value of k_{az}/k_{solv} of 130 M^{-1} for the reaction of 1-(*p*-nitrophenyl)ethyl chloride requires $k_d > 130(k_{-d}' + k_s')$. An estimated rate constant[8] for diffusion of $k_d = 5 \times 10^9$ M^{-1} s^{-1} sets a limit of 5×10^7 s^{-1} on k_{-d}' and k_s'. The value of 5×10^7 s^{-1} for diffusional separation in water is unlikely, since when combined with a rate constant of 5×10^9 M^{-1} s^{-1} for encounter complex formation it gives an unreasonably large value of 10^2 M^{-1} for the equilibrium constant for ion-pair formation in water.[9]

The required value of $k_s' \leq 5 \times 10^7$ s^{-1} for the reaction of the carbocation–chloride anion pair of 1-(*p*-nitrophenyl)ethyl chloride is 10^6 times smaller than the extrapolated rate constant of $\sim 10^{14}$ s^{-1} for the reaction of the free carbocation with solvent.[10] A large decrease in reactivity for an intimate ion pair is unlikely in view of the similar reactivities of an intramolecular triarylmethyl carbocation–sulfonate anion ion pair and an analogous compound in which an uncharged sulfone is substituted for the sulfonate.[11]

(2) The rate-determining step for a preassociation reaction of reactive nucleophiles, with $k_{Nuc} > k_{-1}'$, is substrate ionization in the presence of Nuc, k_1'. The observed ρ^+ value for this step may be slightly less than ρ^+ for k_1 due to electrostatic interactions between azide and phenyl ring substituents in the encounter complex. An estimate for this interaction, $\rho = 1.1$ for the ionization of trifluoroacetophenone hydrates,[12] is substantially smaller than the observed change in effective charge as measured by $\rho^+(k_{az}) - \rho^+(k_{solv}) = 2.4$.[2] This shows that at least part of the increase in $\rho^+(k_{az})$ is due to bonding of azide to the central carbon atom in the transition state for the reaction of azide.

(3) The observed positive value of $\rho^+ = 2.4$ for k_{az}/k_{solv} is inconsistent with a diffusion-controlled trapping mechanism (k_d, Scheme I), because k_d is constant whereas k_s' should follow $\rho \geq 0$ with changing substituents on R^+Cl^-.

(4) The second-order rate constants for the reaction of nucleophiles by a stepwise mechanism through the ion-pair intermediate $Nuc{\cdot}R^+{\cdot}Cl^-$ will be independent of the nature of the nucleophile for a diffusion-controlled trapping mechanism (k_d rate determining) and for a preassociation mechanism when formation of the intermediate is rate determining ($k_{Nuc} > k_{-1}'$) and there is no nucleophilic assistance in the k_1' step. The intermediate $N_3^-{\cdot}R^+{\cdot}Cl^-$ will partition preferentially to products since azide is more nucleophilic than chloride, so that $k_{az} = K_{as}k_1'$. The intermediate $CN^-{\cdot}R^+{\cdot}Cl^-$ will also partition favorably to products since cyanide is at least as nucleophilic as chloride toward free carbocations,[13] so that k_{CN} will be ≥ 0.5 $K_{as}k_1'$. In fact, the values of k_{az} are up to 200 times larger than k_{CN}. This must reflect either a concerted pathway for k_{az} or nucleophilic assistance to substrate ionization, k_1'. If there is nucleophilic assistance at the time that the C–Cl bond is breaking, the reaction is S_N2 in the Ingold sense, unless there is an intermediate.

(5) Extrapolated "rate constants" for the reactions of substituted 1-phenylethyl carbocations with solvent range from 10^{10} s^{-1} for the *p*-F substituted compound to 10^{14} s^{-1} for the *p*-NO_2 compound.[10] Combining these values with a rate constant ratio k_{az}/k_s of 10^6 M^{-1} for the activation-limited reactions of azide and solvent with free carbocations[14] and an estimated association constant of $K_a = 0.1$ M^{-1} for ion-pair formation[9] (eq 1) gives a range of "rate constants" of $k_{Nuc} = 10^{17}$–10^{21} s^{-1} for the reaction of an encounter complex containing azide and a 1-phenylethyl carbocation intermediate. The rate constant for the reaction of the intimate ion pair is not expected to be substantially different.[11] These values exceed the frequency of a bond vibration. Thus a mechanism involving nucleophilic assistance to substrate ionization must be effectively a concerted mechanism, because the intermediate formed in the stepwise pathway cannot exist. In other words, the concerted mechanism is "enforced".

$$R^+ + N_3^- \underset{}{\overset{K_a}{\rightleftharpoons}} R^+{\cdot}N_3^- \xrightarrow{k_{Nuc}} R{-}N_3 \qquad (1)$$

Registry No. 1-(*p*-Nitrophenyl)ethyl chloride, 19935-75-2; CN^-, 57-12-5; N_3^-, 14343-69-2.

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(8) Reference 2, footnote 13.

(9) Davies, C. W. "Ion Association"; Butterworth: London, 1962; pp 77–87.

(10) Reference 2, Figure 1.

(11) Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039–7044.

(12) Stewart, R.; Van der Linden, R. *Can. J. Chem.* **1960**, *38*, 399–406.

(13) The N^+ value for cyanide in water is 3.8 (Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966–4971). Values of log k_{Cl^-}/k_s (M^{-1}), obtained by analysis of the common ion effect on the solvolysis of alkyl chlorides in mixed aqueous/organic solvents are 10^2–10^3 M^{-1} (Bateman, L. C.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1940**, 974–978. Swain, C. G.; Scott, C. B.; Lohmann, K. H. *J. Am. Chem. Soc.* **1953**, *75*, 136–140. Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *Chem. Commun.* **1966**, 122–123. Royer, R. E.; Daub, G. H.; Vander Jagt, D. L. *J. Org. Chem.* **1979**, *44*, 3196–3201.).

(14) Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536–3544. Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354.

Actinide Tris(hydrocarbyls). Synthesis, Properties, Structure, and Molecular Dynamics of Thorium and Uranium Pentamethylcyclopentadienyl Tris(η^n-benzyls)

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The chemical characteristics of actinide-to-carbon σ bonds are a sensitive function of the number and nature of the other ligands within the metal coordination sphere (cf. $M(\eta^5\text{-}C_5H_5)_3R$ vs. $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ chemistry).[1] In our continuing effort to "tune" the actinide ligation environment with respect to such factors, we have recently explored approaches to the unknown and potentially highly coordinatively unsaturated class of compounds containing a single permethylcyclopentadienyl ligand and three hydrocarbyl functionalities ($M[\eta^5\text{-}(CH_3)_5C_5]R_3$).[2] We report here on the synthesis, unusual molecular structure(s), and other interesting properties of the first members of this series, the trisbenzyl derivatives of thorium and uranium.[3]

The precursor complexes $M[\eta^5\text{-}(CH_3)_5C_5]Cl_3{\cdot}2THF$ (M = Th, U) were synthesized (60–80% isolated yield) as shown in eq 1.[4]

$$MCl_4 + Mg[(CH_3)_5C_5]Cl{\cdot}THF \xrightarrow[\text{(2) } CH_2Cl_2\text{/excess dioxane}]{\text{(1) THF, 25 °C, 8 h}} M[\eta^5\text{-}(CH_3)_5C_5]Cl_3{\cdot}2THF + MgCl_2(C_4H_8O_2) \qquad (1)$$

1,M = Th, colorless crystals
2,M = U, dark red needles

Purification was accomplished by evaporation of the solvent, followed by extraction of the residue with CH_2Cl_2/dioxane (>20 equiv of dioxane), filtration, and recrystallization from cold (−78 °C) THF/pentane.[4b] The new complexes were characterized by

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(1) (a) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, in press. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J. In "Organometallics of the f-Elements"; Marks, T. J., Fischer, R. D., Eds.; Reidel Publishing: Dordrecht, Holland, 1979; Chapter 4. (c) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 224–333. (d) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(2) See ref 1b for preliminary studies (e.g., $Th[\eta^5\text{-}(CH_3)_5C_5][CH_2Si(CH_3)_3]Cl_2$).

(3) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D.C., 1981; INOR 224.

(4) (a) Bagnall, K. W.; Beheshti, A.; Heatley, F.; Tempest, A. C. *J. Less-Common Met.* **1979**, *64*, 267–275 ($(CH_3)_4(C_2H_5)C_5$ analogues). (b) Fagan, P. J.; Manriquez, J. M.; Mintz, E. A.; Moloy, K. G.; Marks, T. J., to be submitted for publication.

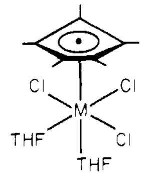
0002-7863/82/1504-4692$01.25/0

Table I. NMR Data for Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ (**3**) and U[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ (**4**)[a,b]

	temp,	η^5-$(CH_3)_5C_5$			benzyl											
compd	°C	H_{Me}	C_{Me}	C	H_A	$H_{A'}$	H_C	$H_{C'}$	H_D	$H_{D'}$	H_E	C_A	C_B	C_C $C_{C'}$	C_D $C_{D'}$	C_E
3	25	2.32	12.6	145.2	1.22		6.40 (d, 7)		7.05–7.4 (m)			80.4	69.1	125.9	131.9	122.7
			(q, 127)									(t, 134)		(d, 152)	(d, 162)	(d, 160)
	−92	2.32			0.32	2.13	6.06	6.74	7.06–7.7							
4	25	−0.44	−54.1	5.10	3.52		−21.15		6.56		−0.16	1129	51.6	72.0	158.9	180.0
			(q, 122)				(d, 4.0)		(t, 3.5)		(t. 3.5)	(t, 134)		(d, 159)	(d, 159)	(d, 159)
	−92	−2.55			1.50		−12.2	−106.5	29.7	33.7	−1.52					

[a] All chemical shifts relative to internal Me_4Si. Relative intensities are those appropriate for the assignments. [b] Quantities in parentheses are multiplicities (d = doublet, t = triplet, q = quartet) followed by observed coupling constants ($^3J_{H\text{-}H}$, $^1J_{C\text{-}H}$, Hz).

standard techniques;[5] ^1H NMR spectra suggest the pseudooctahedral structure A established previously for U(η^5-$CH_3C_5H_4$)-



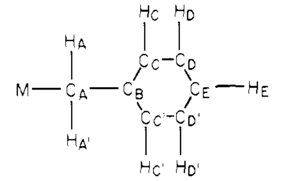
A

Cl_3·2THF.[6] Alkylation of **1** and **2** with benzyllithium proceeds cleanly (40–75% isolated yield; eq 2) and the resulting trisbenzyl

$$M[\eta^5\text{-}(CH_3)_5C_5]Cl_3\cdot 2THF + 3LiCH_2C_6H_5 \xrightarrow[\text{(1) }-78\ ^\circ\text{C, 1 h; (2) 25 }^\circ\text{C, 3 h}]{\text{THF}} M[\eta^5\text{-}(CH_3)_5C_5](CH_2C_6H_5)_3 + 3LiCl + 2THF \quad (2)$$

3, M = Th, yellow crystals
4, M = U, black crystals

compounds can be isolated by evaporation of the THF, extraction with toluene, and subsequent, repeated recrystallization from toluene/diethyl ether at −78 °C. The new compounds were characterized by infrared and ^1H and ^{13}C NMR spectroscopy, elemental analysis,[7] and in the case of **3**, by single-crystal X-ray diffraction (vide infra). Infrared spectra[8] are in accord with metal-bound benzyl functionalities and η^5-$(CH_3)_5C_5$ ligands.[1d,9] Room-temperature ^1H, ^{13}C, and $^{13}C\{^1H\}$ NMR spectra (Table I) indicate π-bonded cyclopentadienyl units and magnetically equivalent, mirror-symmetrical benzyl ligands (B).



B

The $5f^2$ uranium complex exhibits large isotropic shifts and relatively narrow line widths; the comparatively small displacement of the H_A resonance despite the close proximity to the U(IV) ion suggests (along with the large displacement of C_A) a fortuitous cancellation of contact and dipolar terms.[1d,10a,b] Variable-temperature ^1H NMR studies (e.g., **3** in Figure 1) indicate that the instantaneous

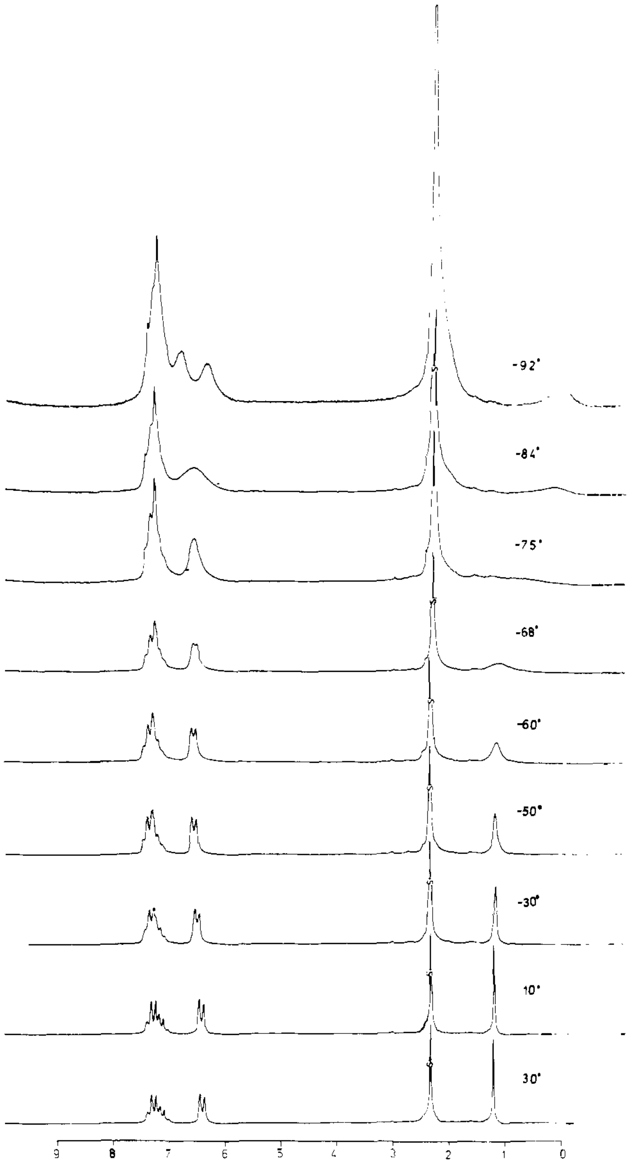


Figure 1. Variable-temperature ^1H NMR spectra (FT, 90 MHz) of a solution of Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ in toluene-d_8.

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(5) (a) IR (Nujol, cm^{-1}) (**1**) 1343 w, 1297 w, 1248 w, 1175 w, 1039 m, 1005 s, 952 w, 922 m, 853 s, 720 w, 668 m; (**2**) 1344 w, 1298 w, 1247 w, 1171 w, 1040 m, 1007 s, 952 w, 925 m, 858 s, 722 m, 680 m, 612 w, 522 w. (b) NMR ($CDCl_3$, 90 MHz) δ (**1**) 1.96 (8 H, m, br), 2.27 (15 H, s), 4.13 (8 H, m, br); (**2**) −9.67 (4 H, br), −5.38 (4 H, br), −3.16 (4 H, m, br), 10.35 (4 H, m, br)), 17.34 (15 H, br). (c) **1**: Anal. Calcd for $C_{18}H_{31}ThCl_3O_2$: C, 34.99; H, 5.06; Cl, 17.21; Mg, 0.00. Found: C, 35.01; H, 5.15; Cl, 17.10; Mg, 0.03. **2**: Anal. Calcd for $C_{18}H_{31}UCl_3O_2$: C, 34.66; H, 5.01; Cl, 17.05; Mg, 0.00. Found: C, 34.89; H, 5.13; Cl, 16.98; Mg, 0.01.

(6) (a) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656–2664. (b) The structure of Zr(η^5-C_5H_5)Cl_3(1,2-dimethoxyethane) is similar: Wells, N. J.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1981**, *213*, C17–C20. (c) The structure of Er(η^5-C_5H_5)Cl_3·2THF is also similar: Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics*, in press.

(7) **3**: Anal. Calcd for $C_{31}H_{36}Th$: C, 58.11; H, 5.67. Found: C, 57.95; H, 5.83. **4**: Anal. Calcd for $C_{31}H_{36}U$: C, 57.57; H, 5.62. Found: C, 57.86; H, 5.83.

(8) IR (Nujol, cm^{-1}) (**3**) 3043 w, 1588 s, 1553 w, 1293 w, 1209 m, 1090 w, 1021 m, 893 m, 840 m, 792 s, 739 s, 696 s; (**4**) 3050 w, 1570 ms, 1295 w, 1258 w, 1210 m, 1170 w, 1020 m, 895 m, 840 m, 790 ms, 740 s, 692 s.

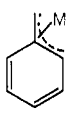
(9) (a) Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley-Interscience: New York, 1977; p 34. (b) Brüser, W.; Thiele, K.-H.; Zdunneck, P.; Brune, F. *J. Organomet. Chem.* **1971**, *32*, 335–341 (Th$(CH_2C_6H_5)_4$).

(10) (a) Fischer, R. D., in ref 1b, Chapter 11. (b) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529–5539 and references therein. (c) In the −93 °C ^1H spectrum of **4**, one of the benzylic (H_A, $H_{A'}$) proton resonances appears to be coincident with the CHD_2 signal of the solvent.

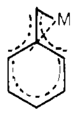
benzyl coordination environment is of lower symmetry than indicated in the 25 °C spectrum. At −92 °C (Table I), the benzyl ligands in **3** and **4** appear magnetically equivalent but lack C_s local symmetry (A ≠ A′, C ≠ C′, D ≠ D′). The precise reason for the nonequivalence follows from the structural study of **3**.[10c]

Single crystals of Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$, grown by slow evaporation of a toluene solution, are tetragonal at 20 ± 1 °C with space group $I4_1/a$-C_{4h}^6 (No. 88), a = 16.785 (4) Å, c = 37.427 (7) Å, and Z = 16 (ρ_{calcd} = 1.614 g cm^{-3}; μ_a (Mo K$\bar{\alpha}$) = 5.87 mm^{-1}). Three-dimensional X-ray diffraction data were collected for 6051 independent reflections having $2\theta_{Mo K\bar{\alpha}}$ <55° on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (0.90° wide) ω scans. The structure was solved by using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence [R (unweighted, based on F) = 0.050 for 2479 independent absorption-corrected reflections havng $I > 3\sigma(I)$ and $2\theta_{Mo K\bar{\alpha}}$ <55°] by using empirically weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms. All calculations were performed on a Data General Eclipse S-200 computer using locally modified versions of the Nicolet EXTL interactive software system.

The structural analysis reveals that the crystal is composed of discrete, mononuclear Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ units (Figure 2). The Th(IV) ion is π bonded to a pentamethylcyclopentadienyl ligand with unexceptional internal dimensions (C–C = 1.43 (3, 2, 3, 5) Å, C–CH_3 = 1.51 (3, 1, 3, 5) Å, all ring carbon atoms coplanar to within 0.02 Å) and Th–C contacts (2.79 (2, 2, 4, 5) Å).[11,12] Although the internal structure of the benzyl ligands is not unusual (C_1–C_2 = 1.47 (3, 2, 4, 3) Å, aromatic C–C = 1.40 (3, 3, 6, 18) Å, all carbons coplanar to within 0.05 Å), the η^n mode of ligation is. Thus, the magnitude of the metal–ligand metrical parameters (Figure 2) suggests that the bonding is not as localized as in typical middle and late transition metal[13] or lithium[14] η^3-benzyls (C). Rather, the bond distances and angles are more in accord with a strong Th–C_1 σ interaction[15,16] (ca. 60% of the benzyl$^-$ negative charge is localized on C_1[17]) together with a more diffuse, unsymmetrical secondary interaction involving the C_2,C_3,C_7 part of the π system (D) (ca. 30% of the benzyl$^-$ charge is localized on C_3,C_7[17]). The relatively narrow range of Th–C_1 and ∠Th–C_1–C_2 parameters together with the greater range of Th–C_2,C_3,C_7 contacts suggests that the potential-energy surface for the latter interaction is relatively flat; this is in accord with the dynamic NMR results. Interestingly, the structures of M$(CH_2C_6H_5)_4$, M = Ti, Zr, Hf,[18] exhibit similar distortions from classical η^1-benzyl structures (as in Sn$(CH_2C_6H_5)_4$[18c]), although nothing is known about the molecular dynamics.



C



D

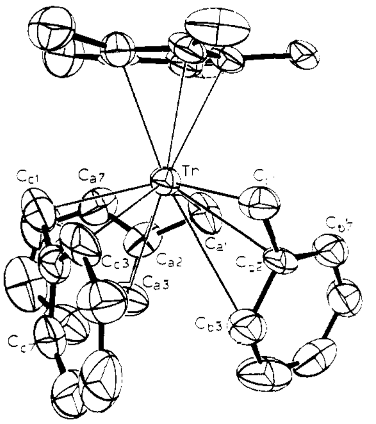


Figure 2. Perspective ORTEP drawing of the nonhydrogen atoms in Th[η^5-$(CH_3)_5C_5$]$(CH_2C_6H_5)_3$ (**3**). All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. Important metal–ligand bond distances are as follows (Å): Th–C_{a1} = 2.581 (19), Th–C_{b1} = 2.579 (17), Th–C_{c1} = 2.578 (21) (2.58 (2, 0, 0, 3) average[12a]); Th–C_{a2} = 2.913 (18), Th–C_{b2} = 2.865 (18), Th–C_{c2} = 2.979 (18) (2.92 (2, 4, 6, 3) average[12a]); Th–C_{a3} = 3.413 (21), Th–C_{b3} = 3.352 (19), Th–C_{c3} = 3.325 (18) (3.36 (2, 3, 5, 3) average); Th–C_{a7} = 3.501 (20), Th–C_{b7} = 3.574 (19), Th–C_{c7} = 3.852 (20), Th–C(cyclopentadienyl) = 2.79 (2, 2, 4, 5)[12a] average. Important bond angles are as follows (deg): Th–C_{a1}–C_{a2} = 87 (1), Th–C_{b1}–C_{b2} = 86 (1), Th–C_{c1}–C_{c2} = 91 (1); C_{a1}–Th–C_{b1} = 112.6 (6), C_{a1}–Th–C_{c1} = 116.2 (6), C_{b1}–Th–C_{c1} = 117.3 (6); C_g–Th–C_{a1} = 104.9, C_g–Th–C_{b1} = 99.1, C_g–Th–C_{c1} = 103.7.[12b]

For **3** and by inference **4**, it appears that the solid-state symmetry (nonequivalent benzyl ligands) is slightly lower than surmised in solution or that a second averaging process is still rapid at −90 °C. At higher temperatures, the dynamic process observed ($\Delta G_c^\ddagger$ = 9.1 ± 0.3 and 8.5 ± 0.2 kcal/mol for **3** and **4**, respectively) can be ascribed to $\eta^n \rightleftharpoons \eta^1 \rightleftharpoons \eta^n$ equilibration[19] (with rapid rotation about M–C_1 and/or C_1–C_2 in the η^1 state) or to combined (in view of the low symmetry of the Th–benzyl ligation) rotation of the benzyl units about the M–C_2 axes and suprafacial M shifting.[13f]

The chemistry of **3** and **4** is currently under investigation. With polarity-sensitive reagents such as alcohols and formaldehyde, rapid reaction occurs at room temperature to yield the corresponding M[η^5-$(CH_3)_5C_5$]$(OR)_3$ and M[η^5-$(CH_3)_5C_5$]$(OCH_2CH_2C_6H_5)_3$ derivatives, respectively. Reaction with H_2 and CO is rapid, the former cleanly producing toluene and what we presume[1d] to be hydrides, while the latter results in complex mixtures of oxygenates. Further studies with these and other actinide tris(hydrocarbyls) are in progress.

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(11) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220. (b) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112–7114.

(12) (a) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value. (b) C_g refers to the center of gravity for the five-membered ring of the $(CH_3)_5C_5^-$ ligand.

(13) (a) Cotton, F. A.; La Prade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418–5422. (b) Sonada, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 346–350. (c) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 399–434. (d) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 435–450. (e) Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt, B. C. *Inorg. Chem.* **1981**, *20*, 1316–1318. (f) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics*, **1982**, *1*, 188–197.

(14) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150–1157.

(15) Compare, Th–C(σ) = 2.484 (12, 27, 27, 2) Å in Th[η^5-$(CH_3)_5C_5$]$_2$[$CH_2Si(CH_3)_3$]$_2$ and 2.474 (14, 11, 11, 2) Å in Th[η^5-$(CH_3)_5C_5$]$_2$$(CH_2)_2Si(CH_3)_2$: Bruno, J. W.; Marks, T. J.; Day, V. W., submitted for publication.

(16) (M–C_3)–(M–C_1) differences fall in the range 0.060–0.38 Å for typical η^3-benzyls.[13,14]

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Supplementary Material Available: Tables of fractional atomic coordinates and of anisotropic thermal parameters for nonhydrogen atoms of $Th[\eta^5\text{-}(CH_3)_5C_5](CH_2C_6H_5)_3$ (**3**) (2 pages). Ordering information is given on any current masthead page.

Fluoride-Promoted, Dye-Sensitized Photooxidation of Enols

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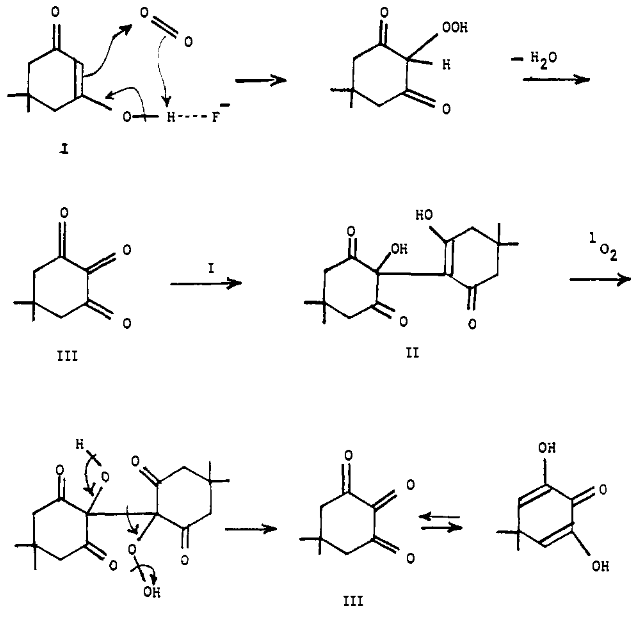
Among the reactions of singlet oxygen ($^1O_2$) with organic substrates, additions to carbon–carbon double bonds provide methods for the oxygenation of many types of compounds that have had numerous applications in synthesis.[1,2] The reactions of the electrophilic $^1O_2$ take place most readily with electron-rich systems such as enamines,[3,4] enol ethers,[5] and highly substituted olefins,[6] and the oxygenations of these substrates have been extensively investigated. By contrast, enolic tautomers of carbonyl compounds have received very little attention in singlet oxygen reactions beyond the observations that a few such compounds react slowly with $^1O_2$ to yield cleavage products.[7]

Recent findings showing that fluoride ion enhances the nucleophilicity of enols in alkylation and condensation reactions[8] prompted us to investigate the possibility of a related effect in enol–singlet oxygen reactions. It might be anticipated that hydrogen bonding or other electron-releasing phenomena associated with fluoride ion participation could operate to facilitate uptake of electrophilic $^1O_2$ by the donor enol component.

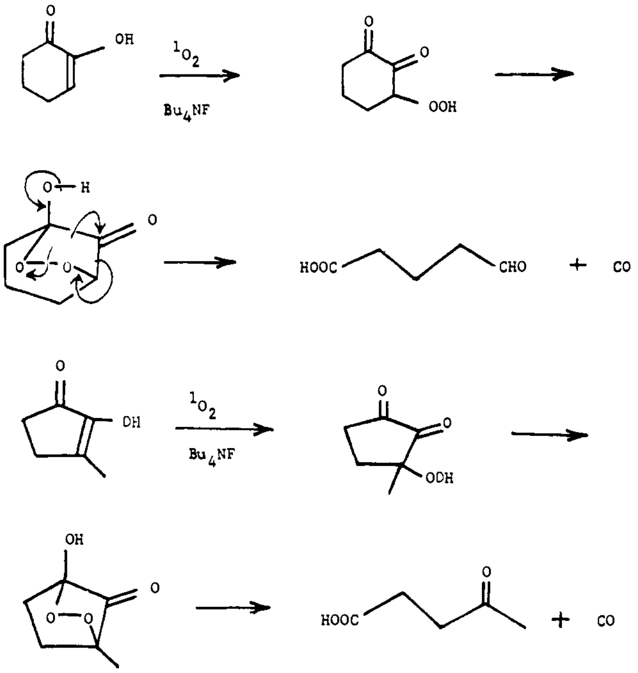
We now report a remarkable fluoride ion effect taking place in the reactions of a series of enolic compounds with $^1O_2$. Among the substrates are β-diketones, β-keto esters, and α-diketones. As is summarized in Table I, dye-sensitized photooxidations of all of these systems proceeded very sluggishly or failed completely in the absence of fluoride ion. In the presence of fluoride, however, the photooxidations were complete within a few hours, yielding ketonic products or other derivatives resulting from α-hydroperoxide formation.

In a typical procedure, the compound was dissolved in chloroform, tetrabutylammonium fluoride (1.1 equiv, as a 1 M solution in ethanol) was added, and the solvent was evaporated. The resulting oil was taken up in chloroform and injected into a dried, oxygen-purged well. Polymer-bound rose bengal[10] was added, and the solution was irradiated with visible light (650-W tungsten-halogen lamp, Pyrex-filtered) at 0 °C while O_2 was circulated. The course of the reaction was followed by O_2 uptake and by thin-layer chromatography. Workup consisted of filtration to remove the sensitizer and evaporation of solvent, followed by either partition between ether and water or chromatography on silica gel with chloroform.

Scheme I



Scheme II



Photooxidation of the β-dicarbonyl compounds shown in the table most probably takes place by an initial "ene"-type reaction followed by dehydration to a tricarbonyl compound which may then undergo hydration or enolization. With certain of the β-diketones studied, the triketone first formed appeared to take part in a second-stage reaction with unreacted starting material to yield an isolable intermediate. This product then underwent further oxygenation with $^1O_2$. This sequence is illustrated in the case of dimedone (I) (Scheme I) where oxidation with $^1O_2$ yielded the enolized triketone (III). Interruption of the reaction yielded II (the addition product of I and III), mp 133–134 °C,[12] which could

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(12) Product II, fully characterized by NMR, IR, and elemental analysis, could be prepared by addition of dimedone I to the triketone III.