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C_β becomes dominant and maximizes at rotation of the $C_\gamma H_2$ unit of 88° with respect to the CH_2 plane in the ground state. Concomitantly, a positive charge develops on C_β, while C_α and C_γ still bear negative charges. Thus, nucleophilic attack at C_β appears to be favored by both charge and orbital factors.

These preliminary results suggest a rich chemistry for μ-η^1:η^2-allenyl complexes as a source of three-carbon fragments in synthesis.

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Supplementary Material Available: Tables of structure determination details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **2a**, **3a**, and **5** (26 pages); tables of observed and calculated structure factors (86 pages). Ordering information is given on any current masthead page.

Models for Organometallic Molecule–Support Complexes. Very Large Counterion Modulation of Cationic Actinide Alkyl Reactivity

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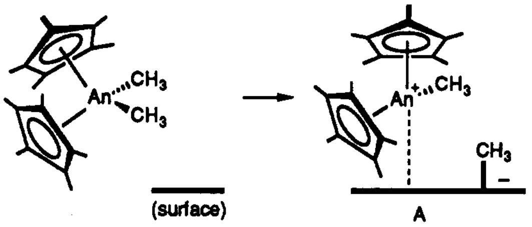
Summary: The reaction of $Cp'_2Th(CH_3)_2$ ($Cp' = \eta^5$-$(CH_3)_5C_5$) with $HN^nBu_3{}^+B(C_6F_5)_4{}^-$ yields the crystallographically characterized, cationic thorium alkyl $Cp'_2ThCH_3{}^+B(C_6F_5)_4{}^-$. The $B(C_6F_5)_4{}^-$ anion is weakly coordinated, the NMR spectroscopic parameters are similar to those of $Cp'_2Th(CH_3)_2$ adsorbed on dehydroxylated alumina, and the complex is a highly active catalyst for ethylene polymerization and 1-hexene hydrogenation.

Surface spectroscopic[1] and chemical[2] evidence argue that cationic alkyls play a major role in facile olefin transformations catalyzed by organoactinides adsorbed on electron-deficient supports (e.g., A in eq 1). Furthermore,



(1)

An = Th, U

analogous group 4 species[3,4] are thought to be important in homogeneous Ziegler–Natta catalysis.[5] Nevertheless, an *isolable, structurally characterized, base-free* complex that models both the salient spectroscopic and catalytic properties of A has not been available. We report here on

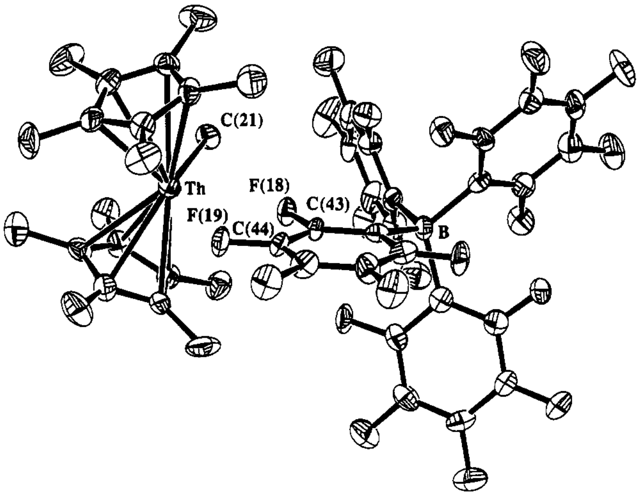


Figure 1. Molecular structure of $Cp'_2ThCH_3{}^+B(C_6F_5)_4{}^-$ (**1**). Important bond distances (Å) and angles (deg) are as follows: Th–C(21) = 2.399 (8), Th–C_{ring} = 2.754 (3) (av), Th–F(18) = 2.757 (4), Th–F(19) = 2.675 (5), C(43)–F(18) = 1.325 (6), C(44)–F(19) = 1.344 (7); ring centroid–Th–ring centroid = 140.1 (3). Thermal ellipsoids are drawn at the 35% probability level.

Table I. Solution-Phase Catalytic Activity of $Cp_2'ThCH_3{}^+X^-$ Complexes[a]

	X^-			
reaction	$CH_3{}^-$	$^1/_2$ Fe(1,2-$C_2B_9H_{11})_2{}^{2-}$	$BPh_4{}^-$	$B(C_6F_5)_4{}^-$
ethylene polymerization[b]	0	0	1.1×10^{-2}	36
1-hexene hydrogenation[c]	1.4×10^{-4}	0	1.1×10^{-3}	4.57

[a] As expressed in turnover frequencies (N_t, s^{-1}). [b] Procedure of ref 15: $P_{ethylene} = 1.0$ atm, $T = 25$ °C, solvent toluene or benzene. [c] Procedure of ref 15: $P_{H_2} = 1.0$ atm, $T = 25$ °C, solvent toluene or benzene.

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the synthesis, crystal structure, and catalytic properties of such a highly reactive thorium alkyl cation, stabilized/activated by the weakly coordinated $B(C_6F_5)_4^-$ counterion.[6,7]

Protonolytic reaction[2] of tri-*n*-butylammonium tetrakis(pentafluorophenyl)borate[8] with thorium alkyls in noncoordinating solvents affords cationic complexes in high yields (eq 2, Cp′ = η^5-$(CH_3)_5C_5$). Less bulky amines yield

$$Cp'_2ThR_2 + HN^nBu_3^+B(C_6F_5)_4^- \xrightarrow[-N^nBu_3]{C_6H_6} Cp'_2ThR^+B(C_6F_5)_4^- + RH \tag{2}$$

1, R = CH_3, 90% isolated yield;
2, R = $CH_2C_6H_5$, 70% isolated yield

cationic amine complexes. Complexes **1** and **2** were characterized by standard spectroscopic/analytical techniques.[9] A low-field Th–$^{13}CH_3$ signal as in **1** has previously been proposed[1a,c,e,2] to be diagnostic of "cation-like" A structures. The crystal structure of **1**[10] (Figure 1) consists of loosely associated "bent-sandwich" $Cp'_2ThCH_3^+$ cations and $B(C_6F_5)_4^-$ anions. Conspicuous in the former are the *short* Th–CH_3 (cf. 2.49 (1) Å in $Cp'_2Th(CH_3)(THF)_2^+BPh_4^-$ (**3**),[2] 2.480 (3) Å in $Fe[(1,2\text{-}C_2B_9H_{11}^-)Th^+(CH_3)Cp'_2]_2$ (**4**)[6,11]) and Th–C_{ring}(av) distances (vs 2.80 (1) Å in **3** and 2.817 (3) Å in **4**[6,11]). The shortest Th–F contacts (Th–F(18),F(19)) are significantly longer than the sums of relevant Th^{4+} and F^- ionic radii[12a] (~2.28 Å), the length assigned to a F→Yb dative bond[13] after correction for differences in Th^{4+}/Yb^{2+} ionic radii[12a] (~2.29 Å), and a Th←O(THF) bond distance[2a] after correction for differences in F/O covalent radii[12b] (~2.56 Å). The present C–F(18),F(19) distances are unexceptional[14] (1.323 (8) Å average in **1**), and the ^{19}F NMR spectrum shows magnetically equivalent C_6F_5 rings down to −70 °C in toluene-d_8.

As measured[15] by ethylene polymerization and 1-hexene hydrogenation activity in solution (Table I), the catalytic properties of $Cp'_2ThCH_3^+X^-$ species are remarkably sensitive to X^-. Thus, **1** is far more reactive than $Cp'_2ThCH_3^+BPh_4^-$ (~3300× more reactive for ethylene polymerization; ~4100 more reactive for 1-hexene hydrogenation), for which low-temperature NMR spectroscopy suggests π-arene coordination,[2] and **4**, where there are two sets of three close B–H···$Th^+(CH_3)Cp'_2$ contacts.[6,11] Indeed, the α-olefin hydrogenation activity of **1** approaches that of $Cp'_2Th(CH_3)_2$–dehydroxylated alumina ($N_t \approx 3\ s^{-1}$ per active site at −45 °C; E_a = 3.6 (2) kcal mol^{-1}).[1b] This marked counterion sensitivity offers an appealing explanation for the wide variation in adsorbate cation heterogeneous catalytic activity both as a function of support (in this case the counterion) and as a function of site on the same support.[1b,f] Interestingly, finely ground powders of **1** are also heterogeneous catalysts for olefin hydrogenation ($N_t \approx 0.1\ s^{-1}$ at 0 °C for propylene).

Chemically, **1** is a strong Lewis acid and forms μ-alkyl complexes with hydrocarbyls such as $Cp'_2Th(CH_3)_2$ (eq 3).

$$\mathbf{1} + Cp'_2Th(CH_3)_2 \rightleftharpoons \underset{\mathbf{5}}{Cp'_2(CH_3)Th(\mu\text{-}CH_3)Th(CH_3)Cp'^+_2B(C_6F_5)_4^-} \tag{3}$$

At room temperature in solution, bridge and terminal methyl groups of **5** are in rapid exchange; however, discrete CH_3 signals (in a 2:1 ratio) are observable below ca. −20 °C or in the solid.[16] The large $^1J_{C-H}$ = 132.3 Hz value for the bridging CH_3 is characteristic of electron-deficient μ-alkyls.[17,18]

These structural and catalytic results demonstrate that, and suggest the means by which, the reactivity of cationic acetinide hydrocarbyls is strongly controlled by the nature of the charge-compensating environment. Furthermore, the $B(C_6F_5)_4^-$ anion exhibits unprecedented activating characteristics in such systems and may find a variety of other applications in the quest for minimally coordinating anions.[19]

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(6) Communicated in part at the XIVth International Conference on Organometallic Chemistry, Detroit, MI, Aug 1990, Abstract 120.

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(9) Analytical and spectroscopic data for **1** are as follows. NMR (C_6D_6, room temperature): ^1H, δ 1.54 (s, 30 H), 0.34 (s, 3 H); ^{13}C, δ 77.27 (q, $^1J_{C-H}$ = 116.1 Hz, Th–CH_3), 10.77 (q, $^1J_{C-H}$ = 126.2 Hz, Cp′); ^{19}F, δ −132.63 (s, br, 8 F, *o*-F), −162.11 (t, $^3J_{F-F}$ = 21.2 Hz, 4 F, *p*-F), −166.03 (m, 8 F, *m*-F); ^{11}B (in C_6D_6 + THF, vs $BF_3{\cdot}OEt_2$), δ −16.6 (s). Anal. Calcd for $C_{45}H_{33}BF_{20}Th$: C, 45.17; H, 2.78; N, 0.00. Found: C, 44.53; H, 2.88; N, 0.00. Analytical and spectroscopic data for **2** are as follows. NMR (C_6D_6, room temperature): ^1H, δ 6.82 (t, $^3J_{H-H}$ = 7.6 Hz, 2 H, *m* Ph), 6.75 (t, $^3J_{H-H}$ = 7.2 H, 1 H, *p* Ph), 6.23 (d, $^3J_{H-H}$ = 2 H, *o* Ph), 2.11 (s, 2 H), 1.50 (s, 30 H); ^{19}F, δ −131.91 (s, br, 8 F, *o*-F), −161.53 (t, $^3J_{F-F}$ = 21.5 Hz, 4 F, *p*-F), −167.00 (m, 8 F, *m*-F). Anal. Calcd for $C_{51}H_{37}BF_{20}Th$: C, 48.13; H, 2.93; N, 0.00. Found: C, 47.64; H, 3.07; N, 0.11.

(10) Crystal data: $ThF_{20}C_{45}BH_{33}{\cdot}2.5C_6H_6$; monoclinic, space group $P2_1/c$; a = 18.390 (7) Å, b = 16.444 (4) Å, c = 18.731 (6) Å, β = 99.20 (3)° at −120 °C; V = 5592 (3) A^3; Z = 4, d_{calcd} = 1.653 g cm^{-3}. The structure was solved by Patterson methods (SHELXS-86) and refined with weighted and unweighted difference Fourier syntheses and blocked-matrix least squares (SHELX-76). $R(F)$ and $R_w(F)$ = 0.035 and 0.037, respectively, for 4074 absorption-corrected reflections with $I > 2.58\sigma(I)$ measured on a CAD4 diffractometer (Mo Kα radiation, λ = 0.710 69 Å, 2θ = 42°).

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(16) Spectroscopic data for **5**($^{13}CH_3$) are as follows. NMR (toluene-d_8, −27 °C): ^1H, δ 1.74 (s, 30 H), 0.070 (d, 6 H, $J_{^{13}C-H}$ = 113.8 Hz), −1.20 (d, 3 H, $J_{^{13}C-H}$ = 132.3 Hz); ^{13}C (CPMAS), δ 127.3 (Cp C), 76.5 (s, CH_3), 56.6 (s, CH_3), 10.9 (Cp′ (CH_3)).

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Supplementary Material Available: Details of the crystal data collection and structure refinement, a fully labeled diagram, and tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for 1 (15 pages); a table of structure factors (34 pages). Ordering information is given on any current masthead page.

Photochemistry of Permethyloligosilanes

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Summary: Primary photochemical pathways have been identified in the irradiation of three oligosilanes at 254 nm. These pathways include a reductive elimination not previously observed in oligosilanes but closely analogous to a chain-scission process that has been observed in polysilane materials.

Investigation of the thermal and photochemical breakdown of polysilanes is of topical interest because of the importance of these compounds as photoresists.[1] To complement work on the photoablation of these materials,[2] we are undertaking separate pyrolysis[3] and photochemical studies on a number of permethyloligosilanes as simple models for polysilanes; we now report preliminary results of our photochemical experiments.

The compounds we have studied so far are 2,3-bis(trimethylsilyl)octamethyltetrasilane (I), $(Me_3Si)_2Si(Me)Si(Me)(Me_3Si)_2$, 2-(trimethylsilyl)heptamethyltrisilane (II), $(Me_3Si)_3SiMe$, and 2,2-diethylhexamethyltrisilane (III), $(Me_3Si)_2SiEt_2$. Ishikawa and Kumada have published a preliminary account[4] of the photochemistry of the branched oligosilanes I and II and a more detailed account[5] of the photochemistry of the series of linear oligosilanes $Me(Me_2Si)_nMe$, where $n = 4–8$, in cyclohexane solution at 254 nm, using diethylmethylsilane as a silylene trap. They found extrusion of dimethylsilylene, $:SiMe_2$, to be the main primary photochemical pathway, together with some homolytic Si–Si bond rupture; e.g., irradiation of the permethylated tetrasilane gave 84% Me_8Si_3 (the stable product concomitant with extrusion of $:SiMe_2$), with 11% Si–Si bond rupture. Likewise,[6] dimesitylsilylene was formed photochemically from the trisilane $(Me_3Si)_2SiMes_2$, although Wilking and Gaspar recently reported that irradiation at 254 nm of the mesityl-substituted disilane and trisilane $(MesMe_2Si)_2$ and $(MesMe_2Si)_2SiMe_2$ mainly caused Si–Si bond rupture followed by radical reactions.[7]

Photochemical studies of polysilanes have revealed that three types of simultaneous primary processes may occur:

(A) chain scission by homolytic Si–Si bond cleavage[8]

$$\text{-RR'Si-RR'Si-RR'Si-RR'Si-} \rightarrow \text{-RR'Si-RR'Si}^{\bullet} + {}^{\bullet}\text{RR'Si-RR'Si-}$$

(B) chain abridgement by elimination of a silylene from the polysilane chain[8]

$$\text{-RR'Si-RR'Si-RR'Si-RR'Si-} \rightarrow \text{-RR'Si-RR'Si-RR'Si-} + \text{:SiRR'}$$

(C) chain scission with formation of a silylene on the polysilane chain[9]

$$\text{-RR'Si-RR'Si-RR'Si-RR'Si-} \rightarrow \text{-RR'Si-RR'SiR} + \text{:Si(R')-RR'Si-}$$

$$\text{-RR'Si-RR'Si-RR'Si-RR'Si-} \rightarrow \text{-RR'Si-RR'SiR'} + \text{:Si(R)-RR'Si-}$$

Processes B and C occur by reductive elimination. It has been proposed that the silylenes formed in process C readily isomerize to disilenes, e.g. $\text{:SiR'-RR'Si-RR'Si-} \rightarrow \text{RR'Si-SiR'=SiRR'}$, and that these disilenes can then add to polysilyl radicals generated by process A to form new radicals.[9] It has been established[10] that photochemically produced silyl radicals abstract hydrogen originally attached to the α- position of alkyl chains in the polysilane material (presumably in a radical disproportionation process), rather than from the solvent or from silylene traps such as Et_3SiH or Et_3SiD.

Our experiments were carried out in rigorously purified *n*-hexane solution with concentrations of oligosilanes in the range of 0.02–0.05 mol dm^{-3}; most irradiations were carried out with a low-pressure mercury lamp at 254 nm, but some were with a cadmium lamp at 228 nm. Products were separated and identified by GC/mass spectrometry. Information about the nature of the intermediates produced was obtained by irradiating solutions of oligosilane in 1:1 *n*-hexane–triethylsilane; silylenes insert into the Si–H bond in Et_3SiH to form photochemically stable hydridodisilanes, while characteristic products are also

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