Table I. The Inactivation of Acetylcholinesterase by
Decamethoxonium[a]

Experiment no.	$II\text{-}(PF_6)_2$ (μM)	V_i/V_0
1	0.5	<0.05
	0.25	0.05
	0.05	0.37
	0.025	0.46
	0.005	0.69
	0.0025	0.89
2[b]	2.5	<0.05
	2.5	0.50
3[c]	0.50	0.14
	0.50	0.78

[a] A small aliquot of a freshly prepared 20 mM II-(PF$_6$)$_2$ in dry nitromethane was vigorously mixed with ice-cold water. A minute or less later, a small aliquot of this aqueous solution was added to electric eel acetylcholinesterase (type V, Sigma Chemical Co.) in 1 mM potassium phosphate buffer, pH 7.0, at 2°. After 2 hr or more, an aliquot of the modified enzyme solution was assayed for activity by measuring the rate of hydrolysis of acetylcholine as described in ref 6. The extent of inactivation is expressed as the ratio of the rate with the treated enzyme (V_i) to that with the same amount of untreated enzyme (V_0). The initial concentration of acetylcholinesterase in the modification reaction mixtures, calculated on the basis of the specific activity of the purified enzyme (ref 7), was about 0.0015 μM. When the reagent was allowed to hydrolyze in buffer and then the enzyme was added, no inactivation occurred. [b] The first entry is the result of treatment with II in the presence of 10 mM NaCl, and the second entry is the result of treatment with II in the presence of 10 mM tetramethylammonium chloride. [c] Same as b, except 20 mM NaCl and tetramethylammonium chloride.

(3.0 ml) were added to a solution of 7.7 g of dry silver hexafluorophosphate (Cationics, Inc.) in 30 ml of dry 1,2-dichloroethane. The mixture was stirred for 1 hr, and the precipitate (a mixture of silver iodide and II-(PF$_6$)$_2$) was collected on a sintered-glass funnel. The precipitate was mixed with 10 ml of dry nitromethane. The slurry was filtered through a fine-sintered-glass funnel, and 50 ml of dry 1,2-dichloroethane was added to the filtrate. This mixture was put in a desiccator over P$_2$O$_5$, and the desiccator was placed at $-20°$ for several hours. Colorless crystals of II-(PF$_6$)$_2$ formed. They were collected rapidly by suction filtration and were stored at 2° in a desiccator over P$_2$O$_5$. The yield was 3.2 g. The compound was recrystallized from nitromethane-1,2-dichloroethane in the same way. Analysis for C, H, F, and P gave 32.3, 5.7, 43.6, and 11.8%, respectively; the theoretical values are 32.2, 6.1, 43.7, and 11.9%. The pmr spectrum, taken within 15 min after solution in dry deuterated nitromethane, was the following, expressed as δ (apparent multiplicity, relative integrated intensity, assignment to hydrogen atoms in the compound): 0.78 (broad singlet, 12 H, -[CH$_2$]$_6$-), 1.43 (multiplet, 4 H, OCH$_2$CH_2), 3.88 (singlet, 12 H, [CH$_3$]$_2$O), 4.20 (triplet with $J = 7$ Hz, 4 H, OCH$_2$). The signals in this spectrum are the ones expected on the basis of the pmr spectrum of the related ion, dimethylethyloxonium ion.[5] II-(PF$_6$)$_2$ dissolves in water only very slowly. Aqueous solutions were prepared by dissolving it in dry nitromethane, in which it dissolves in a few seconds, and vigorously mixing a small aliquot of the concentrated solution in nitromethane with water. Trialkyloxonium ions react rapidly with water to yield an ether, an alcohol, and hydronium ion.[2] The rate of hydrolysis of 0.15 mM II-(PF$_6$)$_2$ in 1% nitromethane at pH 7.0 and 5.5° was followed in a pH-stat apparatus. The reaction was first-order with a half-time of 5 min; 2 equiv of base were consumed. We have also synthesized the tetrafluoroborate salt of II by a procedure identical with that for the preparation of the hexafluorophosphate salt, except for the substitution of dry silver tetrafluoroborate (Cationics, Inc.) for silver hexafluorophosphate.[3]

The data in Table I show that II is an extremely potent inactivating agent against eel acetylcholinesterase. It causes about 50% inactivation when present at an initial concentration of 0.025 μM (experiment 1). Tetramethylammonium ion, a competitive inhibitor of the enzyme with a dissociation constant of 1.2×10^{-3} M,[8] blocks the irreversible inactivation by II (experiment 2 and 3). These results suggest that II acts by alkylation of a group at the active site. Other studies[1] have indicated that the high affinity of acetylcholinesterase for decamethonium is due to decamethonium bridging the active site and a peripheral anionic site. Thus, II may also alkylate the peripheral site. We have reported earlier that the monofunctional reagent, trimethyloxonium ion, inactivates the enzyme at concentrations near 1 mM.[6]

Another protein that has a high affinity for decamethonium is acetylcholine receptor. The value of the dissociation constant for I with solubilized receptor from *Electrophorus electricus* is 2×10^{-8} M.[9] The binding of I is competitive with the binding *Naja naja* α-neurotoxin.[10] We have examined the effect of II upon the capacity of purified receptor from *Electrophorus electricus*[10] to bind α-neurotoxin. This activity was measured using radioactively labeled toxin in the antibody precipitation assay that has been reported previously.[11] Treatments of 10^{-8} M receptor at pH 7.4 and 4° with II at initial concentrations of 5.0, 0.50, and 0.05 mM resulted in the loss of 98, 60, and 10% of the toxin-binding activity, respectively. We then determined the ability of decamethonium to protect against inactivation of receptor by II. At a concentration of 5 mM, decamethonium reduced the extent of inactivation produced by 0.5 mM II from 60 to 20%.

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Isolation and Structural Characterization of a μ-Di(η^5:η^1-cyclopentadienyl)dithorium(IV) Complex

Sir:

Considerable interest has recently been focused on those factors which determine the stability of both d and f transition metal to carbon σ bonds.[1-4] Studies of organometallic decomposition mechanisms have principally involved exam-

Table I. Positional and Thermal^a Parameters for Nonhydrogen Atoms

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th	0.3169 (1)	0.3536 (1)	0.0 (0)	70.0 (14)	64.3 (15)	26.3 (6)	4.6 (17)	0.0 (0)	0.0 (0)

	x	y	z	B			x	y	z	B
C11^b	0.577 (3)	0.341 (3)	0.0 (0)	1.4 (5)	C22		0.278 (3)	0.084 (3)	0.888 (2)	5.2 (6)
C12	0.170 (3)	0.146 (3)	0.578 (2)	4.4 (5)	C23		0.147 (3)	0.180 (3)	0.876 (2)	6.5 (8)
C13	0.317 (4)	0.142 (3)	0.536 (2)	6.8 (9)	C24		0.187 (3)	0.313 (3)	0.826 (2)	5.7 (6)
C21	0.381 (3)	0.168 (3)	0.841 (2)	4.4 (5)	C25		0.329 (3)	0.306 (3)	0.807 (2)	5.5 (6)

^{a} The anisotropic thermal parameters are multiplied by 10^4. ^{b} The subscripts on carbon atoms specify first the ring number and then the atom number. Ring 1 is the bridging ring with C11 bonded to both thorium atoms.

ination of organic reaction products; in many cases the nature of the metal-containing product, essential to a complete understanding of the reaction, has remained unclear. The remarkably thermally stable actinide organometallics, $(\eta^5\text{-}C_5H_5)_3U\text{-}R^{5-7}$ and $(\eta^5\text{-}C_5H_5)_3Th\text{-}R$,[8] R = alkyl or aryl group, thermolyze predominantly via intramolecular abstraction of a cyclopentadienyl hydrogen to yield $R\text{-}H$.[5,8] We report here the isolation and structural characterization of the thorium-containing $(C_5H_5)_3Th\text{-}R$ thermolysis product.[9] Besides affording a complete delineation of the thermolysis reaction species, the structure and mode of formation of this unique organoactinide may be of considerable consequence in understanding certain aspects of transition metal $\eta^5\text{-}C_5H_5$ chemistry.

Toluene solutions of $(C_5H_5)_3Th(n\text{-}Bu)$ at 170° slowly deposit colorless crystals which analyze as $[(C_5H_5)_2ThC_5H_4]_2$;[10] the yield is essentially quantitative.

Several crystals were carefully sealed in thin-walled glass capillaries under a nitrogen atmosphere for X-ray diffraction analysis. They were found to conform to the orthorhombic space group *Pnnm* with unit cell dimensions a = 9.758 (4), b = 8.528 (3), and c = 14.397 (5) Å. The calculated density for four formula units per unit cell was 2.45 g cm^{-3}. Data were measured out to 2θ = 55° on a Picker four-circle automatic diffractometer using a θ-2θ scan technique and monochromatic Mo $K\alpha$ radiation. As the linear absorption coefficient is 191.3 cm^{-1}, the data were corrected for absorption effects. The structure was solved by heavy atom techniques. Refinement has resulted in a weighted R factor of 0.07 for the 790 independent reflections with $F^2 \geq 3\sigma(F^2)$. Positional and thermal parameters for the nonhydrogen atoms are listed in Table I.

The molecular structure is that of a dimeric complex. Each thorium is π (η^5) bonded to three cyclopentadienyl rings as well as σ bonded to one of the cyclopentadienyl rings of the other thorium (Figure 1). The bridging unit thus consists of two thorium atoms and two η^1:η^5 cyclopentadienyl rings. The thorium and bridging carbon atoms lie on a crystallographic mirror plane. Perpendicular to this plane and passing through the center of the dimer is a crystallographic twofold axis, so that the two halves of the complex are twofold related and the dimer as a whole possesses C_{2h} point symmetry.

The coordination about the thorium is approximately the same as in other actinide $Ac(C_5H_5)_3X$ structures.[11,12] The centers of the rings and the σ-bonded carbon form the apices of an approximate tetrahedron with the inter-ring angles ranging from 115 to 122°. The angle from the bridging carbon to the center of the other bridging ring is 68.5° due to the steric requirements of the bridge. The terminal C_5H_5 rings are planar within 0.02 Å and equidistant from the metal, with an average Th-C distance of 2.83 Å. This can be compared with the uranium-carbon distance of 2.68 Å in $U(C_5H_5)_3C \equiv C_6H_5$,[12] which also has three π-bonded rings and a σ bond. The bridging C_5H_4 ring is not as well defined and shows greater fluctuation in Th-C distances.
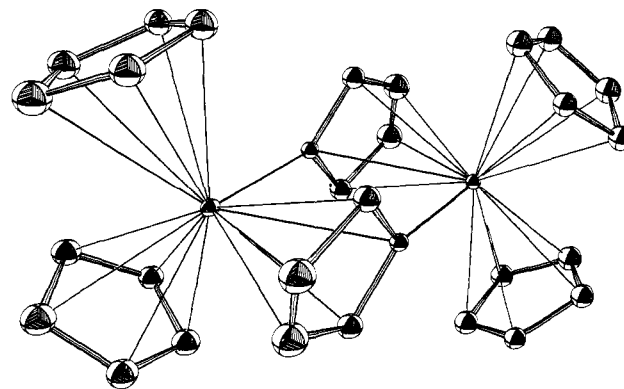

Figure 1. A perspective view of the μ-di(η^5:η^1-cyclopentadienyl)dithorium(IV) complex, $[Th(C_5H_5)_2(C_5H_4)]_2$.

The Th-C σ bond length is 2.55 Å and represents the first determination of a metal-carbon σ bond distance for a thorium compound.

Thorium organometallic compounds have not been extensively investigated to date. Structural data exist for bis(cyclooctatetraene)thorium,[13] but the present structure represents the first cyclopentadienyl complex of thorium studied by X-ray diffraction methods and the first ligand-bridged organoactinide dimer. As with most of the uranium organometallics, the thorium is formally ten coordinate but achieves coordinative saturation in an unusual way, via ring metalation, heretofore unobserved in organoactinides or lanthanides.

The transformation of $(\eta^5\text{-}C_5H_5)M$ functionalities to $M\text{-}(\eta^5\text{:}\eta^1\text{-}C_5H_4)_2M$, $M\text{-}(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)M$, and related systems is now recognized as an important facet of low-valent organotransition metal chemistry.[14-22] The present work indicates that it may be equally important in organoactinide chemistry. Furthermore, the intramolecularity of R–H elimination[5,8] suggests that the carbene complex[23-25]–ylid[26-28] species I is the precursor of the complex reported

Ia   Ib   Ic
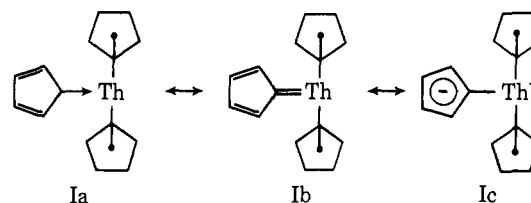
here. This complex is coordinatively unsaturated, with a formal coordination number of 7 for the Th(IV) ion. On a general level, species similar to I may be extensively involved in thermolyses and group transfer reactions of numerous $\eta^5\text{-}C_5H_5$ transition metal compounds.

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Synthesis of Perfluoro-1,4-dioxane, Perfluoro(ethyl acetate), and Perfluoropivaloyl Fluoride by Direct Fluorination

Sir:

Recent advances in direct fluorination[1-3] will make possible the synthesis of many important new oxygen-containing functional fluorocarbon molecules and provide a valuable synthetic route to complement existing synthetic methods. To demonstrate this potential for handling three separate functional groups, we wish to report the first successful fluorination of 1,4-dioxane, of pivaloyl fluoride, (CH₃)₃CCFO, and of a hydrocarbon ester to produce the

Chart I. Reactions
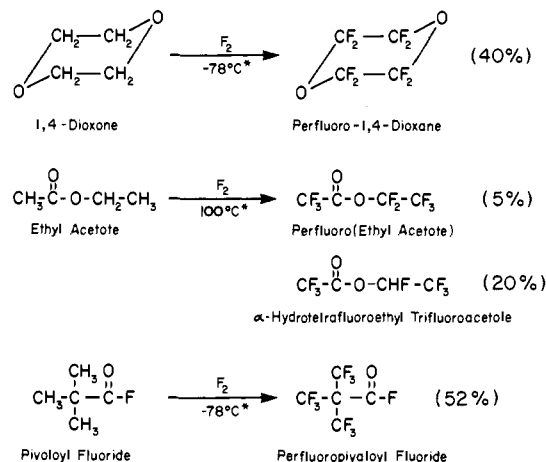
* Lowest temperature of gradient

corresponding perfluorocarbon analogs (see Chart I) in good yields.

Previous attempts to fluorinate 1,4-dioxane electrolytically in anhydrous hydrogen fluoride yielded the acyclic ether perfluoro-1,2-dimethoxyethane in 4% yield but no perfluoro-1,4-dioxane.[4] Perfluoro-1,4-dioxane has been prepared previously in 4% yield by dimerization of tetrafluoroethylene oxide.[5]

Only recently have studies indicated that acyclic perfluoroesters and α-hydrofluoroesters are stable as a class of compounds.[6-8] However, no direct synthesis of a perfluoroester from a hydrocarbon ester has been reported previously. Perfluoropivaloyl fluoride has not been prepared.

The direct fluorination of acyl fluorides as a class of compounds represents an important route to the perfluoroacids. Pivaloyl fluoride was selected as an example of a sterically crowded system which is difficult to prepare by other methods.[9]

In a typical experiment for the preparation of perfluoro-1,4-dioxane a 3.3-g sample of 1,4-dioxane was evaporated over a 20-hr period by a 160-cm³/min flow of helium into a four-zone cryogenic reactor[2] which was maintained at 0°. The reactor was cooled to −78° and a 0.5 cm³/min flow (approximately 30 mmol per day) of fluorine diluted with a 20-cm³/min flow of helium was passed over the solid dioxane. After 12 hr, the rate was increased to 1.0 cm³/min for 1 day and then further increased to 1.5 cm³/min where it was maintained for 6 days. During this period the helium flow was reduced to zero, and reactor zones one through four were warmed sequentially to their equilibrium temperature until all were at ambient at the end of the 6-day period. Similar programs were used for ethyl acetate and pivaloyl fluoride. The crude product was hydrolyzed in 2.0 *M* KOH, separated from the aqueous layer and fractionated. Glc assay of the contents of the −95 and −131° traps yielded 3.37 g (38.5%) of perfluoro-1,4-dioxane and 0.4 g (4%) of perfluoro-1,2-dimethoxyethane. The −196° trap contained 4.23 g (58%) of essentially pure perfluorodimethyl ether.

Anal. Calcd for C₄F₈O₂: C, 20.706; F, 65.503. Found: C, 20.63; F, 65.67.

Perfluoro-1,4-dioxane is a gas at room temperature (bp 15.9°). The molecular weight determined by the ideal gas method was 232.7, *vs.* 232.0 for C₄F₈O₂. The ¹⁹F nmr consisted of a singlet at φ +90.78 ppm (relative to CFCl₃, external). The infrared spectrum exhibits bands at 1435 (w), 1369 (w), 1311 (sh), 1303 (s), 1232 (vs), 1163 (sh), 1149 (s), 1113 (3), 890 (m), 665 (m) wave numbers. The mass