.

[3] (a) Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1988**, *7*, 237. (b) Corriu, R. J. P. *Pure Appl. Chem.* **1988**, *60*, 99 and references cited therein.

[4] Timms, R. E. *J. Chem. Soc. A* **1971**, 1969.

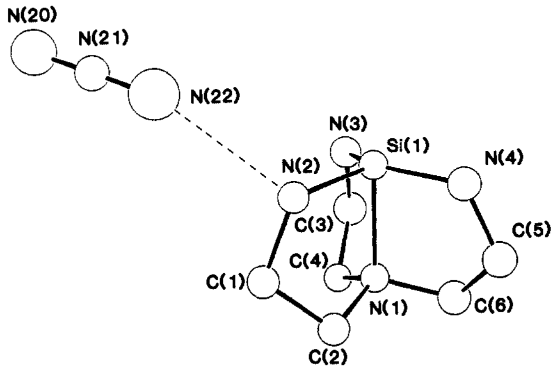
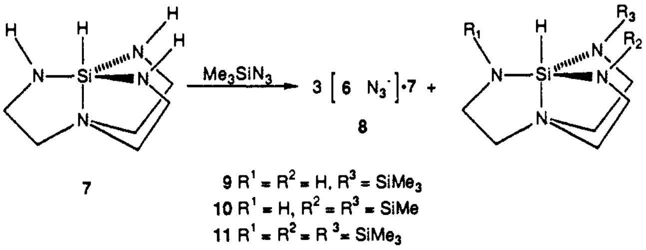


Figure 1. ORTEP drawing of one of the cations (**6**) and azide anions in **8**. Electron probability spheres are drawn at the 50% level.

in 49% yield.[5] Products **9–11**[6,7] arise presumably by nucleophilic attack of **7** on Me_3SiN_3, thereby releasing HN_3, which then reacts



with unreacted **7** to yield **8**. X-ray diffraction studies[8] on **8** reveal the presence of cations **6** (Figure 1) and azide ions. From Figure 1 it is seen that one nitrogen of the azide ion lies within hydrogen bonding distance (283 pm, average) of the protonated nitrogen in cation **6**. Whereas the azido groups in covalent silyl and organic azides are usually bent,[9] those in **8** are essentially linear, with an average NNN angle of 178.2°. The average bond lengths (114 and 118 pm) in the azide ions of **8** are close to those reported for covalent silyl azides but also for the free azide ion.[9] Although the hydrogen atoms in **8** could not be located, the site of protonation is signalled by a significantly longer SiN(2) bond (189 pm, average) compared with the two other $Si-N_{eq}$ bond lengths (169 pm, average) in cation **6** and the $Si-N_{eq}$ bond lengths (173 pm, average) in the cocrystallized molecule of **7**. The $Si-N_{ax}$ bond lengths (208 pm) in the protonated and in the neutral silatrane molecule of **8** are equal. The constitution of **8** is further confirmed by its IR, chemical ionization mass, ^1H NMR, and solid-state ^{29}Si NMR spectra.[5] The latter spectrum exhibits resonances at −83.0 and −86.3 ppm (ratio 1:3) characteristic of pentacoordinated silicon in the neutral and protonated azasilatrane molecule, respectively, the chemical shift value of the former being in excellent agreement with that reported for **7** in solution (−82.3 ppm).[10]

Attempts to generate cation **6** by protonation of **7** with CF_3SO_3H or, indirectly, by reacting **7** with the strong electrophiles CF_3SO_3Me or $CF_3SO_3SiMe_3$ resulted in the destruction of the atrane moiety of **7**.

Acknowledgment. We thank the AFOSR for financial support and the W. R. Grace company for samples of tren.

Supplementary Material Available: Description of the data collection and structure solution and tables of positional and isotropic thermal parameters, bond distances and angles, and least-squares planes (14 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(5) To a filtered solution of 0.71 g (4.1 mmol) of **7** in 20 mL of dry CH_3CN was added 0.55 mL (4.2 mmol) of Me_3SiN_3. Over a period of ca. 2 h, crystalline **8** was formed (mp 138–140 °C dec; FT-IR (KBr, cm^{-1}) 3375 m, 3325 m, 2900 s (br, NH str), 2000 s (br, N≡N and SiH str); MS (Cl, NH_3) 214 (1.1%, M + 1 of $N_3Si(HNCH_2CH_2)_3N$), 173 (100%, M^+ of **6** or M + 1 of **7**); MS (Cl, CH_4) 341 (2%, M + 1 of $C_{12}H_{26}N_8Si_2$), 213 (0.5% M^+ of $N_3Si(HNCH_2CH_2)_3N$), 173 (59%, M^+ of **6** or M + 1 of **7**), 171 (100%, $M^+ - 2$ of **6** or $M^+ - 1$ of **7**); ^1H NMR ($CDCl_3$): 2.61 t, 2.86 t (CH_2 cage protons of **7**), 2.65 t, 2.99 t (CH_2 cage protons of **6**, ratio cage proton sets of **7**:**6** = 1:3), 4.27 s (br, NH, NH_2), 4.67 s (SiH of **6**). Elemental anal. Calcd (found) for $C_{24}H_{67}N_{25}Si_4$: C, 35.44 (35.22); H, 8.25 (8.56); N, 42.79 (42.79); Si, 13.73 (13.45).

(6) Compounds in the supernatant were characterized by GLC, high-resolution mass spectroscopy, and ^1H NMR (yield (GC-MS): **8**, 17%; **10**, 47%; **11**, 26%; **12**, 10%). Authentic samples of **10** and **11** were available for comparison (see ref 7).

(7) (a) Gudat, D.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 8520. (b) Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.

(8) **7**: monoclinic, space group *I*a, $Z = 4$; $a = 13.400\ (3)$ Å, $b = 22.645\ (3)$ Å, $c = 13.812\ (2)$ Å; $\beta = 108.85\ (1)°$; $V = 3966\ (1)$ Å^3; $d_{calcd} = 1.370$ g/cm^3; $4° < 2\theta < 45°$, (Mo Kα, λ) = 0.71073 Å; $\mu = 1.99$ cm^{-1}). A total of 2588 unique reflections collected at −20 °C were used to solve (direct methods) the structure; 1823 reflections having $I > 3\sigma(I)$ were used in the refinement, which converged to $R = 5.98\%$, $R_w = 7.48\%$ ($w = 1/(\sigma^2/(|F_o|))$). Non-hydrogen atoms were refined with isotropic temperature factors. Hydrogen atoms were used in idealized positions for the carbon atoms only. Details are given in the supplementary material.

(9) Zigler, S. S.; Haller, K. J.; West, R. *Organometallics* **1989**, *8*, 1656 and references cited therein.

(10) Kupce, E.; Liepins, E.; Lapsina, G.; Zelcans, G.; Lukevics, E. *J. Organomet. Chem.* **1987**, *333*, 1.

Ketone Perfluoroenolates: Regioselective and Stereoselective Synthesis, Unique Reactivities, and Electronic Properties

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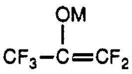
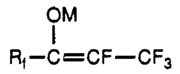
Despite the prominent role of metal enolates in organic synthesis, the chemistry of perfluoroenolates (*F*-enolates) remains relatively unexplored. We recently introduced a new, practical method to generate the parent ketone *F*-enolate **1** and described its unique spectrum of reactivity.[1] For this method to be generally useful in organofluorine synthesis, its scope and other fundamental aspects of *F*-enolate chemistry need to be explored. We now report the highly regio- and stereoselective generation of β-trifluoromethyl-substituted *F*-enolates **2**, whose kinetic reactivities differ significantly from those of **1**.



$$CF_3-\overset{\displaystyle OM}{\overset{|}{C}}=CF_2$$

1



$$R_f-\overset{\displaystyle OM}{\overset{|}{C}}=CF-CF_3$$

2

The regio- and stereoselectivities observed in the generation of **2** from alcohols **3**[2] (eq 1) are summarized in Table I. For the Li enolates (entries 1–5), only the *Z* isomers are formed in ether, whereas in THF the selectivity decreases and in THF/HMPA it reverses to favor the *E* isomer. "Internal" enolates **2b** are produced almost exclusively, irrespective of solvent and metal ion

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(1) Qian, C.-P.; Nakai, T. *Tetrahedron Lett.* **1988**, *29*, 4119.

(2) The alcohols **3** were obtained in ca. 70% distilled yields by $LiAlH_4$ reduction of the corresponding *F*-ketones, which were prepared from R_fCO_2Et and CF_3CF_2I according to the literature procedure: Chen, L. S.; Chen, G. J.; Tamborski, C. *J. Fluorine Chem.* **1984**, *26*, 341.

0002-7863/90/1512-4602$02.50/0