cation flux ca. 40-fold greater than the simple carrier but ca. 100-fold poorer than gramicidin at this concentration.

It should be noted that, after incubation of the vesicles with **2**, a decrease in the $[\text{Na}]_{\text{inside}}/[\text{Na}]_{\text{outside}}$ ratio from 1:4.5 to 1:9 was observed. This is not troubling since the dynamic NMR method is solely dependent on the rate of exchange between internal and external sodium ions which are at the same equilibrium concentration. The only concern would be if such vesicular rupture leads to increased ionophore concentration in the vesicles. Although this seems unlikely to us, the maximum effect would only be a factor of 2.

Tentative confirmation that sodium transport is mediated differently by **1** and **2** can be found in the respective kinetic orders. Carrier-mediated transport (**1**) exhibits second-order kinetics, but the tris(macrocycle) **2** shows first-order kinetics. As noted above, gramicidin is second order, due to the fact that the channel is dimeric. We think **1** exhibits second-order kinetics due to the requirement of a flip-flop mechanism for transport utilizing this ionophore. Monensin, also a carrier, shows first-order kinetics but is capable of simple diffusion of a kind that seems unlikely with **1**.[1]

Finally, it should be noted that the structure of gramicidin channels makes one associate a tunnel shape with the term "channel". The gramicidin channel is an excellent channel, but it is not the only one and should be regarded as an example rather than a definition. The present channel may be flatter and more like, as the dictionary says, a "groove" or a "trench". Relay from ring to ring, although obviously involving distances longer than known for gramicidin, does not disqualify this system from the designation channel.

Acknowledgment. We thank the National Institutes of Health for grants (GM-33940 to L.E. and G.W.G. and GM-36262 to G.W.G.) The synthetic effort was sponsored by the latter and characterization by the former.

Supplementary Material Available: Experimental details of the ^{23}Na NMR measurements, NMR sample preparation, materials, vesicle preparations, and the synthesis of compound **2** (4 pages). Ordering information is given on any current masthead page.

β-Agostic Interactions in $(C_5H_4Me)_2Zr(CH_2CH_2R)(PMe_3)^+$ Complexes

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Agostic C–H–M interactions are potentially important structural features of unsaturated metal complexes that are intermediates in olefin polymerization, C–H activation, and other metal-mediated or -catalyzed reactions.[1,2] Here we report observations that establish the presence of β-agostic interactions in $(C_5H_4Me)_2Zr(CH_2CH_2R)(PMe_3)^+$ complexes. These results suggest that similar interactions may be present in the $Cp_2M(R)^+$ and $Cp_2M(R)(olefin)^+$ ions which are believed to be key intermediates in metallocene-based Ziegler–Natta olefin polymerization catalyst systems.[3]

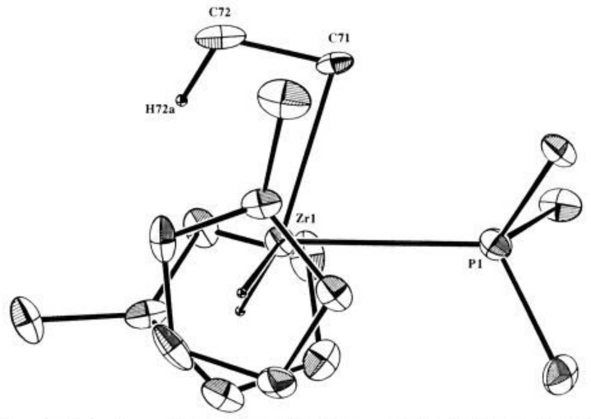
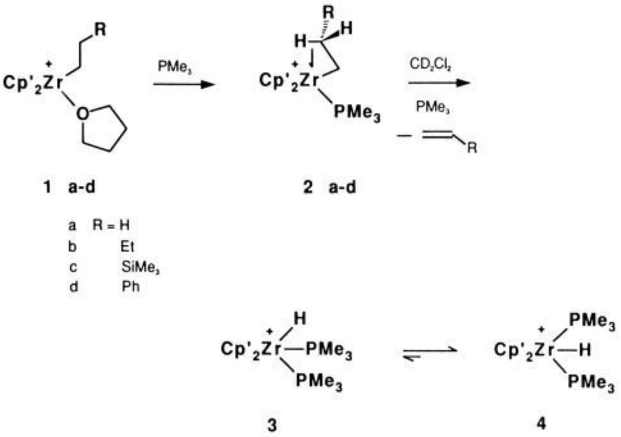


Figure 1. Structure of the cation of **2a**. Key bond distances (angstroms) and angles (degrees): Zr1–C71, 2.290 (9); Zr1–C72, 2.629 (9); Zr1–H72a, 2.16; Zr1–P1, 2.691 (3); C71–C72, 1.47 (2); Zr–C1C, 2.21; Zr–C2C, 2.21; P1–Zr1–C71, 73.6 (3); Zr1–C71–C72, 84.7 (5); C1C–Zr1–C2C, 132.3 (CnC denotes centroid of Cp′ ring).

Scheme I



The cationic THF complexes $Cp'_2Zr(CH_2CH_2R)(THF)^+$ (**1a–d**, Scheme I, Cp′ = C_5H_4Me) are prepared by reaction of the cationic hydride $Cp'_2Zr(H)(THF)^+$ with the appropriate olefin.[4] Complexes **1a,b,d** have normal, undistorted alkyl ligands as established by NMR and IR spectroscopies (normal ^{1}H and ^{13}C shifts, $J_{C\alpha-H} = 115$ Hz, $J_{C\beta-H} = 122$–129 Hz, no low-frequency ν_{C-H}).[5] Reaction of **1a–d** with PMe_3 in CD_2Cl_2 or THF at −78

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(1) Reviews: (a) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(2) Leading references: (a) Bailey, N. A.; Jenkins, J. M.; Mason, R.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1965**, 237. (b) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. (c) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410. (d) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (e) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326. (f) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (g) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (h) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109. (i) Kanamori, K.; Broderick, W. E.; Jordan, R. F.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7122. (j) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629. (k) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210.

(3) (a) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219 and references therein. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (e) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148 and references therein. (h) Lin, Z.; LeMarechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (i) Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1647. (j) Giannetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2117. (k) Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* **1967**, *16*, 2333.

(4) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892.

(5) All complexes are studied as the BPh_4^- salts. The spectroscopic data for **1c** do not allow unambigious assignment of the structure of the alkyl ligand. Full characterization data are given as supplementary material. Mechanistic details of the β-H elimination reactions will be reported separately (P. K. Bradley and R. F. Jordan, in preparation).

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°C and above yields the corresponding PMe_3 complexes $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ **2a–d** and free THF. Butyl derivative **2b** and phenethyl derivative **2d** undergo β-H elimination above 0 and −20 °C, respectively, in CH_2Cl_2, yielding the bis-PMe_3 hydride **4** and olefin in the presence of excess PMe_3 (the isomer **3** is the kinetic product, Scheme I). Ethyl complex **2a** decomposes slowly at 25 °C by a similar process. In THF solvent, **2b**,**d** decompose to yield mixtures of **4** and **1**.

The solid-state structure of **2a** was determined by X-ray diffraction at 170 K, Figure 1.[6] The acute Zr–Cα–Cβ angle (84.7 (5)°) and the short Zr–Cβ distance (2.629 (9) Å) establish the presence of a β-agostic interaction. The agostic β-hydrogen was located (Zr–H72a, 2.16 Å) and lies in the plane containing the Zr LUMO[7] as required for a three-center, $2e^-$ interaction. The Zr–Cα bond distance (2.290 (9) Å) is similar to those in related cationic complexes (e.g., $Cp_2Zr(CH_3)(THF)^+$, Zr–C = 2.256 (10) Å),[3b] while the Cα–Cβ bond (1.47 (2) Å) is shorter than the normal C–C single-bond length. The P1–Zr–C71 angle (73.6 (3)°) is significantly smaller than the expected value of 95–99° due to the β-agostic interaction.[8] The Et ligand in **2a** is structurally similar to those in the β-agostic complexes $Ti(dmpe)Cl_3Et$ and $Cp^*Co[P(p\text{-tol})_3](Et)^+$.[2e,j] IR studies confirm the β-agostic structure of **2a** in the solid state at ambient temperature. The IR spectrum of **2a** (Nujol) exhibits bands at 2395 and 2312 cm⁻¹, at the low end of the range exhibited by agostic C–H stretches.[1a] These bands are absent from the spectrum of THF complex **1a** and shift to 1750–1680 cm⁻¹ in the spectrum of the analogous $ZrCD_2CD_3^+$ complex **2a**-d_5.[9] The IR spectrum of Cp^*_2ScEt, which has been assigned a β-agostic structure, exhibits ν_{C-H} bands at 2593–2440 cm⁻¹.[10]

NMR spectroscopic studies establish that **2a–d** maintain β-agostic structures in solution and that exchange of agostic and terminal β-hydrogens is rapid.[11] For **2a–d**, high-field shifts of the β-CH_2R ^1H and ^{13}C NMR resonances (vs those of **1a–d**), and large values for $J_{C\alpha-H}$ (141–145 Hz for **2a–c**, 135 Hz for **2d**), consistent with significant sp^2 character at the α-C, are observed. For **2a**,**b**, ^{31}P coupling to the α and β hydrogens is also observed. Low-temperature ^1H NMR spectra (to −120 °C) of **2a–c** exhibit broadening of the alkyl and Cp′–CH_3 resonances but no splitting, indicating that exchange of the β-agostic and β-terminal hydrogens (rotation about the Cα–Cβ bond) is rapid. The observed $J_{C\beta-H}$ values for **2a** (124 Hz) and for **2b**,**c** (111, 110 Hz) are the expected averages of one or two large and one reduced J_{CH} values, consistent with rapid exchange of terminal and agostic β-hydrogens. Comparison of ^1H NMR spectra of **2b** and **2b**-d_1 reveals a substantial, temperature-dependent isotopic perturbation (δ($ZrCH_2CH_2Et$) − δ(ZrCH₂CHDEt) = 0.40 ppm at 0 °C, 0.63 ppm at −90 °C).[12] A similar effect is seen in the spectra of **2a** and **2a**-d_1 (δ($ZrCH_2CH_3$) − δ($ZrCH_2CH_2D$) = 0.13 ppm at 25 °C, 0.19 ppm at −60 °C).

Unlike most other reported β-agostic complexes, **2a–d** do not react with PMe_3 to yield bis-PMe_3 adducts with anagostic (normal) alkyl ligands (Scheme I). This may reflect the steric crowding in the expected $Cp'_2Zr(CH_2CH_2R)(PMe_3)_2^+$ products. However, the PMe_3 ligands of **2a–d** do undergo rapid associative exchange with free PMe_3 at ambient temperature. For comparison, the bis-PMe_3 complex $Cp_2Zr(Me)(PMe_3)_2^+$ can be isolated but undergoes extensive PMe_3 dissociation at ambient temperature.[13] Solutions of **2a** in CH_2Cl_2 catalyze ethylene polymerization.

The electronic properties of the ligand L exert a key influence on the structures and reactivity of $Cp_2Zr(R)(L)^+$ complexes.[13,14] In the 16-electron PMe_3 complexes **2a–d**, an empty orbital is available on Zr for coordination of a β C–H bond and for ultimate transfer of the β-H in the elimination reaction. In contrast, π-donation from the THF ligand in **1a**,**b**,**d** utilizes the Zr-centered LUMO, precluding an agostic interaction. This analysis, along with previous reports of agostic structures for Cp^*_2ScEt,[10] Hlatky and Turner's zwitterionic permethylzirconocene complex,[3f] and several other metallocene systems,[4,15,16] suggests that β-agostic interactions may be a general feature of the $Cp_2M(R)^+$ and $Cp_2M(R)(olefin)^+$ ions (R = growing polymer chain) which are believed to play a key role in metallocene-based olefin polymerization catalysts.[3] Such interactions may influence the relative rates of insertion and β-H elimination (chain propagation vs chain transfer) in these systems.[17] Also, β-agostic interactions may help determine the preferred conformation of the β-C of the growing polymer chain and thus may influence stereoselectivity in α-olefin polymerizations by chiral metallocene-based catalysts.[18,19]

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(6) Crystals of **2a** were obtained by slow cooling of a THF solution. Crystallographic data (170 K): a = 25.512 (4) Å, b = 10.247 (4) Å, c = 29.949 (6) Å, β = 113.70 (2)°, V = 6929.6 (5.8) Å³, Z = 8, space group $P2_1/n$; R_F = 0.058, R_{wF} = 0.093 for 3945 unique reflections with $I > 3\sigma(I)$. Structural parameters discussed in the text are for one of two unique molecules which differ slightly in the conformations of the Cp′ rings; structural parameters for the other are similar (Cα–Cβ, 1.52 (1) Å; Zr–Cα–Cβ, 83.0 (6)°). The β-agostic H atom H72a was located on electron density maps, but the terminal α- and β-H atoms were not. Their positions were calculated on the basis of that of H72a. A β-terminal H atom of the second unique molecule was found and its position used to calculate those of other α- and β-H atoms. The positions of the β-agostic H atoms of the two unique molecules, as determined in this manner, are similar.

(7) Leading references: (a) Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421. (b) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (c) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(8) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood, Ltd.: West Sussex, U.K., 1986.

(9) The IR spectrum of **2a**-d_5 also contains bands at 2260 and 2170 cm⁻¹ assignable to isotopically shifted Cα–D stretches.

(10) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(11) Key NMR data for **2a–d**. ^1H NMR: **2a** (CD_2Cl_2, 24 °C) δ 0.91 (quintet, $J_{HH} = J_{PH}$ = 8.5, $ZrCH_2$), −1.26 (td, J_{HH} = 8.6, J_{PH} = 5.4, $ZrCH_2CH_3$); **2b** (CD_2Cl_2, 0 °C) δ 0.87 (m, $ZrCH_2$), −1.93 (sx, $J_{HH} = J_{PH}$ = 6.7, $ZrCH_2CH_2Et$); **2c** (CD_2Cl_2, 25 °C) δ 1.28 (m, $ZrCH_2$), −2.15 (m, $ZrCH_2CH_2SiMe_3$); **2d** (CD_2Cl_2, −30 °C, rapid PMe_3 exchange) δ 1.14 (t, J_{HH} = 8.2, $ZrCH_2$), −0.05 (br t, J_{HH} = 8.2). ^{13}C NMR: **2a** (CD_2Cl_2, −50 °C) δ 26.5 (td, J_{CH} = 141, J_{CP} = 17, $ZrCH_2$), −7.6 (q, J_{CH} = 124, $ZrCH_2CH_3$); **2b** (THF-d_8, −80 °C) δ 33.1 (br t, J_{CH} = 143, J_{CP} = 15 from {^1H} spectrum, $ZrCH_2$), 11.2 (t, J_{CH} = 111, $ZrCH_2CH_2Et$); **2c** (CD_2Cl_2, −40 °C) δ 33.2 (t, J_{CH} = 143, $ZrCH_2$), −16.9 (t, J_{CH} = 110, $ZrCH_2CH_2SiMe_3$); **2d** (CD_2Cl_2, −30 °C, rapid PMe_3 exchange) δ 36.9 (br t, J_{CH} = 135, $ZrCH_2$), 19.4 (br t, J_{CH} = ca. 120, $ZrCH_2CH_2Ph$).

(12) The corresponding chemical shift difference between the THF analogues is 0.02 δ at 24 °C.

(13) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041.

(14) (a) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (b) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C., manuscript submitted.

(15) (a) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402. (b) Erker, G.; Fromberg, W.; Angermund, K.; Schlund, R.; Kruger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372. (c) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389. (d) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (e) Erker, G.; Zwettler, R.; Kruger, C.; Schlund, R.; Hyla-Kryspin, I.; Gleiter, R. *J. Organomet. Chem.* **1988**, *346*, C15.

(16) α-Agostic interactions have been observed in several metallocenes which lack β-hydrogens[16a,b] and have been invoked to explain electrochemical results for Cp_2WR_2 complexes.[16c] (a) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (c) Asaro, M. F.; Cooper, S. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 5187.

(17) The slower rate of ethylene insertion of Cp^*_2ScEt vs the corresponding Pr complex is ascribed to the β-agostic structure of the former complex. Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(18) (a) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Ewen, J.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (d) Erker, G.; Nolte, R.; Tsay, Y.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628. (e) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

(19) (a) In their XPS study of Cp_2ZrX_2/methylaluminoxane catalyst systems,[3e] Gassman and Callstrom observed formation of a species with Zr($3d_{5/2}$) binding energy of 182.4 eV after mixture of the catalyst precursors, followed by formation of a species with Zr($3d_{5/2}$) binding energy of 182.1 eV after ethylene addition. These species were proposed to be $Cp_2Zr(CH_3)^+$ and $Cp_2Zr(H)^+$, respectively. Our results support Brookhart's suggestion[19b] that the latter species is $Cp_2Zr(CH_2CH_2R)^+$ (R = polymer chain) which is stabilized by an agostic interaction. (b) M. Brookhart, private communication.

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Supplementary Material Available: Tables of spectroscopic and analytical data for **1a–d**, **2a–d**, **3**, and **4** and details of the X-ray structure determination for **2a** (25 pages); listing of observed and calculated structure factors for **2a** (15 pages). Ordering information is given on any current masthead page.

Solvolysis of 2-(Trifluoromethyl)-2-adamantyl Tosylate. Unexpectedly High Reactivity in Carbocation Formation

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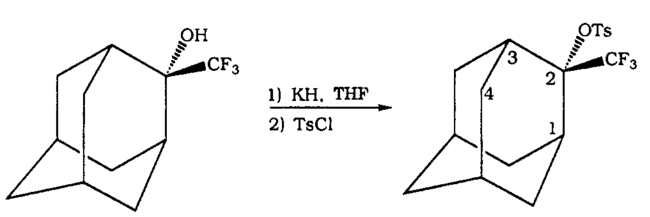
The destabilizing effect of the α-trifluoromethyl substituent on the formation of carbocations relative to hydrogen typically leads to rate decelerations $k(\mathrm{H})/k(\mathrm{CF_3})$ of up to 10^6, although these can be decreased in the presence of strong donor groups.[2] The 2-adamantyl system has been proposed to be a structure in which nucleophilic solvent stabilization of developing positive charge is minimized and carbocation character is maximized in solvolysis,[3] and therefore, this appeared to be a good place to seek a maximal $k(\mathrm{H})/k(\mathrm{CF_3})$ rate ratio. On the contrary, this system gives the smallest such ratio known to us.

2-(Trifluoromethyl)-2-adamantyl tosylate (**1**)[4] was obtained by treatment of the corresponding alcohol[5] with KH followed by TsCl. Solvolytic rate constants in four solvents (Table I) are well correlated by Y_{OTs}[6a] values at 25 °C by the relation $\log k = 0.940\,(\pm 0.069)\,Y_{\mathrm{OTs}} - 7.70\,(\pm 0.24)$, $r = 0.995$.

The major products (>90%) from the solvolysis of **1** in CF_3CO_2H and CF_3CD_2OD were the corresponding 3-(trifluoromethyl)-4-*exo*-protoadamantyl derivatives **3a**, together with 2% of unrearranged **1a**. Interruption of the solvolysis of **1** in CF_3CO_2H showed that rearrangement to the isomeric 3-(trifluoromethyl)-4-*exo*-protoadamantyl tosylate **3** occurs, and this reacts further to give the same product mixture of **1a** and **3a** (eq 1). Solvolytic rate constants measured beginning with pure **3** were the same as those observed for **1**, and ^{1}H NMR observation of the course of the reaction revealed that **1** converts to **3** at a rate 3 times more rapid than the rate of formation of **3a** from **3**. The results are interpreted in terms of the mechanism of eq 1 involving the ion pair **2**. The existence of equilibrating structures corresponding to the delocalized ion **2** is not excluded.



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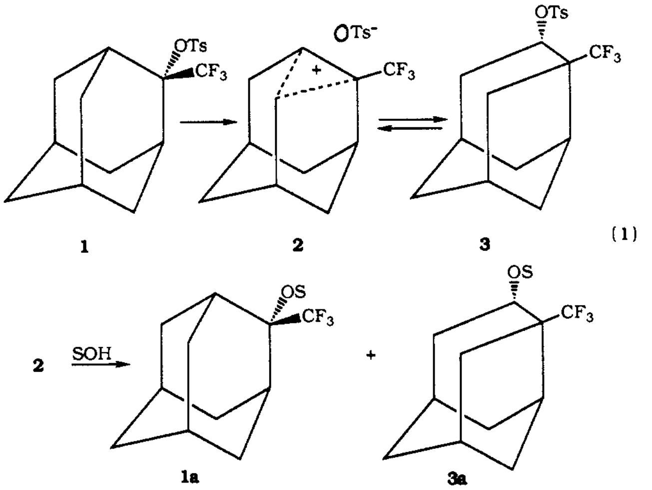
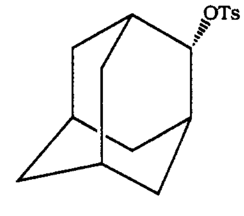


1 **2** **3** (1)

1a **3a**

The reactivity of **1** in the four solvents averages a factor of 2.0 less than that of 2-adamantyl tosylate (**4**), and the rate of **1** calculated for 100% TFE is 700 times greater than that[6b] of 2-cyano-2-adamantyl tosylate (**5**)! Both the small size of the $k(\mathrm{H})/k(\mathrm{CF_3})$ rate ratio $[k(\mathbf{4})/k(\mathbf{1})]$ and the $k(\mathrm{CF_3})/k(\mathrm{CN})$ ratio greater than unity are unprecedented; the smallest previous example of the former was 40,[2e] in the presence of the strongly donating pyrrolyl group, and the largest example of the latter was 0.02, in the doubly destabilized system $\mathrm{ArCR(OTs)CF_3}$.[2a]



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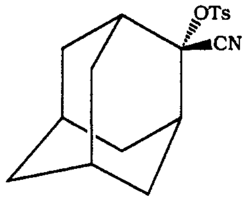

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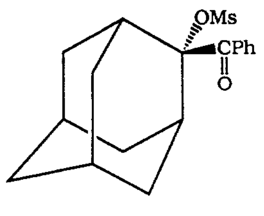

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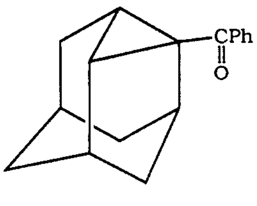

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Solvolysis of **4** in AcOH[3d,6e] and **5** in TFE[6b] give predominantly unrearranged products, with 0.4% and 9%, respectively, of the rearranged products corresponding to **3**. Reaction of **6** in several solvents also gave predominantly unrearranged products together with small amounts of the 1,3-elimination product **7**.[6c,d]

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(1) (a) University of Toronto. (b) University of Southern California.

(2) (a) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1986**, *108*, 3470–3474. (b) Allen, A. D.; Ambidge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *Ibid.* **1983**, *105*, 2343–2350. (c) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285. (d) Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1–44. (e) Kwong-Chip, J. M.; Tidwell, T. T. *Tetrahedron Lett.* **1989**, *30*, 1319–1322.

(3) (a) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538–2540. (b) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 2540–2542. (c) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 4628–4634. (d) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *Ibid.* **1974**, *96*, 2138–2148. (e) Fărcasiu, D. *Ibid.* **1976**, *98*, 5301–5305. (f) Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *Ibid.* **1977**, *99*, 5478–5480. (g) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244–1252.

(4) Mp 120–121 °C, characterized by ^{1}H and ^{13}C NMR, IR, high-resolution MS, and an X-ray crystal structure.

(5) Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393–395.

(6) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674. (b) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613–7615. (c) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151–4162. (d) Creary, X. *Ibid.* **1984**, *106*, 5568–5577. (e) Sinnott, M. L.; Storesund, H. J.; Whiting, M. C. *Chem. Commun.* **1969**, 1000–1001.

0002-7863/90/1512-1291$02.50/0