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Influence of electronic factors on the structure and stability of uranium compounds. Tri-tert-butyl methoxide uranium(IV) complexes

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Abstract

The complexes (tritox)$UCl_3(THF)_x$ (I) and $(tritox)_2UCl_2(THF)_2$ (II) (tritox = $^tBu_3CO$, THF = tetrahydrofuran) have been prepared by treating UCl_4 with (tritox)Li. Compound II was a precursor for a series of $(tritox)_2UX_2$ compounds (X = BH_4, $CH_3COCHCOCH_3$, η-C_3H_5, CH_2Ph). The uranium borohydride derivative (tritox)$U(BH_4)_3$(THF) (IX) was isolated from the reaction of $U(BH_4)_4(THF)_2$ with (tritox)H and was successively transformed into $(tritox)_2U(BH_4)_2$ (IV) and $(tritox)_3U(BH_4)$ (XI) by treatment with (tritox)Li. The crystal structures of the trigonal bipyramidal compound IX and the pseudo tetrahedral complex XI provide clear evidence of the strong $O\pi \rightarrow U$ contribution to the metal–oxygen bonds. The structure and stability of these tritox compounds are quite different from those of the isosteric cylopentadienyl analogues, and reveal the determining role of the electronic factors.

Introduction

It is generally accepted that steric factors play a dominant role in determining the structure and stability of *f*-transition metal complexes. Evaluation of the steric crowding about the metal centre in many structurally characterized compounds led recently to the new definition of a steric coordination number [1] after the proposal of a cone angle packing model [2]. According to this model, the coordination saturation in *f*-group chemistry is explained on the basis of filling up the coordination space, the sum of the ligand cone angles being equal to a value which represents the criterion for the relevant packing. Bonding in *f*-transition element compounds is generally considered to be highly ionic in character [3], and the structure of the complexes should be very similar to the packing in an ionic lattice, the size and the shape of the ions being crucial factors in their arrangement. In the series of the cyclopentadienyl uranium chlorides $Cp_{4-n}UCl_n$ (Cp = C_5H_5), the stability of Cp_4U [4] and Cp_3UCl [5], the failure to isolate Cp_2UCl_2 [6] although $(C_5Me_5)_2UCl_2$ is quite stable [7], the fact that $CpUCl_3$ only exists under the form of 1 : 2 Lewis base adducts $CpUCl_3L_2$ (L = oxygen or nitrogen donor ligand) [8] are in full agreement with the predictions of the cone angle packing model, which have also been verified for a majority of actinide complexes.However, some facts cannot be easily explained in terms of such steric parameters. Why cannot Cp_2UCl_2 be stabilized by coordination of a Lewis base, Cp_2UCl_2L being expected to have a satisfactory steric environment? Since the chloride and the tridentate borohydride groups have similar cone angles [2], why are the sterically unsaturated derivatives $Cp_2U(BH_4)_2$ [9] and $CpU(BH_4)_3$ [10] so stable, and not the adducts $CpU(BH_4)_3L_2$ [11]? Clearly steric factors alone do not suffice to account for the relative stability of these complexes.

In order to obtain more detailed information on the electronic effects of the ancillary ligands on the properties of uranium compounds, we decided to use the tri-t-butylmethoxide group, denoted by tritox, which is a steric mimic of the ubiquitous cyclopentadienyl ligand [12] while rendering the metal centre more electrophilic. We report here on the synthesis and behaviour of the tritoxuranium(IV) chloride and borohydride compounds $(tritox)_{4-n}UX_n(THF)_x$ (X = Cl, BH_4; THF = tetrahydrofuran; $n = 1-3$) and a series of bis(tritox)uranium derivatives [13]. We also describe the X-ray crystal structures of $(tritox)U(BH_4)_3(THF)$ (IX) and $(tritox)_3U(BH_4)$ (XI).

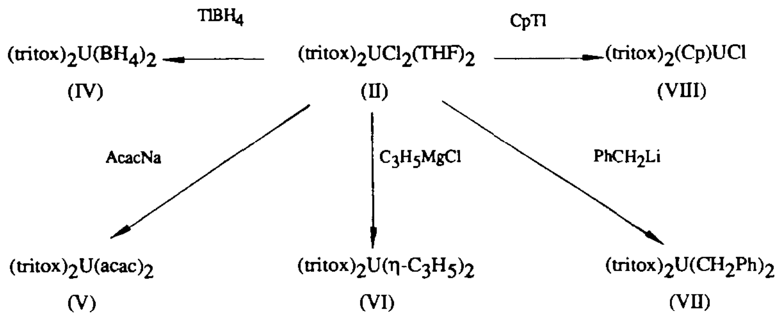
Results

The tritox uranium chloride complexes

The complexes $(tritox)UCl_3(THF)_x$ (I) and $(tritox)_2UCl_2(THF)_2$ (II) were respectively obtained by treatment of UCl_4 with 1 or 2 equivalents of (tritox)Li in tetrahydrofuran. Although the reactions were shown by ^1H NMR spectroscopic monitoring to proceed without detectable formation ($< 5\%$) of side products, the compounds could not be isolated analytically pure because of solvation/desolvation problems and contamination by LiCl. Thus, the NMR spectrum of I, freshly prepared in THF, exhibited a single resonance at 25.60 ppm corresponding to the tritox ligand but evaporation of the solution gave a green powder which was then insoluble in usual organic solvents; it is possible that this insolubility arises from a polymeric structure with chlorine bridges. Crystallization of II from THF–toluene afforded pink crystals that were judged from the NMR spectrum to be the solvate II, 2THF; when dried *in vacuo* or washed with toluene these crystals were reconverted into a green powder of II. Elemental analysis of II revealed the presence of LiCl, and formation of $(tritox)_2UCl_3Li(THF)_2$ cannot be ruled out, especially as $(tritox)_2ZrCl_3Li(OEt_2)_2$ was isolated from the reaction of $ZrCl_4$ with 2 equivalents of (tritox)Li in diethyl ether [12]. Treatment of II with 1 equivalent of (tritox)Li in toluene gave $(tritox)_3UCl$ (III) as the major product (NMR experiment). Reactions of the tritox uranium chlorides I–III with $TlBH_4$ gave the corresponding borohydride derivatives (*vide infra*), and II was a precursor for a series of bis(tritox) uranium complexes.

The bis(tritox) uranium derivatives

Replacement of chloride ligands of II by treatment with $TlBH_4$, $CH_3COCHCOCH_3Na$, $CH_2{=}CHCH_2MgCl$, $PhCH_2Li$ and CpTl afforded the bis(tritox) derivatives IV–VIII shown in Scheme 1. These crystalline compounds were obtained in satisfactory yields (40–70%) and identified from their elemental analyses and ^1H



Scheme 1. Synthesis of the bis(tritox) uranium derivatives (Acac = $CH_3COCHCOCH_3$).

NMR spectra (Table 1). The spectrum of VI exhibited at 30 °C a simple A_4X pattern, characteristic of fluxional allyl ligands [14]. The high field doublet was replaced at −80 °C by two broad resonances, indicating that the ground state structure of the allyl ligands is trihapto, as found for the related complexes $(\eta\text{-}C_3H_5)_2U(OR)_2$ (R = Et, ^{i}Pr, ^{t}Bu) [15]. If the latter are dimeric in toluene and in the solid state, the bulk of the tritox unit would prevent the formation of alkoxide

Table 1

NMR spectra for the complexes [a]

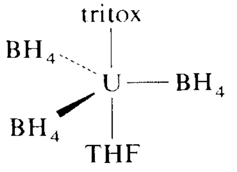
Compound	tritox ligand	Other ligands
(tritox)UCl$_3$(THF)$_x$ (I)	25.60	
(tritox)$_2$UCl$_2$(THF)$_2$ (II)	19.02 (s, 54H)	−3.10 (s, 8H, α-THF); −7.73 (s, 8H, β-THF)
(tritox)$_3$UCl (III)	6.52	
(tritox)$_2$U(BH$_4$)$_2$ (IV)	16.97 (s, 54H)	−84.65 (q, 85, 8H, BH$_4$)
(tritox)$_2$U(acac)$_2$ (V)	16.46 (s, 54H)	−17.65 (s, 2H, CH); −23.24 (s, 12H, CH$_3$)
(tritox)$_2$U(η-C$_3$H$_5$)$_2$ (VI)	7.25 (s, 54H)	−30.27 (s, 2H, CH); −66.81 (d, 11, 8H, CH$_2$)
at −80 °C [c]	17.15 (s, 18H) 100 (br, 300, 36H)	−63.18 (s, 2H, CH); −113.7 and −123.1 (br, 300, 4H = 4H, CH$_2$)
(tritox)$_2$U(CH$_2$Ph)$_2$ (VII)	16.66 (s, 54H)	−1.84 (t, 7, 4H, *m*-Ph); −8.58 (t, 7, 2H, *p*-Ph); −20.03 (d, 7, 4H, *o*-Ph); −173.9 (s, 4H, CH$_2$)
(tritox)$_2$(Cp)UCl (VIII)	14.17 (s, 54H)	−35.97 (s, 5H, Cp)
(tritox)U(BH$_4$)$_3$(THF) (IX)	26.20 (s, 27H)	43.25 (s, 4H, β-THF); 85.39 (s, 4H, α-THF) −86.42 (q, 80, 12H, BH$_4$)
(tritox)U(BH$_4$)$_3$(THF)$_2$ (X) [b,c]	37.7 (br, 30, 9H)	
	50.3 (br, 100, 9H)	−232.1 (br, 240, 4H, BH$_4$)
	57.6 (br, 30, 9H)	−266.0 (br, 240, 8H, BH$_4$)
(tritox)$_3$U(BH$_4$) (XI)	6.14 (s, 81H)	−96.09 (q, 80, 4H, BH$_4$)

[a] At 30 °C, in toluene-d_8 except I and X in THF-d_8. δ relative to TMS (multiplicity, J or half height width in Hz, intensity, assignment). [b] At −100 °C. [c] The tritox ligand gives rise to 2 or 3 signals at low temperature, because of the blocking of methyl rotations.

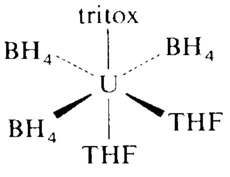
bridges [12], and the low temperature NMR spectra of complexes II and IV–VIII exhibited the signals corresponding to two equivalent tritox ligands. These bis(tritox) uranium(IV) compounds are quite stable in the solid state and in toluene or THF solution; in particular, they do not undergo any redistribution.

The tritox uranium borohydride complexes

The mono(tritox) compound (tritox)$U(BH_4)_3(THF)$ (IX) was prepared in 70% yield by treatment of $U(BH_4)_4(THF)_2$ with 1 equivalent of (tritox)H in toluene. When (tritox)Li was used instead of (tritox)H, a mixture of IX and IV, in the ratio 85 : 15, was obtained. The NMR spectrum of IX in toluene-d_8 (Table 1) showed that only one molecule of THF is coordinated to (tritox)$U(BH_4)_3$ and that the three borohydride ligands are equivalent, even at low temperature; the paramagnetic shifts of the signals corresponding to the tritox and THF ligands are in the opposite direction from those of the BH_4 groups. From consideration of the theoretical expression for the pseudo-contact shifts in axial symmetry [16], it is likely that IX adopts in solution the trigonal bipyramidal configuration **A** in which the BH_4 ligands occupy the equatorial positions; this geometry was found in the crystalline form of IX (*vide infra*). The two resonances at 85.39 and 43.25 ppm were shifted towards the diamagnetic region of the spectrum upon addition of tetrahydrofuran (ca 3 equivalents) because of the rapid exchange between the free and coordinated THF ligands. This exchange was slowed down at low temperature, and at −80 °C, the slow limit NMR spectrum revealed that no additional THF molecule had been coordinated to IX. However, formation of the hexacoordinated compound (tritox)$U(BH_4)_3(THF)_2$(X) was observed in THF-d_8 at low temperature. Below −90 °C, the borohydride ligands of X gave rise to two signals of relative intensity 8/4; both of these resonances are located in the high field region of the spectrum, indicating that X adopts the *mer* octahedral configuration **B**, with the three BH_4 groups in the equatorial plane and the two THF molecules in *cis* positions. That one of the two tetrahydrofuran ligands of X is not firmly attached to the metal centre was further demonstrated by evaporation of THF solutions of this complex, which gave crystals of IX. As is usually observed for organouranium complexes, triphenylphosphine oxide ligands are more strongly bonded than THF, and addition of $OPPh_3$ to a toluene solution of IX led to the successive formation of (tritox)$U(BH_4)_3(OPPh_3)$ and (tritox)$U(BH_4)_3(OPPh_3)_2$ in configuration **A** and **B**, respectively; these derivatives were characterized only from their NMR spectra.



(**A**)



(**B**)

We have tried to synthesize the tetracoordinated complex (tritox)$U(BH_4)_3$, the tritox analogue of $CpU(BH_4)_3$ [10]. It was not possible to prepare this compound from IX by refluxing in toluene [17], and treatment of $U(BH_4)_4$ with 1 equivalent of (tritox)H gave a mixture of unidentified products. Reaction of the uranium tetraborohydride with 1 equivalent of (tritox)Li in toluene was more encouraging: the bis(tritox) derivative IV, which was formed in ca 15% yield, was removed by successive crystallizations from pentane, but the major product, obtained as a green powder, could not be isolated analytically pure, free from a small amount of impurity having similar solubility in pentane. The NMR spectra of dilute solutions of this powder in toluene-d_8 (ca 5 mg per ml) correspond to the formula of the expected compound, but when the concentration is increased the spectra became very complicated, and suggest the formation of associated species. After addition of THF, the spectrum was identical to that of IX, thus confirming the possible existence of (tritox)U$(BH_4)_3$.

Treatment of $U(BH_4)_4$ with 2 equivalents of (tritox)Li afforded the bis(tritox) derivative IV (almost quantitative yield as indicated by NMR spectroscopy). The latter further reacted with 1 equivalent of (tritox)Li in toluene to give the tris(tritox) compound $(tritox)_3U(BH_4)$ (XI), which was isolated as pink crystals in 33% yield. In contrast to $Cp_2U(BH_4)_2$ and $Cp_3U(BH_4)$ which, in the presence of $U(BH_4)_4$, were respectively transformed into $CpU(BH_4)_3$ and $Cp_2U(BH_4)_2$ [10], no ligand exchange reactions were observed between IV or XI and the uranium tetraborohydride.

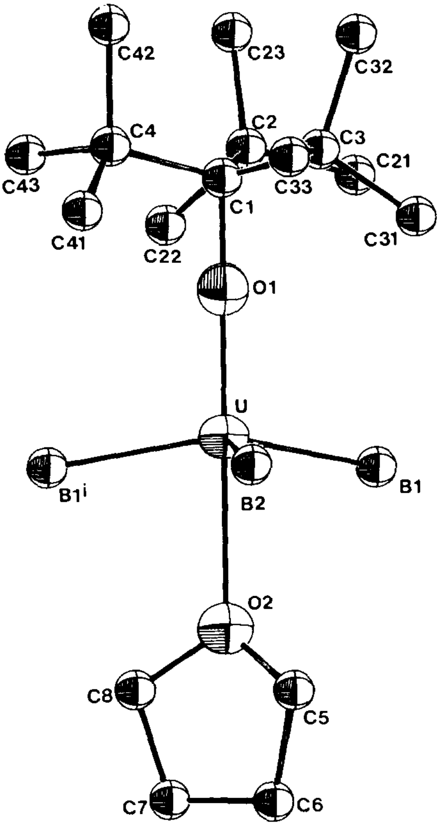


Fig. 1. View of molecule IX.

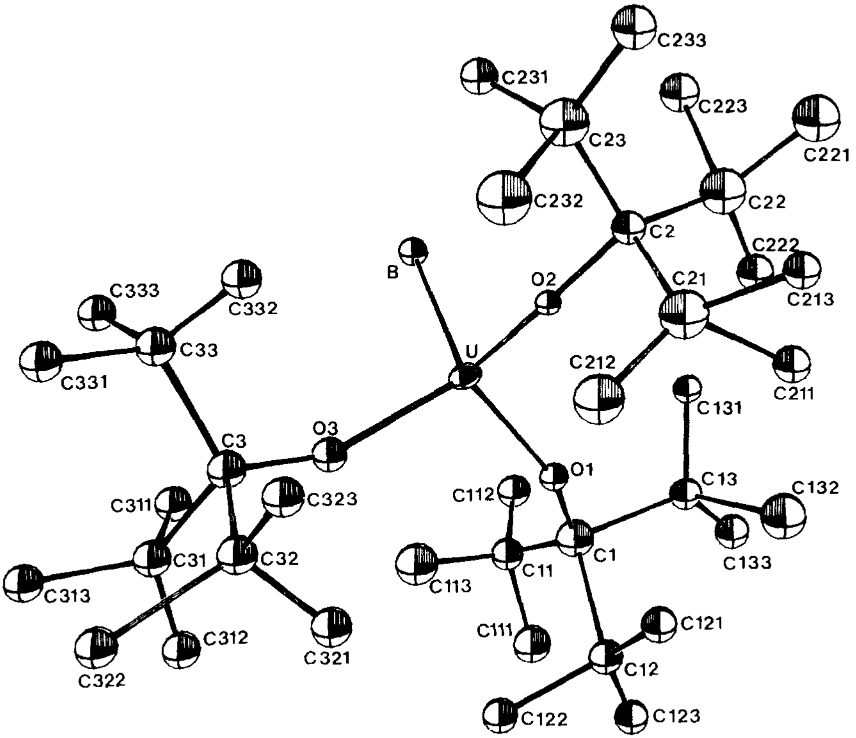


Fig. 2. View of molecule XI.

Crystal structures of (tritox)U(BH_4)$_3$(THF) (IX) and (tritox)$_3$U(BH_4) (XI)

The tritox uranium compounds IV, IX and XI are the first examples of mixed alkoxo-borohydride transition metal complexes and it was of interest to determine their crystal structures. ORTEP drawings [18] of IX and XI are shown in Figs. 1 and 2, respectively; selected bond distances and angles are listed in Table 2. The structure of IX consists of discrete molecules in which the U atom is five coordinate in a slightly deformed trigonal bipyramidal arrangement with the equatorial base consisting of the three BH_4 groups. The pyramid axis, defined by the U atom and the apical positions occupied by the oxygen atoms of the tritox and THF ligands, is essentially linear (178.3(5)°) and perpendicular to the trigonal base. Such five coordination is not common for uranium compounds, and was previously encountered only in dimeric or sterically saturated complexes [19]. The U atom is out of the plane of the three B atoms by 0.4 Å towards the tritox ligand. The linear U–O(1)–C(1) angle (178.6(5)°) and the very short U–O(1) distance (1.97(1) Å) provide a clear manifestation of strong π-bonding between the U and O atoms. Such interaction of oxygen atoms with the metal centre in alkoxide complexes is well established [20], and is also observed in compound XI, where the U–O–C angles and the U–O distances average 170° and 2.07 Å, respectively. The borohydride and the three tritox ligands of XI form a distorted tetrahedron around the uranium atom. The B–U–O angles (104° average) and O–U–O angles (114.5° average) are very close to the X–U–Cp(centroid) and Cp(centroid)–U–Cp(centroid) angles in the Cp_3UX derivatives [21], reflecting the similar conical shape and steric

Table 2

Selected bond distances (Å) and angles (°)

$(tritox)U(BH_4)_3(THF)$ (IX)		$(tritox)_3U(BH_4)$ (XI)	
U environment			
U–B(1)	2.51(2)	U–B	2.58(2)
U–B(2)	2.65(2)	U–O(1)	2.074(7)
U–O(1)	1.97(1)	U–O(2)	2.073(6)
U–O(2)	2.57(2)	U–O(3)	2.077(7)
O(1)–U–B(1)	99.1(4)	O(1)–U–B	103.4(4)
O(1)–U–B(2)	98.6(5)	O(2)–U–B	104.2(4)
O(1)–U–O(2)	178.3(5)	O(3)–U–B	104.4(4)
B(1)–U–B(2)	114.8(4)	O(1)–U–O(2)	113.5(3)
$B(1)–U–B(1^i)$	123.2(5)	O(1)–U–O(3)	111.5(3)
O(2)–U–B(1)	81.6(4)	O(2)–U–O(3)	118.1(3)
O(2)–U–B(2)	79.7(5)	U–O(1)–C(1)	171.1(6)
U–O(1)–C(1)	178.6(5)	U–O(2)–C(2)	172.8(6)
		U–O(3)–C(3)	167.9(6)
Tritox ligand			
O(1)–C(1)	1.49(2)	⟨O–C⟩	1.45(1)
$\langle C(1)–C_{tert} \rangle$	1.62(5)	$\langle C(1,2,3)–C_{tert} \rangle$	1.62(2)
$\langle C_{tert}–C_{Me} \rangle$	1.62(9)	$\langle C_{tert}–C_{Me} \rangle$	1.56(6)

bulk of the tritox and cyclopentadienyl ligands. In both complexes IX and XI, the short U–B distances are characteristic of tridentate BH_4 ligands [22] and the geometry of the bulky alkoxide ligand is identical to that found in other tritox transition metal derivatives [12,23].

Discussion

It is interesting to compare the coordination chemistry of the isosteric units $CpUCl_3$, $CpU(BH_4)_3$ and $(tritox)U(BH_4)_3$. The structure and stability of their adducts with the same Lewis base, tetrahydrofuran, are quite different and, obviously, are not determined solely by the steric parameters. The only stable compound which satisfies to the criteria of the cone angle packing model is $CpUCl_3(THF)_2$ [2,8]; the latter has not tendency to undergo dissociation of a THF molecule, and was found to undergo a facile ligand exchange via the heptacoordinated intermediate $CpUCl_3(THF)_3$ [8]. In contrast, we have previously shown that the THF ligands are not so strongly bonded to the metal centre in the borohydride analogue $CpU(BH_4)_3(THF)_2$ [11], which could not be isolated because of its rapid transformation into an equimolar mixture of $Cp_2U(BH_4)_2$ and $U(BH_4)_4(THF)_2$. However, the monocyclopentadienyl compound $CpU(BH_4)_3$, which is sterically very unsaturated, is quite stable in non-coordinating solvents; it is monomeric in the solid state and can be easily sublimed [10]. The pentadienyl and cyclohexadienyl analogues (1,4-dimethylpentadienyl)$U(BH_4)_3$ and (6,6-dimethylcyclohexadienyl)U-$(BH_4)_3$ exhibited similar properties [24]. The difference in behaviour between $CpUCl_3$ and $CpU(BH_4)_3$ can be attributed to the higher electron-donating ability of the borohydride ligands [28]; the $CpUCl_3$ species, which is electronically unsaturated, has been isolated only in the form of adducts with donor ligands, whereas the bis-tetrahydrofuran adduct $CpU(BH_4)_3(THF)_2$ should be destabilized because of the two much important electron density on the metal. It is likely, for both steric and electronic reasons, that $(tritox)UCl_3$ would readily coordinate THF molecules or form polymers with chlorine bridges; unfortunately, it was not possible to determine the exact structure of $(tritox)UCl_3(THF)_x$. In contrast to $CpU(BH_4)_3$, the more electrophilic metal centre of the tritox species $(tritox)U(BH_4)_3$ favours the formation of stable adducts with tetrahydrofuran. The most striking feature is the remarkable stability of the sterically unsaturated complex $(tritox)U(BH_4)_3(THF)$ (IX), which is resistant towards both dissociation and coordination of a THF ligand. Thus it appears that the electron-richness of $(tritox)U(BH_4)_3$ is intermediate between those of $CpUCl_3$ and $CpU(BH_4)_3$, and we judge that the metal charge density is close to "ideal" in compound IX.

The same electronic effects should be responsible for the difference in behaviour of the Cp_2UCl_2 and $(tritox)_2UCl_2$ units. Like $CpU(BH_4)_3$, Cp_2UCl_2 disproportionates in THF, presumally by the intermediacy of $Cp_2UCl_2(THF)_x$, and is transformed into an equimolar mixture of $CpUCl_3(THF)_2$ and Cp_3UCl [6]; the less electron-rich tritox species forms the stable adduct $(tritox)_2UCl_2(THF)_2$ (or the anion $(tritox)_2UCl_3^-$).

It is noteworthy that no rearrangement of $(tritox)U(BH_4)_3(THF)_2$ was observed in THF, whereas $CpU(BH_4)_3(THF)_2$ and $Cp_2UCl_2(THF)_x$ readily disproportionate in this solvent. On the other hand, in contrast to $Cp_2U(BH_4)_2$ and $Cp_3U(BH_4)$ which comproportionate with $U(BH_4)_4$ in toluene, the tritox analogues are inert under such conditions. It is conceivable that the ligand exchange reactions of the cyclopentadienyl derivatives are facilitated by the accessibility of Cp-bridged intermediates or transition states [25], and that the bulky tritox ligand fails to provide low energy pathways to the formation of stable rearranged products.

Conclusion

The series of complexes listed in Table 3 clearly illustrate that steric parameters are not the only factors that must be taken into account in to explaining and or predicting the structure and the stability of actinide compounds. It is evident that the electron density on the metal centre plays a determining role, and must not exceed an upper limit. An important consequence of this result is that synthesis of sterically unsaturated species should be favoured by the use of electron-donating

Table 3

Stability of isosteric units and their THF adducts

Isosteric units	Stable compound
$CpU(BH_4)_3$	$CpU(BH_4)_3$
$(tritox)U(BH_4)_3$	$(tritox)U(BH_4)_3(THF)$
$CpUCl_3$	$CpUCl_3(THF)_2$
$(tritox)UCl_3$	$(tritox)UCl_3(THF)_x$
$Cp_2U(BH_4)_2$	$Cp_2U(BH_4)_2$
$(tritox)_2U(BH_4)_2$	$(tritox)_2U(BH_4)_2$
Cp_2UCl_2	
$(tritox)_2UCl_2$	$(tritox)_2UCl_2(THF)_2$

ligands. Such species could be prepared in and isolated from coordinating solvents like THF, which is commonly used in organoactinide chemistry, if the eventual formation of electron-rich adducts is reversible; this situation was encountered, for example, with (tritox)U$(BH_4)_3$(THF). In some cases, the adducts will readily undergo facile rearrangements, as observed for CpU$(BH_4)_3$$(THF)_2$ and Cp_2UCl_2 $(THF)_x$, and the desired sterically unsaturated compound can be isolated only if they can be synthesized in non-coordinating solvents.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (Germany). The ^{1}H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The chemical shifts are given as δ values relative to tetramethylsilane. The ^{1}H NMR spectra are given in Table 1.

All experiments were carried out under argon in Schlenk type glassware on a high vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by the standard methods and distilled immediately prior to use. UCl_4 [26], $U(BH_4)_4$ [27], (tritox)H [28], (tritox)Li [12], TlCp [29] and $TlBH_4$ [30] were prepared by published methods.

Syntheses

(tritox)$UCl_3$$(THF)_x$ (I). An NMR tube was charged with UCl_4 (15 mg) and (tritox)Li (8.2 mg) in THF-d_8 (0.5 ml). After 20 min at 80 ° C, the NMR spectrum of the blue-green solution exhibited a singlet at 25.60 ppm. Evaporation of the solution gave a green powder which was insoluble in THF, toluene, or CH_2Cl_2. $TlBH_4$ (3.5 equivalents) was added to a freshly prepared solution of I in THF-d_8 and after 10 h at 80 ° C, the NMR spectrum showed the formation of (tritox)U$(BH_4)_3$(THF) (ca 50% yield).

$(tritox)_2$$UCl_2$$(THF)_2$ (II). A 50 ml round bottom flask was charged with UCl_4 (0.92 g) and (tritox)Li (1.00 g) and THF (25 ml) was condensed into it under vacuum at −78 ° C. After 24 h at 20 ° C, the volume of the orange solution was reduced to 10 ml and addition of toluene (10 ml) led to precipitation of pink crystals, which were filtered off and rapidly dried under vacuum. The NMR spectrum of these crystals in toluene-d_8 corresponds to the formula II · 2THF. (δ: 19.04 (54H, s, tritox); −1.25 (16H, s, β-THF); −3.40 (16H, s, α-THF).) The pink crystals were washed with toluene and dried under vacuum to give II as a green powder (1.59 g, 80%).

$(tritox)_3$UCl (III). An NMR tube was charged with II (15 mg) and (tritox)Li (4 mg) in toluene-d_8 (0.5 ml). After 1 h at 20 ° C, the NMR spectrum showed two signals at 6.5 and 4.5 ppm with intensities in the ratio 60 : 40. $TlBH_4$ (4 mg) was introduced into the tube which was kept at 80 ° C for 10 h; in the NMR spectrum, the signal at 6.5 ppm was replaced by the resonances corresponding to $(tritox)_3$U(BH_4).

$(tritox)_2$U$(BH_4)_2$ (IV). A 50 ml round bottom flask was charged with II (300 mg) and $TlBH_4$ (174 mg) and toluene (25 ml) was condensed into it under vacuum at −78 ° C. The mixture was stirred at room temperature for 48 h. The green solution was filtered and the solvent was evaporated off, leaving a green powder

(140 mg, 60%). An analytical sample was obtained by crystallization from cold pentane. Analysis. Found: C, 46.75; H, 9.21; B, 3.16. $C_{26}H_{22}B_2O_2U$ calcd.: C, 46.84; H, 9.31; B, 3.30%.

(tritox)$_2$U(CH$_3$COCHCOCH$_3$)$_2$ (V). A 50 ml round bottom flask was charged with II (300 mg) and $CH_3COCHCOCH_3Na$ (90 mg) and toluene (25 ml) was condensed into it under vacuum at −78° C. The mixture was stirred at 20° C for 4 h. The red solution was filtered and evaporated to dryness, to give V as an orange-red powder (175 mg, 60%). The analytical sample was obtained by crystallization from cold toluene. Analysis. Found: C, 51.52; H, 7.98. $C_{36}H_{68}O_4U$ calcd.: C, 51.80; H, 8.15%.

(tritox)$_2$U(η-C$_3$H$_5$)$_2$ (VI). A 50 ml round bottom flask was charged with II (333 mg) in toluene (25 ml) and $CH_2{=}CHCH_2MgCl$ (390 μl of a 2 *M* solution in THF) was added via a microsyringe. After 2 h at room temperature, the red solution was filtered and evaporated, to give VI as a brown powder (197 mg, 70%). Analytically pure crystals were obtained from cold pentane. Analysis. Found: C, 53.11; H, 8.78. $C_{32}H_{64}O_2U$ calc.: C, 53.48; H, 8.91%.

(tritox)$_2$U(CH$_2$Ph)$_2$ (VII). A 50 ml round bottom flask was charged with II (300 mg) and $PhCH_2Li$ (70 mg) and toluene (25 ml) was added at −78° C under vacuum. After 2 h at room temperature, the red solution was filtered and evaporated, to give VII as a red powder (175 mg, 61%). The analytical sample was obtained by crystallization from cold pentane. Analysis. Found: C, 58.48; H, 8.24. $C_{40}H_{68}O_2U$ calc.: C, 58.68; H, 8.31%.

(tritox)$_2$U(Cp)UCl (VIII). A 50 ml round bottom flask was charged with II (300 mg) and CpTl (95 mg) and toluene (25 ml) was condensed into it at −78° C under vacuum. After 12 h at room temperature, the pink solution was filtered and evaporated, to give VIII as a pink powder (104 mg, 40%). The analytical sample was obtained by crystallization from toluene. Analysis. Found: C, 50.27; H, 7.92; Cl, 4.62. $C_{31}H_{59}ClO_2U$ calcd.: C, 50.51; H, 8.01; Cl, 4.82%.

(tritox)U(BH$_4$)$_3$(THF) (IX). A 50 ml round bottom flask was charged with $U(BH_4)_4$ (300 mg); toluene (10 ml) and THF (5 ml) were condensed into it at −78° C under vacuum. Evaporation of the solution afforded $U(BH_4)_4(THF)_2$ as a green powder. (Tritox)H (200 mg) was added and toluene (25 ml) was condensed into the flask. After 16 h at 110° C, the solvent was evaporated off and the residue was washed with pentane (5 ml) and extracted in hot pentane (20 ml). Upon cooling, the solution deposited green microcrystals of IX, which were filtered off and dried under vacuum (235 mg, 42%). Slow evaporation of the mother liquors afforded crystals of IX suitable for X-ray diffraction studies. The analytical sample of IX was obtained by recrystallization from pentane. Analysis. Found: C, 36.69; H, 8.38; B, 5.82. $C_{17}H_{44}B_3O_3U$ calcd.: C, 36.82; H, 8.48; B, 5.96%.

(tritox)U(BH$_4$)$_3$. A solution of (tritox)Li (205 mg) in toluene (10 ml) was slowly introduced into a 50 ml round bottom flask containing $U(BH_4)_4$ (300 mg) in toluene (10 ml). After the addition, the solvent was evaporated off, leaving a yellowish powder, the NMR spectrum of which in toluene-d_8 showed the tritox signal of IV and another signal at 22.79 ppm. After extraction with pentane (2 × 20 ml), a green microcrystalline powder (70 mg) was obtained by 3 successive crystallizations from this solvent; the NMR spectrum in toluene-d_8 exhibited signals which were assigned to (tritox)$U(BH_4)_3$ (δ(30° C): 22.79 (s, 27H, tritox); 7 (br, $W_{1/2}$ 600 Hz, 12H, BH_4)), and other small peaks which were not attributed. The low

temperature NMR spectra of dilute solutions of this powder (ca 5 mg per ml) also correspond to the proposed formulation (δ ($-80\,°$C): 50.1, 38.9 and 16.6 (br, $W_{1/2}$ 50–100 Hz, 3 × 9H, tritox); 7 (br, $W_{1/2}$ 600 Hz, 12H, BH_4)); the low temperature spectra of more concentrated solutions (> 20 mg per ml) were not interpretable. The spectrum of the powder in THF-d_8 was identical to that of IX.

(tritox)U(BH$_4$)$_3$(OPPh$_3$)$_n$ (n = 1, 2). An NMR tube was charged with IX (10 mg) and $OPPh_3$ (5 mg) in toluene-d_8 (0.4 ml). The mixture was heated at 60 °C for 2 min, after which the NMR spectrum showed the quantitative formation of (tritox)U$(BH_4)_3(OPPh_3)$.

(δ(30 °C): 41.79 (s, 6H, *o*-Ph); 28.39 (s, 27H, tritox); 12.88 (s, 6H, *m*-Ph); 11.34 (s, 3H, *p*-Ph); −112.41 (br, $W_{1/2}$ 300 Hz, 12H, BH_4)). Green microcrystals separated upon addition of $OPPh_3$ (10 mg); after evaporation of toluene-d_8, the spectrum in CD_2Cl_2 showed the formation of (tritox)U$(BH_4)_3(OPPh_3)_2$.

(δ(-20 °C): 52.10 (s, 6H, *ortho*-axial); 45.34 and 35.88 (m, 27H, tritox); 15.16 (s, 6H, *meta*-axial); 13.81 (s, 3H, *para*-axial); 4.66 (s, 3H, *para*-equatorial), 3.00 (s, 6H,

Table 4

Crystallographic data and experimental details

Crystal data	IX	XI
Crystal dimensions (mm)	0.6 × 0.35 × 0.30	0.65 × 0.25 × 0.10
Color	green	pink
Crystal system	orthorhombic	monoclinic
Space group	$Pmn2_1$	$P2_1/a$
a (Å)	12.543(3)	16.867(9)
b (Å)	8.804(3)	12.532(4)
c (Å)	11.070(2)	21.122(6)
β (°)		109.46(4)
V (Å^3)	1222.6	4209.8
Z	2	4
D_{calc} (g cm^{-3})	1.483	1.343
μ(Mo-K_α) (cm^{-1})	56.5	36.8
Data collection		
θ limits (°)	1, 28	1, 20
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$
Range absc. trans.	0.888, 0.997	0.552, 0.999
Range h, k, l	$0 < h < 11$	$0 < h < 16$
	$0 < k < 14$	$0 < k < 12$
	$0 < l < 16$	$-20 < l < 20$
Reflections collected		
total	1717	4090
unique	1472	3722
with	$> 2.5\sigma(I)$: 941	$> 3\sigma(I)$: 2465
Final values		
$R(F) = \Sigma\|\|F_o\| - \|F_o\|\|/\Sigma\|F_o\|$	0.047	0.038
$R_w(F) = [\Sigma_w\|\|F_o\| - \|F_c\|\|^2/\Sigma_w\|F_o\|^2]^{1/2}$	0.045	0.044
max shift/esd	0.07	0.02
max residual (e/Å^3)	< 1	< 1

meta-equatorial); −12.77 (s, 6H, *ortho*-equatorial); −191.1 and −206 (br, $W_{1/2}$ 100 Hz, 8H + 4H, BH_4).

(tritox)$_3$U(BH$_4$)(XI). A 50 ml round bottom flask was charged with IV (155 mg) and (tritox)Li (48 mg) and toluene (20 ml) was condensed into it under vacuum at −78° C. After 1 h at 100° C, the solution was filtered and evaporated to dryness. Crystallization of the oily residue from pentane afforded XI as a pink powder, which was filtered off and dried under vacuum (65 mg, 33%). Analysis. Found: C, 51.27; H, 9.15; B, 1.68. $C_{39}H_{85}OBU$ calcd.: C, 55.05; H, 10.00; B, 1.29%. Crystals of XI suitable for X-ray diffraction studies were obtained by recrystallization from cold pentane.

X-ray analysis

Single crystals of IX and XI were introduced into thin-walled Lindeman glass tubes in the glove box. Data were collected at room temperature on an Enraf Nonius CAD4 diffractometer equipped with a graphite monochromator (λ = 0.71073 Å). The cell dimensions were determined from the setting angles of 25 randomly selected reflections with θ between 8 and 12°. Three standards reflections were measured after each hour to monitor crystal decay, instrumental stability and crystal alignment. No significant variations were observed for both compounds. The data were corrected for Lorentz polarization effects and absorption (using an empirical correction based on ψ scan [31]). For both compounds, the Patterson function

Table 5

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their esd's and occupation factors for compound IX

Atom	x	y	z	B (Å^2)	Occupation factor
U	0.000	0.1787(1)	0.000	4.92(8) [a]	1.0
O(1)	0.000	0.319(1)	−0.139(1)	5.0(5) [a]	1.0
O(2)	0.000	0.004(1)	0.185(2)	6.4(5) [a]	1.0
B(1)	0.176(2)	0.051(2)	−0.035(2)	9.9(2)	0.5
B(2)	0.000	0.382(2)	0.176(2)	9.0(2)	1.0
C(1)	0.000	0.421(1)	−0.245(1)	4.8(2)	1.0
C(3)	0.0932	0.538(1)	−0.214(1)	6.1(2)	0.5
C(31)	0.197(2)	0.468(2)	−0.154(2)	8.5(2)	0.5
C(32)	0.134(2)	0.644(2)	−0.325(2)	9.2(2)	0.5
C(33)	0.044(2)	0.665(2)	−0.119(2)	9.7(2)	0.5
C(4)	−0.122(2)	0.473(2)	−0.261(2)	8.1(2)	0.5
C(41)	−0.167(2)	0.527(2)	−0.126(2)	8.7(2)	0.5
C(42)	−0.127(2)	0.619(2)	−0.354(2)	11.2(2)	0.5
C(43)	−0.198(2)	0.355(2)	−0.324(2)	10.5(2)	0.5
C(2)	0.043(2)	0.315(2)	−0.361(2)	7.5(2)	0.5
C(21)	0.162(2)	0.273(2)	−0.346(2)	11.1(2)	0.5
C(22)	−0.032(2)	0.154(2)	−0.346(2)	10.6(2)	0.5
C(23)	0.033(2)	0.390(2)	−0.492(2)	10.5(2)	0.5
C(5)	0.062(2)	0.025(2)	0.294(2)	12.0(2)	0.5
C(6)	0.047(2)	−0.137(1)	0.363(2)	9.6(2)	0.5
C(7)	−0.055(2)	−0.202(2)	0.318(2)	12.2(2)	0.5
C(8)	−0.094(2)	−0.078(2)	0.226(2)	7.7(2)	0.5

[a] $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$.

revealed the positions of the U atom and the subsequent difference electron density maps gave the position of all the non hydrogen atoms. The structures were refined by full-matrix least-squares (*F*). For IX, the difference electron density maps revealed the coordinates of the atoms which are located in the crystallographic

Table 6

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their esd's for compound XI

Atom	x	y	z	B (Å^2)
U	0.04515(3)	0.05443(4)	0.23159(2)	2.574(9) [a]
O(1)	0.1118(5)	0.1376(6)	0.3177(4)	3.6(2) [a]
O(2)	−0.0295(4)	0.1512(6)	0.1554(3)	3.3(2) [a]
O(3)	−0.0079(4)	−0.0837(6)	0.2543(4)	3.4(2) [a]
B	0.1611(9)	−0.013(1)	0.1867(8)	4.4(4)
C(1)	0.1626(7)	0.180(1)	0.3828(6)	3.6(3)
C(2)	−0.0742(6)	0.2294(9)	0.1060(5)	2.9(2)
C(3)	−0.0525(7)	−0.1813(9)	0.2549(5)	3.4(3)
C(11)	0.0995(8)	0.196(1)	0.4241(7)	4.9(3)
C(12)	0.2046(8)	0.290(1)	0.3690(6)	4.6(3)
C(13)	0.2360(8)	0.090(1)	0.4138(7)	5.0(3)
C(21)	−0.1346(8)	0.291(1)	0.1385(6)	4.8(3)
C(22)	−0.1225(9)	0.167(1)	0.0384(7)	6.6(4)
C(23)	−0.0012(9)	0.307(1)	0.0972(8)	6.9(4)
C(31)	−0.0668(8)	−0.238(1)	0.1830(6)	4.6(3)
C(32)	0.0063(7)	−0.254(1)	0.3171(6)	3.9(3)
C(33)	−0.1402(7)	−0.145(1)	0.2644(6)	4.4(3)
C(111)	0.0128(8)	0.240(1)	0.3799(7)	6.5(4)
C(112)	0.0712(9)	0.087(1)	0.4483(8)	7.3(4)
C(113)	0.1312(9)	0.268(1)	0.4875(7)	7.2(4)
C(121)	0.1411(8)	0.383(1)	0.3493(7)	6.3(4)
C(122)	0.2379(8)	0.279(1)	0.3080(6)	5.0(3)
C(123)	0.2792(9)	0.331(1)	0.4303(7)	6.3(4)
C(131)	0.2787(9)	0.098(1)	0.4912(7)	6.9(4)
C(132)	0.3062(7)	0.084(1)	0.3835(7)	6.9(4)
C(133)	0.1976(9)	−0.026(1)	0.3986(8)	6.8(4)
C(211)	−0.0870(9)	0.370(1)	0.1960(7)	6.9(4)
C(212)	−0.1754(8)	0.215(1)	0.1756(7)	6.2(4)
C(213)	−0.2071(8)	0.356(1)	0.0877(7)	6.1(4)
C(221)	−0.206(1)	0.108(1)	0.0428(8)	8.5(5)
C(222)	−0.1538(9)	0.234(1)	−0.0279(7)	7.3(4)
C(223)	−0.0741(9)	0.073(1)	0.0241(7)	6.7(4)
C(231)	0.071(1)	0.328(1)	0.1612(8)	8.1(5)
C(232)	−0.034(1)	0.418(1)	0.0644(8)	7.9(5)
C(233)	0.047(1)	0.252(1)	0.0529(8)	9.2(5)
C(311)	−0.0871(9)	−0.156(1)	0.1254(7)	6.3(4)
C(312)	0.0147(8)	−0.294(1)	0.1784(7)	5.9(4)
C(313)	−0.1355(8)	−0.325(1)	0.1630(7)	6.5(4)
C(321)	0.1001(8)	−0.255(1)	0.3210(7)	5.6(3)
C(322)	−0.0214(8)	−0.374(1)	0.3151(7)	6.6(4)
C(323)	0.0103(8)	−0.210(1)	0.3867(6)	6.3(4)
C(331)	−0.1912(8)	−0.232(1)	0.2873(7)	5.9(4)
C(332)	−0.1252(8)	−0.051(1)	0.3165(7)	6.0(3)
C(333)	−0.2051(9)	−0.093(1)	0.2010(7)	7.3(4)

[a] $B_{\mathrm{eq}} = 4/3\Sigma_i\Sigma_j\beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$.

symmetry plane m(U, O(1), O(2), B(2) and C(1)) and showed a statistical disorder of both tritox and THF ligands about this plane. It was difficult to separate the two positions of these two ligands since some atoms were very close to the m plane. Because of this disorder, the distances C–C, C–O in THF and C–C in tritox were constrained to 1.54(5), 1.43(5) and 1.55(2) Å, respectively, during the full-matrix least-squares refinement using the SHELX computing program [32]. Only U and O atoms were refined anisotropically for both compounds. H atoms, not introduced in the refinement for IX, were introduced at calculated positions for XI (C–H = 0.95 Å and $B = 6$ Å^2) and were not refined but constrained to ride on their C atoms. All calculations were performed on a Micro Vax II computer with the Enraf–Nonius Structure Determination Package [33]. Analytical scattering factors for neutral atoms [34] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 4; final positional and thermal parameters are listed in Tables 5 and 6 for compounds IX (with occupation factors), and XI, respectively.

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