For further investigation of the effect of carboxylate anions on the isomerization rate, we protonated **2** with trichloroacetic acid (TCA), dichloroacetic acid, and bromoacetic acid (all up to 0.35 M solution of the corresponding acid). We clearly observed a decrease in the isomerization rate of the $C_{13}{=}C_{14}$ double bond ($t_{1/2}$ = 1 and 13 h for **2b** and **2c**) and no isomerization in the case of bromoacetic acid.

The interaction between the positively charged nitrogen and its counteranion can also be controlled by introducing counteranions of different sizes. Thus, protonation of RSB with $HClO_4$ in $CDCl_3$ caused a red shift relative to HCl.[9] Similarly, *n*-butylamine 13-cis PRSB salt of perchlorate underwent isomerization to all-trans (in $CDCl_3$) with $t_{1/2}$ = 50 min, while with corresponding chloride and bromide salts $t_{1/2}$ is 8 h. Charge delocalization can also be influenced by changing the substituent on the nitrogen. Substitution of the *n*-butyl group by *tert*-butyl slowed down the isomerization. *tert*-Butyl perchlorate salt of 13-cis showed only 20% isomerization after 10 h at 25 °C, while HCl salt **2e** exhibited a negligible amount of isomerization. All 13-cis PRSB salts described above exhibited no isomerization of C=C bond (after 6 h at 25 °C) but did show that of $C{=}N^+$ using methanol as a solvent.

Interaction through space with external charges may influence charge delocalization controlling the rate of thermal isomerization[10,11] of $C_{13}{=}C_{14}$ cis to trans. To investigate this possibility, we followed the thermal isomerization (in $CDCl_3$) of **3a** salt[12] carrying a positive charge in the neighborhood of the β-ionone ring. We could not observe either C=C or $C{=}N^+$ isomerization even after 5 h at 25 °C, using a 0.6 M concentration of TFA. On the contrary, a positive charge in the vicinity of the positively charged nitrogen **4a**[13] enhanced the thermal isomerization of 13-cis PRSB to all trans. This isomerization was observed even using 0.35 M solution of bromoacetic acid in $CDCl_3$ or TFA in CD_3OD ($t_{1/2}$ = 66 min), conditions that failed to isomerize 13-cis PRBS **1**.

Strong interaction between the counteranion and the positively charged nitrogen will stabilize the positive charge on the nitrogen and will decrease charge delocalization. This effect will slow down the isomerization rate of 13-cis to trans. Excess TFA will weaken the interaction between the carboxylate anion and the positive charge due to the homoconjugation effect, causing enhancement of charge delocalization. Similarly, this effect can be achieved by introducing a large counteranion like perchlorate or periodate. Carboxylate anions exhibiting a weak homoconjugation effect will cause slow isomerization. Indeed, we observed an isomerization rate in the order TFA, TCA, dichloroacetic acid, and bromoacetic acid. In all these cases we observed $C{=}N^+$ isomerization, indicating sufficient charge distribution along this bond to allow relatively fast thermal isomerization. Methanol, a leveling solvent, will cancel the effect of the counteranion on the positively charged nitrogen[9] as well as the homoconjugation effect. However, it will stabilize the positive charge on the nitrogen by strong solvolysis and thus will reduce charge delocalization toward the C_{13}–C_{14} double bond, resulting in a slow isomerization. The positive charge on the nitrogen can also be stabilized by a *tert*-butyl group attached to the nitrogen.[14] Thus, no isomerization was observed in **2e** and **2g**.

External positive charge in the neighborhood of the β-ionone ring reduces charge delocalization[12,15] and bond alternation. Therefore, no thermal isomerization was observed in **3a**. A positive charge close to the nitrogen will cause the opposite effect. Thus, isomerization in **4** was observed, even in methanol, which prevents isomerization in the case of **1** and **2**.

In this study, we have shown that thermal isomerization of 13-cis to all-trans PRSB is controlled by charge delocalization, which is influenced by interaction through space with external charges and by the nature of the counteranion. This isomerization is accompanied by a fast $C{=}N^+$ isomerization of anti to syn.[16] Thus, our results strongly support the suggestion that 13-cis bR can isomerize smoothly to all trans due to interaction with a negative charge in the vicinity of the ring which will increase charge delocalization.[10,11,17] The isomerization can also be enhanced by separation of the positively charged nitrogen from its counteranion.[18-20] It should be noted that steric hindrance imposed by the protein might also influence the barrier for thermal isomerization. Our results point strongly to a protonation of the M_{412} intermediate of bR prior to thermal isomerization from 13-cis to all trans.[21]

Acknowledgment. We thank the Fund for Basic Research (Administered by the Israeli Academy of Sciences and Humanities) and the Committee for Scientific Cooperation between German and Israeli Research Institution (Minerva Grant) for supporting this work.

Registry No. *anti*-**1**, 68737-92-8; *syn*-**1a**, 92216-31-4; *syn-trans*-**1a**, 92098-19-6; *anti*-**1e**, 68737-89-3; *syn-trans*-**1e**, 92098-24-3; *anti*-**1f**, 92098-25-4; *syn-trans*-**1f**, 92098-26-5; *anti*-**1g**, 92098-22-1; *syn-trans*-**1g**, 92098-23-2; *anti*-**2**, 92098-20-9; *anti-trans*-**2a**, 92216-33-6; *syn-trans*-**2b**, 92098-21-0; *syn-trans*-**2c**, 92125-63-8; *anti*-**2d**, 92098-34-5; *anti*-**2g**, 92098-27-6; *syn-trans*-**2g**, 92125-64-9; *anti*-**3a**, 92098-29-8; *anti*-**4a**, 92098-31-2; *syn-trans*-**4a**, 92098-33-4.

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Synthesis and Characterization of a Homoleptic Actinide Alkyl. The Heptamethylthorate(IV) Ion: A Complex with Seven Metal–Carbon σ Bonds

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Although interest in preparing homoleptic actinide peralkyls dates back to the 1940s,[1] all synthetic attempts (principally involving uranium) have resulted in thermally unstable and largely uncharacterized/uncharacterizable products.[2-4] We reasoned

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(3) The course(s) of the complicated UCl_4 + RLi reaction(s) have been controversial. See ref 2b,c for critical comments on ref 2a, ref 1b,c for critical comments on ref 2b, and ref 2d for critical comments on ref 2c.

that the greater metal–ligand bond disruption enthalpies[5] and more difficultly accessible +3 oxidation state[1b,c] would favor the isolability of analogous thorium(IV) peralkyls. We report here the first synthesis and structural characterization of a reasonbly stable homoleptic actinide alkyl, $Th(CH_3)_7^{3-}$, which is also, to our knowledge, the only mononuclear d- or f-block complex with greater than six hydrocarbonyl ligands to be completely (structurally) characterized.[2,6] Despite apparent coordinative saturation, initial indications are that $Th(CH_3)_7^{3-}$ is rather reactive.

By use of an organolanthanide approach originally developed by Schumann,[7] a suspension of 3.20 g (8.56 mmol) of $ThCl_4$ in 100 mL of diethyl ether and 3.90 g (34.2 mmol) of tetramethylethylenediamine (TMEDA) at −78 °C was treated dropwise with 52.6 mL (68.4 mmol) of a 1.3 M solution of CH_3Li in diethyl ether (eq 1). After it was stirred for 1 h, the clear yellow solution

$$ThCl_4 + 7CH_3Li + 4TMEDA \xrightarrow[-78\ ^\circ C]{ether} [Li(TMEDA)]_3Th(CH_3)_7{\cdot}TMEDA + 4LiCl \quad (1)$$

was warmed to 20 °C, stirred an additional 2 h, and filtered and the filtrate slowly cooled to −30 °C overnight. Isolation and vacuum drying produced 3.0 g (45% yield) of $[Li(TMEDA)]_3Th(CH_3)_7{\cdot}TMEDA$ (**1**) as yellow, pyrophoric needles, mp 82–88 °C dec, stable at room temperature for hours.[8] The complex was characterized by standard analytical techniques[9] and by single-crystal X-ray diffraction (vide infra). The room temperature ^1H NMR spectrum[9] exhibits magnetically equivalent $ThCH_3$ groups and magnetically equivalent TMEDA units; cooling to −90 °C only results in broadening and collapse of the TMEDA NCH_2 resonances.

Single crystals of **1** at −110 °C are monoclinic, space group $P2_1/c$ with a = 14.311 (2) Å, b = 12.458 (4) Å, and c = 22.757 (3) Å, β = 99.38 (1)°, Z = 4, μ_a(Mo K$\bar{\alpha}$) = 38.77 cm^{-1}, and d_{calcd} = 1.27 g cm^{-3}. Three-dimensional data were collected (7009 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} < 50°$) on a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo radiation and ω–2θ scans (ω scan width = [0.9 + 0.35 tan θ]°). All calculations were performed on a VAX 11/730 computer with the Enraf-Nonius SDP crystallographic software package and programs standard in this Laboratory. The structure was solved using Patterson and direct methods techniques.[10] Structural parameters were refined to convergence [R(unweighted, based on F) = 0.040 for 4744 independent, absorption-corrected reflections with $I > 3\sigma(E)$] with anisotropic thermal parameters for all non-hydrogen atoms. Electron density peaks around the inversion center were interpreted in terms of a disordered, unbound TMEDA molecule and were included in the model as fixed contributors to the structure factors.

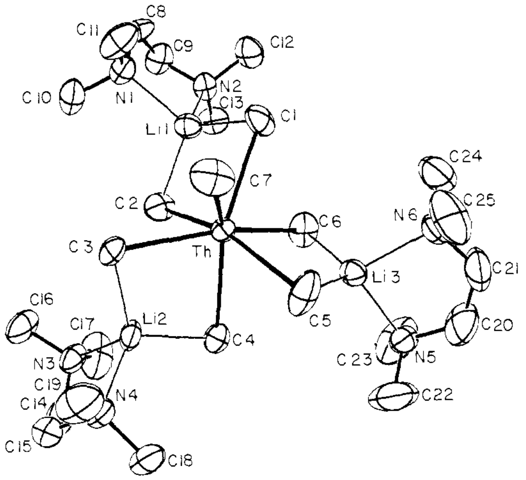

Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms in $[Li(TMEDA)]_3Th(CH_3)_7{\cdot}TMEDA$ (**1**). All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density. Individual bond lengths (Å) and angles (deg) of interest: Th–C(1), 2.698 (8); Th–C(2), 2.700 (8); Th–C(3), 2.655 (8); Th–C(4), 2.765 (9); Th–C(5), 2.667 (8); Th–C(6), 2.723 (8); Th–C(7), 2.571 (9); mean Li–C(methyl), 2.18 (3); mean Li–N, 2.12 (2). C(1)–Th–C(2), 84.1 (2); C(2)–Th–C(3), 74.8 (3); C(3)–Th–C(4), 84.6 (2); C(4)–Th–C(5), 76.6 (3); C(5)–Th–C(6), 84.6 (3); C(6)–Th–C(7), 132.9 (3).

In the structure of **1** (Figure 1) thorium is coordinated to seven methyl ligands in a distorted monocapped trigonal prismatic array. The trigonal prism is approximately defined by carbon atoms C(1), C(2), C(3), C(5), C(6), and C(7) while C(4) can be assigned to the capping position. Six of the methyl groups are coordinated in pairs to $Li(TMEDA)^+$ ions while a single methyl (C7) is not coordinated to a lithium ion. The Th–C(7) bond distance (2.571 (9) Å) is slightly shorter than the other Th–methyl distances (range = 2.667 (8)–2.765 (9) Å). These parameters can be compared with Th–C(sp^3) distances of 2.46 (1), 2.51 (1) Å ($Cp'_2Th[CH_2Si(CH_3)_3]_2$,[11] Cp′ = η^5-$(CH_3)_5C_5$); 2.546 (4), 2.478 (4) Å ($Cp'_2Th[CH_2C(CH_3)_3]_2$[12]), 2.581 (19), 2.579 (17), 2.578 (21) Å ($Cp'Th(Bz)_3$[4c]), and 2.54 (2), 2.53 (2), 2.54 (2), 2.57 (2) Å ($Th[(CH_3)_2PCH_2CH_2P(CH_3)_2](benzyl)_4$[13]). The metrical parameters involving the $Li(TMEDA)^+$ units (Li–C(methyl) = 2.18 (3) Å (mean)) and Li–N = 2.12 (2) Å (mean)) are unexceptional.[7] In view of these structural results, the NMR data can be interpreted in terms of rapid permutation of methyl environments and exchange of free and coordinated TMEDA.

In several survey experiments, we find that the reaction of **1** with either CO or H_2 (toluene, 25 °C, 1 atm) is complete in a few minutes. The former reaction absorbs 4.0 (4) equiv of CO (by Toepler pump) to produce a yellow, insoluble precipitate analyzing approximately as $Li_3Th(CH_3)_7(CO)_4{\cdot}0.75TMEDA$.[14a] Infrared spectra[14b] suggest the presence of Th(η^2-$COCH_3$) functionalities rather than enediolate,[15] and hydrolysis yields acetaldehyde as the only carbonylation product. The second reaction liberates 7.0 (1.0) equiv of CH_4 (by Toepler pump) to yield a yellow, insoluble microcrystalline solid having infrared spectral features[16a] in accord with a hydride[1b,c,17] and analyzing

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(10) (a) See supplementary material for details. (b) DIRDIF: Direct methods applied to difference structure factors to strengthen Fourier methods. Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van der Hark, Th. E. M.; Prick, P. A. J. In "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 516.

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approximately as $Li_3ThH_7{\cdot}0.6TMEDA$.[16b] Studies of $Th(CH_3)_7^{3-}$ reactivity are continuing.

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Supplementary Material Available: Tables of fractional atomic coordinates and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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(16) (a) Nujol mulls and KBr pellets exhibit only very weak TMEDA-associated features and a strong, broad ($\nu_{1/2} \approx 700$ cm^{-1}) transition centered at ca. 900 cm^{-1}, which shifts to ca. 630 cm^{-1} ($\nu_{Th\text{-}H}/\nu_{Th\text{-}D} \approx 1.43$) in the analogue prepared with D_2. (b) Anal. Calcd for $Li_3C_{3.60}H_{16.6}N_{1.20}Th$: Li, 6.32; C, 13.11; H, 5.09; N, 5.10. Found: Li, 6.76; C, 12.69; H, 4.38; N, 5.63.

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Photoinduced Electron Transfer between Cytochrome c and Ruthenium/Osmium Bipyridine and Phenanthroline Complexes

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Recently there has been considerable interest in elucidating the mechanism of electron transfer in biological molecules.[2-8] Important information pertaining to this problem is the dependence of the transfer rate on the driving force ΔE for the reaction. Existing data have been obtained mostly from reactions between metalloproteins and inorganic reagents.[5,7] Unfortunately, these are available only within a limited ΔE range around 0.25 V.

An attractive method for measuring electron-transfer rates over a wide ΔE range has been developed in the past few years. Excited inorganic complexes were used as oxidants or reductants[9-11] and the transfer rate was determined by studying the luminescence quenching of the complexes. In such experiments, complications often arise as a result of the presence of other competing processes, such as quenching by energy transfer. To avoid this difficulty, we have employed the transient absorption method to measure directly the kinetics of electron transfer between cytochrome *c* (Cyt-*c*) and several inorganic complexes $X^{2+/3+}$ where X corresponds to $Ru(bpy)_3$ (bpy = 2,2′-bipyridine), $Ru(phen)_3$ (phen = 1,10-phenanthroline), $Os(bpy)_3$, and $Os(phen)_3$. After being photoexcited, a small amount of the complex X^{2+} is converted into X^{3+} while simultaneously Cyt-c^{3+} is reduced to Cyt-c^{2+}. Subsequently, by monitoring the back reaction, the electron-transfer rate between Cyt-c^{2+} and X^{3+} can be directly determined. The results are interesting in that there are very few data in the high driving force regime ($E°$ for $X^{3+}/X^{2+} \simeq 1$ V vs. NHE).

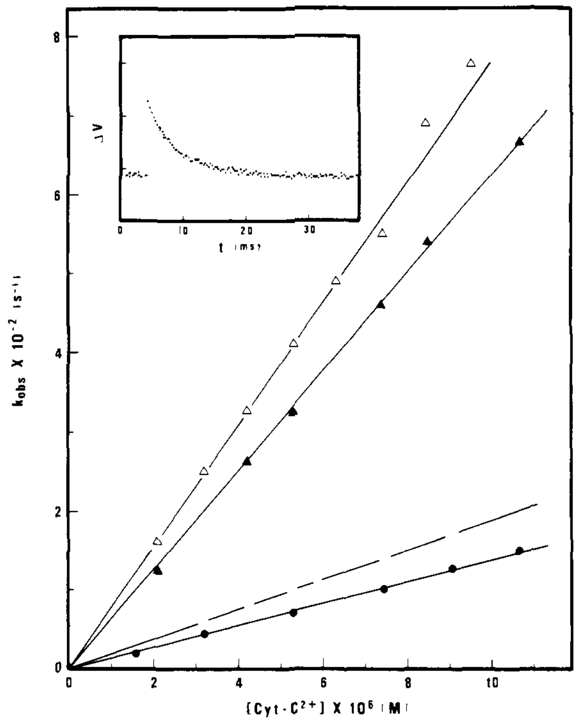

Figure 1. Plot of k_{obsd} vs. Cyt-c^{2+} for the oxidation of ferrocytochrome *c* by $Ru(bpy)_3^{3+}$ (▲), $Ru(phen)_3^{3+}$ (△), $Os(bpy)_3^{3+}$ (●), and $Os(phen)_3^{3+}$ (○) in 5 mM (pH 7) phosphate buffer. The complex concentration was 50 μM, and the reaction was followed at 550 nm. Inset: Typical transient observed for a deoxygenated sample containing 50 μM (oxidized + reduced) cytochrome *c* and 50 μM $Os(bpy)_3^{2+}$ in 50 mM NaCl and 5 mM (pH 7) phosphate buffer. The signal was averaged for 100 laser shots and the laser power was 15 mJ/pulse.

Horse heart cytochrome c (type VI), purchased from Sigma, was used without further purification. The protein as received contained (10.6 ± 0.5)% ferrocytochrome *c* as determined by the addition of a slight excess of $K_3Fe(CN)_6$ to several concentrations of protein while monitoring its optical change at 550 nm. The kinetics was studied by a typical transient absorption setup in which the excitation source was the 355-nm output of a Quanta-Ray DCR-2 Nd:YAG laser. The reaction was initiated by flashing a deoxygenated sample containing cytochrome *c* (concentration varying from 10 to 100 μM, 10.6% reduced) and a complex (X^{2+}) in pH 7 phosphate buffer. The signals were typically averaged for 100 laser shots. The rate of the back reaction was determined by monitoring the transient absorption decay at 550 nm (which reflects changes in Cyt-c^{3+}/Cyt-c^{2+} concentration since the complexes absorb weakly at this wavelength) and 434/504 nm (which reflects changes in X^{3+}/X^{2+} concentration since they correspond to Cyt-c^{3+}/Cyt-c^{2+} isosbestic points).

Following excitation we observe a prompt signal which decays in a millisecond time scale (Figure 1 inset). When the magnitude of the prompt signal is examined at constant laser power as a function of wavelength, the spectrum obtained agrees very well with that predicted from a superposition of the difference spectra of Cyt-c^{3+}/Cyt-c^{2+} and X^{2+}/X^{3+}, indicating that the prompt signal

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