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Tetramethylphospholyluranium complexes and their pentamethylcyclopentadienyl analogues

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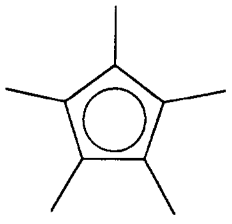
Abstract

The mono- and bis-(tetramethylphospholyl)uranium complexes [U(tmp)(Cl)$_3$(L)$_2$] (tmp = C_4Me_4P, L = tetrahydrofuran or L_2 = dimethoxyethane), [U(tmp)(X)$_3$] (X = BH_4, CH_2Ph) and [U(tmp)$_2$(X)$_2$] (X = Cl, BH_4, alkyl, or alkoxide) were compared with their pentamethylcyclopentadienyl (cp*) analogues. The crystal structures of [U(tmp)(Cl)$_3$(dimethoxyethane)] and [U(cp*)$_2$(BH_4)$_2$] have been determined. Although the structures of the phospholyl compounds are similar to those of their cyclopentadienyl counterparts, the distinct electronic effects of the tmp and cp* ligands (tmp being less electron-donating than cp*) are manifest in the coordinating and redox properties of the complexes.

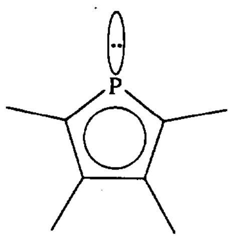
Key words: Uranium; Cyclopentadienyl; Phospholyl

1. Introduction

In order to distinguish between the electronic and steric effects of ancillary ligands on the structures and properties of actinide complexes, we have compared a series of compounds which have ligands of similar size, defined by their cone angle, but with different electron-donating abilities. The pair of isosteric ligands that we have already considered are borohydride and chloride on the one hand, and tri(tertiarybutyl)methoxide and cyclopentadienyl on the other. From these previous studies, it appeared that the electron density on the metal plays a determining role and cannot exceed an upper limit; the synthesis of sterically unsaturated species should be favoured by electron-donating ligands [1]. Here we report a series of mono- and bis-(tetramethylphospholyl)uranium complexes, that are compared with their pentamethylcyclopentadienyl analogues. The two ligands, represented below, have practically the same size, but the C_4Me_4P group (tmp) is less electron-donating than C_5Me_5 (cp*).



cp*



tmp

2. Results and discussion

2.1. Syntheses

The pentamethylcyclopentadienyluranium chlorides [U(cp*)(Cl)$_3$(THF)$_2$] (THF = tetrahydrofuran) and [U(cp*)$_2$(Cl)$_2$], synthesized by Marks *et al.* around 1980 [2,3], are cornerstones in organouranium chemistry, being the precursors of a series of derivatives in the IV and III oxidation states. The tetramethylphospholyl analogues [U(tmp)(Cl)$_3$(DME)] (**1a**) (DME = dimethoxyethane), [U(tmp)(Cl)$_3$(THF)$_2$] (**1b**), and [U(tmp)$_2$(Cl)$_2$] (**2**) were prepared according to Scheme 1.

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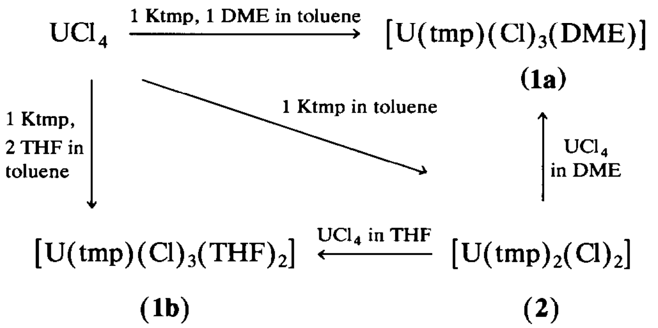


Scheme 1. Preparation of the chloride complexes **1** and **2**.

Treatment of UCl_4 with 1 equiv of Ktmp in toluene readily afforded the bis(phospholyl) complex **2** which, after extraction in pentane, was isolated as brown crystals, in 29% yield. The same reaction in the presence of 1 equiv of DME gave red crystals of **1a** (56%), which was alternatively prepared in almost quantitative yield by comproportionation of **2** and UCl_4 in dimethoxyethane. The THF adduct **1b** was prepared in a manner similar to that for **1a**, but it was contaminated with an oily impurity. Complexes **1** could not be isolated from the reaction of UCl_4 and Ktmp in THF or DME, because in these solvents their synthesis was impeded by the concomitant reduction of the uranium tetrachloride. On the other hand, complex **2** could not be obtained in better yield by using 2 equiv of Ktmp since, under these conditions, competitive formation of $[U(tmp)_3(Cl)]$ occurs [4].

The synthesis and characteristics of the phospholyluranium borohydrides $[U(tmp)(BH_4)_3]$ (**3**) and $[U(tmp)_2(BH_4)_2$ (**4**) were described previously [5]. For comparison, the pentamethylcyclopentadienyl analogues have been prepared (Scheme 2) [6*].

Treatment of $U(BH_4)_4$ with 1 or 2 equiv of Kcp* in toluene gave the red complexes $[U(cp^*)(BH_4)_3]$ (**5**) and $U(cp^*)_2(BH_4)_2]$ (**6**), respectively, which were extracted in pentane and crystallized from this solvent (82 and 58% respectively). The monocyclopentadienyl compound **5** could be easily purified by sublimation, its vapour pressure being of the same order of magnitude as that of **3** or of $[U(C_5H_5)(BH_4)_3]$ [5]. The mixed ring compound $[U(cp^*)(tmp)(BH_4)_2]$ (**7**) was isolated in 90% yield from the reaction of **5** with 1 equiv of Ktmp.

Marks *et al.* prepared a series of alkyl compounds by treatment of $[U(cp^*)(Cl)_3(THF)_2]$ and $[U(cp^*)_2(Cl)_2]$ with alkyl lithium reagents [2,3]. The phospholyl analogues **8**–**10** have been synthesized in toluene from $[U(tmp)(BH_4)_3]$ (**3**) and $[U(tmp)_2(BH_4)_2]$ (**4**), according to eqns. (1) and (2), and the mixed ring derivatives **11** and **12** were obtained from **7** (eqn. 3); after extraction in pentane, the products were isolated as red microcrystalline powders in 50–70% yield. Compounds **8**–**10** could be obtained from the chlorides **1** and **2** but in much lower yield (*ca.* 25%), their formation being impeded by competitive reduction reactions.

$$\underset{\mathbf{3}}{[U(tmp)(BH_4)_3]} + 3LiCH_2Ph \longrightarrow \underset{\mathbf{8}}{[U(tmp)(CH_2Ph)_3]} + 3LiBH_4 \quad (1)$$

$$\underset{\mathbf{4}}{[U(tmp)_2(BH_4)_2]} + 2LiR \longrightarrow [U(tmp)_2(R)_2] + 2LiBH_4 \quad (2)$$

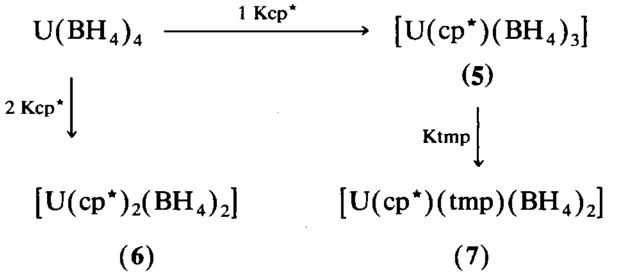
$$\mathbf{9}, R = Me;\ \mathbf{10}, R = CH_2SiMe_3$$

$$\underset{\mathbf{7}}{[U(cp^*)(tmp)(BH_4)_2]} + 2LiR \longrightarrow [U(cp^*)(tmp)(R)_2] + 2LiBH_4 \quad (3)$$

$$\mathbf{11}, R = Me;\ \mathbf{12}, R = CH_2SiMe_3$$

The mixed alkyl borohydride complexes $[U(tmp)_2(BH_4)(R)]$ and $[U(cp^*)(tmp)(BH_4)(R)]$ were observed as intermediates during the synthesis of **9**–**12**. Treatment of **4** with 1 equiv of LiMe gave an equilibrium mixture of **4** (12%), **9** (12%) and $[U(tmp)_2(BH_4)(Me)]$ (76%); the same mixture was obtained by comproportionation of **4** and **9**. The compounds $[U(tmp)_2(BH_4)(R)]$ are not indefinitely stable in toluene and were slowly transformed into the U^{III} complex $[\{U(tmp)_2(BH_4)\}_2]$ [5] (NMR experiments).

No exchange of cp* and tmp between $[U(cp^*)_2(X)_2]$ and $[U(tmp)_2(X)_2]$ (X = Cl, BH_4, or Me) was observed after 12 h at 20°C whereas exchange of Me and Cl groups, or of Me and BH_4 groups, occurred rapidly between $[U(\eta^5\text{-}L)_2(Me)_2]$ and $[U(\eta^5\text{-}L)_2(X)_2]$ (L = cp*, tmp; X = Cl, BH_4), leading to the equilibrium depicted



Scheme 2. Preparation of the borohydride complexes **5**–**7**; all reactions in toluene.

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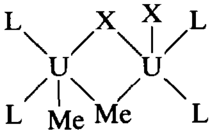
* Reference number with asterisk indicates a note in the list of references.

by eqn. (4). In contrast to its phospholyl analogue, $[U(cp^*)_2(BH_4)(Me)]$ is stable in toluene.

$$[U(\eta^5\text{-L})_2(Me)_2] + [U(\eta^5\text{-L})_2(X)_2] \rightleftharpoons 2[U(\eta^5\text{-L})_2(Me)(X)] \quad (4)$$

L = cp*, tmp; X = Cl or BH_4

As noted previously in the cp* series [3], the distribution reactions were much slower when $[U(tmp)_2(Me)_2]$ was replaced by $[U(tmp)_2(CH_2SiMe_3)_2]$; these ligand exchange reactions certainly involve a dinuclear intermediate such as A, and the results are consistent with the relative abilities of the ligands to bridge two metal centres.



A

Some reactions of the alkyl complexes **9** and **10** have been examined and the products, which are similar to those obtained in the pentamethylcyclopentadienyl series, have been characterized only by their NMR spectra. Hydrogenolysis of these compounds in the presence of 1,2-bis(dimethylphosphino)ethane (DMPE) afforded the uranium(III) hydride complex $[U(tmp)_2(DMPE)(H)]$ (**13**). The hydride resonance of the cp* analogue $[U(cp^*)_2(DMPE)(H)]$ was not detected previously [7]; in fact, we found it at 808 ppm, and that of **13** appeared at 856 ppm. Like $[U(cp^*)_2(Me)_2]$ [3], the dimethyl complex **9** reacted with acetone or tertiary-butyl alcohol to give the di(tertiary butoxide) derivative $[U(tmp)_2(O^tBu)_2]$. The bis(alkoxide) compounds $[U(tmp)_2(OR)_2]$ (**14**, R = Et; R = ^{i}Pr or ^{t}Bu) were easily synthesized by treatment of $[U(tmp)_2(BH_4)_2]$ with the corresponding NaOR.

The new compounds have been characterized by their NMR spectra (Table 1), elemental analyses (except **10** and **13**) and, in the case of **1a** and **6**, by their X-ray crystal structures.

2.2. Crystal structures of $[U(tmp)(Cl)_3(DME)]$ and $[U(cp^*)_2(BH_4)_2]$

Complex **1a** is the first monophospholyluranium compound to have been crystallographically characterized; an ORTEP [8] drawing is shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The coordination geometry about uranium is *mer* pseudo-octahedral with the tmp ligand and one oxygen atom of the DME molecule in *trans* axial positions and the other oxygen and three chlorine atoms, which are coplanar within ±0.07(1) Å, constitute the equatorial plane. The U atom is displaced by 0.60(1) Å from this four-atom mean plane towards the tmp. This is the configuration which is invariably adopted by cyclopentadienyl and indenyl analogues [9]. The U–O (DME) and U–Cl bond distances are unexceptional for U^{IV} compounds. More interesting is the geometry of the phospholyl which is pentahapto-bonded to uranium, the tmp ring being planar within ±0.006(15) Å with the carbon atoms of the methyl groups out of this plane, by an average distance of 0.15(1) Å; the tmp ring is parallel to the equatorial plane. The U–P bond length is 2.926(4) Å and the U–C (ring) distances vary from 2.79(2) to 2.84(1) Å. The average U–C (ring) bond distance (2.82(2) Å) is similar to that determined in $[U(cp^*)(C_4H_7)_3]$ (2.79(1) Å [10]) and slightly longer than that found in $[U(cp^*)_2(Cl)_2(C_3H_4N_2)]$ (2.74(2) Å [11]).

The crystal structure of **6** is shown in Figure 2, selected bond distances and angles are listed in Table 2. The complex adopts the pseudo-tetrahedral bent-sandwich configuration which is quite familiar for $[U(cp^*)_2(X)_2]$ derivatives [12]. The structural parameters of **6** and of its tetramethylphospholyl analogue **4** [5] are very similar: the ring centroid–U–ring centroid angles are 133(1) and 128.6(1)°, respectively, the B–U–B angles are 101(1) and 100.4(2)°. The short U–B distances (2.58(3) Å in **6**, 2.553(1) Å in **4**) are characteristic of tridentate BH_4^- [13]. The average U–C bond length in **6** (2.74(3) Å) is slightly shorter than that in **4** (2.81(4) Å); in the two complexes, the mean U–ring centroid distances are 2.47(5) and 2.50(1) Å, respectively. These structural parameters confirm that the tetramethylphospholyl group is a steric mimic of the ubiquitous pentamethylcyclopentadienyl.

2.3. Differences between the tmp and cp complexes*

Although the structures of the mono- and bis-(tetramethylphospholyl) uranium(IV) compounds $[U(tmp)(Cl)_3(DME)]$, $U[(tmp)(X)_3]$ (X = BH_4 or CH_2Ph) and $[U(tmp)_2(X)_2]$ (X = Cl, BH_4, alkyl, or alkoxide) are quite similar to those of their pentamethylcyclopentadienyl counterparts, the different electronic effects of the cp* and tmp ligands are manifest in the coordination chemistry and redox properties of the complexes.

The species $[U(tmp)(Cl)_3]$, like $[U(C_5H_5)(Cl)_3]$, only exists in the form of a bis(adduct) with oxygen ligands, whereas the stable isosteric compound $[U(tmp)(BH_4)_3]$, like $[U(C_5H_5)(BH_4)_3]$, readily disproportionates in the presence of such Lewis bases [1,14]. This difference has been explained by the greater electron-donating ability of the borohydride group; the adducts $[U(\eta^5\text{-L})(BH_4)_3(THF)_2]$ (L = tmp or C_5H_5) should be too electron-rich and rearrange into more stable products. The pentamethylcyclopentadienyluranium trichloride $[U(cp^*)(Cl)_3(THF)_2]$ is more electron-rich than its tmp

TABLE 1. ^{1}H NMR spectra of the uranium(IV) compounds [a]

Compounds	tmp or cp*	other ligands
$[\mathrm{U(tmp)(Cl)_3(DME)}]$ **(1a)**	16.92 (6H)	−47.68 (3H, $w_{1/2}$ = 85 Hz, Me)
	−2.33 (6H, d, J = 10 Hz)	−36.15 (3H, $w_{1/2}$ = 85 Hz, Me)
		−40.37 (2H, $w_{1/2}$ = 85 Hz, $\mathrm{CH_2}$)
		−33.73 (2H, $w_{1/2}$ = 85 Hz, $\mathrm{CH_2}$)
$[\mathrm{U(tmp)_2(Cl)_2}]$ **(2)**	42.93 (12H)	
	−16.27 (12H)	
$[\mathrm{U(cp^*)(BH_4)_3}]$ **(5)**	6.68 (15H)	42.48 (12H, q, J = 82 Hz, $\mathrm{BH_4}$)
$[\mathrm{U(cp^*)_2(BH_4)_2}]$ **(6)**	12.28 (30H)	−62.58 (8H, q, J = 80 Hz, $\mathrm{BH_4}$)
$[\mathrm{U(cp^*)(tmp)(BH_4)_2}]$ **(7)**	11.21 (15H, cp*)	−48.14 (8H, q, J = 80 Hz, $\mathrm{BH_4}$)
	47.35 (6H, tmp)	
	−20.94 (6H, tmp)	
$[\mathrm{U(tmp)(CH_2Ph)_3}]$ **(8)**	0.17 (6H)	4.52 (6H, $\mathrm{CH_2}$)
	−7.20 (6H, d, J = 7 Hz)	−18.59 (6H, d, J = 7 Hz, *o* − Ph)
		7.85 (6H, t, J = 7 Hz, *m* − Ph)
		0.36 (3H, t, J = 7 Hz, *p* − Ph)
$[\mathrm{U(tmp)_2(Me)_2}]$ **(9)**	6.83 (12H)	−40.73 (6H, Me)
	−5.25 (12H)	
$[\mathrm{U(tmp)_2(CH_2SiMe_3)_2}]$ **(10)**	2.05 (12H)	−24.12 (4H, $\mathrm{CH_2}$)
	−4.00 (12H)	1.88 (18H, $\mathrm{SiMe_3}$)
$[\mathrm{U(cp^*)(tmp)(Me)_2}]$ **(11)**	3.43 (15H, cp*)	−69.81 (6H, Me)
	20.65 (6H, tmp)	
	−10.53 (6H, tmp)	
$[\mathrm{U(cp^*)(tmp)(CH_2SiMe_3)_2}]$ **(12)**	4.61 (15H, cp*)	−32.74 (2H, $\mathrm{CH_2}$)
	12.48 (6H, tmp)	−56.60 (2H, $\mathrm{CH_2}$)
	−9.67 (6H, d, J = 7 Hz, tmp)	0.26 (18H, $\mathrm{SiMe_3}$)
$[\mathrm{U(tmp)_2(OEt)_2}]$ **(14)**	−3.87 (12H, d, J = 5 Hz)	40.05 (4H, q, J = 6 Hz, $\mathrm{CH_2}$)
	−6.96 (12H)	8.06 (6H, t, J = 6 Hz, Me)
$[\mathrm{U(tmp)_2(O^iPr)_2}]$	−3.85 (12H, d, J = 6 Hz)	37.93 (2H, CH)
	−7.18 (12H)	10.76 (12H, d, J = 5 Hz, Me)
$[\mathrm{U(tmp)_2(O^tBu)_2}]$	−2.63 (12H, d, J = 7 Hz)	9.86 (18H, ^{t}Bu)
	−4.80 (12H)	
$[\mathrm{U(cp^*)_2(Me)(Cl)}]$ [b]	9.22 (30H)	−162.15 (3H, Me)
$[\mathrm{U(cp^*)_2(Me)(BH_4)}]$	9.28 (30H)	−171.26 (3H, Me)
		−57.13 (4H, q, J = 81 Hz, $\mathrm{BH_4}$)
$[\mathrm{U(tmp)_2(Me)(Cl)}]$	26.28 (6H)	−66.77 (3H, Me)
	21.00 (6H)	
	−6.52 (6H)	
	−15.37 (6H)	
$[\mathrm{U(tmp)_2(Me)(BH_4)}]$	26.00 (6H)	−103.34 (3H, Me)
	23.39 (6H)	−27.26 (4H, q, J = 82 Hz, $\mathrm{BH_4}$)
	−7.63 (6H)	
	−16.75 (6H)	
$[\mathrm{U(tmp)_2(CH_2SiMe_3)(Cl)}]$	18.32 (6H)	−10.43 (2H, $\mathrm{CH_2}$)
	11.16 (6H)	1.50 (9H, $\mathrm{SiMe_3}$)
	−3.07 (6H)	
	−12.77 (6H)	
$[\mathrm{U(tmp)_2(CH_2SiMe_3)(BH_4)}]$	18.37 (6H)	−90.76 (2H, $\mathrm{CH_2}$)
	16.75 (6H)	1.92 (9H, $\mathrm{SiMe_3}$)
	−7.35 (6H)	−20.04 (4H, q, J = 80 Hz, $\mathrm{BH_4}$)
	−14.27 (6H)	
$[\mathrm{U(cp^*)(tmp)(Me)(BH_4)}]$	7.75 (15H, cp*)	−37.3 (4H, $w_{1/2}$ = 300 Hz, $\mathrm{BH_4}$)
	45.96 (3H, tmp)	−134.47 (3H, Me)
	37.04 (3H, tmp)	
	−21.16 (3H, tmp)	
	−22.08 (3H, tmp)	
$[\mathrm{U(cp^*)(tmp)(CH_2SiMe_3)(BH_4)}]$	8.18 (15H, cp*)	−26.94 (4H, q, J = 80 Hz, $\mathrm{BH_4}$)
	38.76 (3H, tmp)	−110.48 (1H, $\mathrm{CH_2}$)
	33.76 (3H, tmp)	−129.80 (1H, $\mathrm{CH_2}$)
	−18.70 (3H, tmp)	
	−25.22 (3H, tmp)	

[a] At 30°C in toluene-d_8; δ relative to TMS. When not specified, the signals are singlets with half-height widths between 10 and 30 Hz.

[b] This complex and the following mixed alkyl borohydride or alkyl chloride complexes are in equilibrium with the bis(alkyl) and bis(borohydride) or bis(chloride) compounds (see text).

analogue and it was previously noted that this complex readily loses THF under vacuum, giving [U(cp*)(Cl)$_3$], which is soluble and presumably monomeric in toluene [15]. On the other hand, addition of NEt$_4$Cl (1 equiv) to a THF solution of **1b** led to the immediate formation of a new compound, characterized by two NMR signals at 3.6 and −1.99 ppm, attributed to the phospholyl ligand of the anion [U(tmp)(Cl)$_4$]$^-$; no reaction was observed with the cp* analogue. These differences can be explained by the greater electron richness of [U(cp*)(Cl)$_3$(THF)$_2$], which renders the THF more labile and precludes the addition of the chloride ion. The coordinating properties of [U(cp*)(BH$_4$)$_3$] (**5**) are even more unusual since, in contrast to [U(tmp)(BH$_4$)$_3$] and [U(C$_5$H$_5$)(BH$_4$)$_3$], this compound is perfectly stable in tetrahydrofuran. The NMR spectrum in toluene of the pentamethylcyclopentadienyluranium trisborohydride in the presence of 1 equiv of THF revealed that the complex does not coordinate the free Lewis base molecules, certainly a result of its more important electron richness. The distinctive behaviour of **5** provides a further example of the use of electron-donating ligands to stabilize sterically unsaturated compounds.

Bis(tetramethylphospholyl) and bis(pentamethylcyclopentadienyl) complexes should also exhibit differences in their ability to coordinate tetrahydrofuran. As an example, [U(cp*)$_2$(Me)$_2$] and [U(tmp)$_2$(Me)$_2$] (**9**) have similar NMR spectra in THF-d_8 or toluene-d_8 at 30°C, with the methyl resonances at *ca.* −140 and −40 ppm, respectively. The paramagnetic shifts of these signals were temperature-dependent and, as usual, followed the Curie-Weiss law, except in the case of **9** in tetrahydrofuran where initially the signal was first displaced towards the highfield region (−42 ppm at 0°C) and was then dramatically shifted in the opposite sense (32 ppm at −50°C). This suggests structural modification of the tmp complex in THF, presumably because of the formation of a labile adduct.

Sodium amalgam reductions of [U(cp*)$_2$(Cl)$_2$], [U(tmp)(BH$_4$)$_3$], (**3**) and [U(tmp)$_2$(BH$_4$)$_2$] (**4**) to the

TABLE 2. Selected bond distances (Å) and angles (°)

[U(tmp)(Cl)$_3$(DME)] (**1a**)					
U environment					
U–Cl(1)	2.595(3)	U–Cl(2)	2.611(4)	U–Cl(3)	2.601(4)
U–P	2.926(4)	U–C(1)	2.84(1)	U–C(2)	2.84(2)
U–C(3)	2.81(2)	U–C(4)	2.79(2)	U–O(1)	2.52(1)
U–O(2)	2.48(1)	U–1 [a]	2.52(2)		
O(1)–U–Cl(1)	149.1(3)	O(2)–U–1	175.9(4)	Cl(2)–U–Cl(3)	154.4(2)
tmp ligand					
P–C(1)	1.78(2)	P–C(4)	1.76(2)	C(1)–C(2)	1.39(2)
C(2)–C(3)	1.44(2)	C(3)–C(4)	1.40(2)	C(1)–C(5)	1.52(2)
C(2)–C(6)	1.53(2)	C(3)–C(7)	1.49(2)	C(4)–C(8)	1.53(2)
P–C(1)–C(2)	112(1)	C(1)–C(2)–C(3)	113(2)	C(2)–C(3)–C(4)	111(1)
C(3)–C(4)–P	114(1)	C(4)–P–C(1)	89.7(8)		
DME ligand					
O(1)–C(9)	1.44(2)	O(1)–C(10)	1.46(3)	C(10)–C(11)	1.40(3)
O(2)–C(11)	1.47(2)	O(2)–C(12)	1.45(3)		
C(9)–O(1)–C(10)	105(1)	O(1)–C(10)–C(11)	112(2)	C(10)–C(11)–O(2)	115(2)
C(11)–O(2)–C(12)	113(2)				
[U(cp)$_2$(BH$_4$)$_2$]* (**6**)					
U environment					
U–B	2.58(3)				
U–C(1)	2.71(6)	U–C(2)	2.75(3)	U–C(3)	2.71(2)
U–C(10)	2.77(9)	U–C(11)	2.77(2)	U–C(12)	2.73(2)
U–1 [a]	2.46(4)	U–2	2.48(4)		
B–U–1	105(1)	B–U–2	104(1)	1–U–2	133(1)
B–U–B^{i} [b]	101(1)				
cp ligand*					
C(1)–C(2)	1.31(5)	C(1)–C(4)	1.7(1)	C(2)–C(5)	1.52(4)
C(2)–C(3)	1.42(3)	C(3)–C(6)	1.59(4)	C(3)–C(3^{i})	1.41(5)
C(10)–C(11)	1.39(6)	C(10)–C(13)	1.5(1)	C(11)–C(14)	1.47(4)
C(11)–C(12)	1.35(3)	C(12)–C(15)	1.63(4)	C(12)–C(12^{i})	1.46(5)

[a] 1 is the centroid of the phospholyl and cyclopentadienyl rings *etc.*

[b] symmetry code: (i) x, $-y$, z.

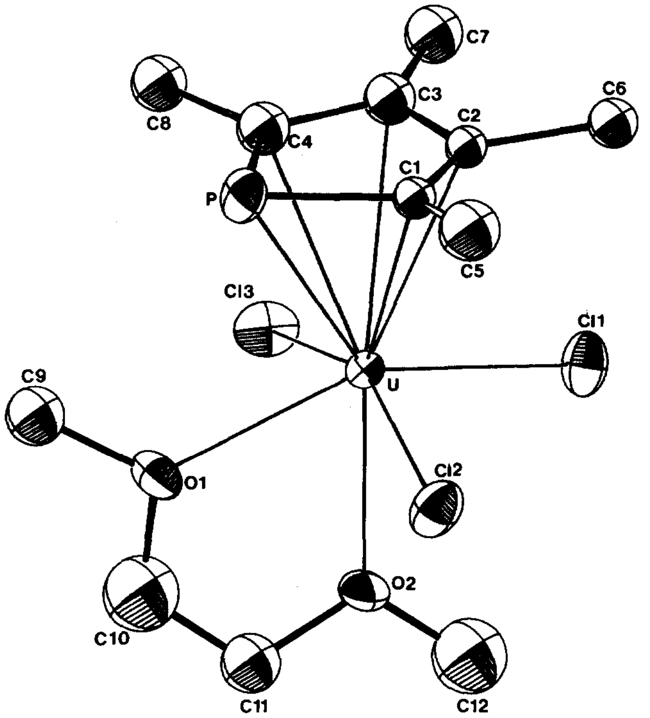
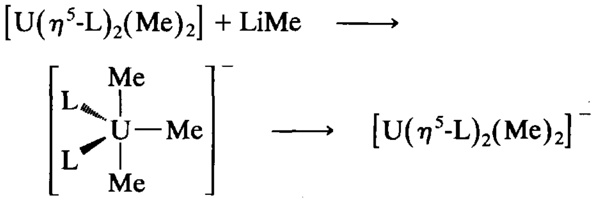


Fig. 1. ORTEP drawing of [U(tmp)(Cl)$_3$(DME)].

corresponding anions [U(cp*)$_2$(Cl)$_2$]$^-$ [16], [U(tmp)(BH$_4$)$_3$]$^-$ and [U(tmp)$_2$(BH$_4$)$_2$]$^-$ [5], have been previously reported. Similar treatment of **2**, **5**, **6** and **7** with Na(Hg) in tetrahydrofuran gave the anions [U(tmp)$_2$(Cl)$_2$]$^-$, [U(cp*)(BH$_4$)$_3$]$^-$ [U(cp*)$_2$(BH$_4$)$_2$]$^-$ and [U(cp*)(tmp)(BH$_4$)$_2$]$^-$. The neutral U^{III} compound [U(cp*)$_2$(BH$_4$)] (**15**) was isolated as a red microcrystalline powder from an equimolar mixture of **6** and [U(cp*)$_2$(H)$_2$] in toluene; the insolubility of **15** in this solvent is presumably due to its polymeric structure. It may possess a trimeric structure like that adopted by [{U(cp*)$_2$(μ-Cl)}$_3$], which was similarly prepared from [U(cp*)$_2$(Cl)$_2$] and [U(cp*)$_2$(H)$_2$] [16]. In the presence of THF, **15** was transformed into [U(cp*)$_2$(BH$_4$)(THF)]. The anions [U(η^5-L)$_2$(R)$_2$]$^-$ (L = cp* or tmp, R = Me, or CH$_2$SiMe$_3$) were formed when the U^{IV} alkyl complexes [U(η^5-L)$_2$(R)$_2$] were reduced by LiR or Na(Hg) in tetrahydrofuran. The reduction of [U(η^5-L)$_2$(Me)$_2$] by LiMe occurred with initial formation of the intermediates [U(η^5-L)$_2$(Me)$_3$]$^-$, followed by homolysis of a U–Me bond (eqn. (5)). These trialkyl intermediates, like the anions [U(C$_5$H$_5$)$_2$(R)$_3$]$^-$ [18], certainly adopt the trigonal configuration C, in which one of the methyl groups is different from the other two; in the NMR spectra, the two axial Me give rise to low field resonances whereas the high field signals correspond to the equatorial ligands.



$$[\mathrm{U}(\eta^5\text{-L})_2(\mathrm{Me})_2] + \mathrm{LiMe} \longrightarrow \left[\mathrm{L}_2\mathrm{U}(\mathrm{Me})_3\right]^- \longrightarrow [\mathrm{U}(\eta^5\text{-L})_2(\mathrm{Me})_2]^- \qquad (5)$$

C

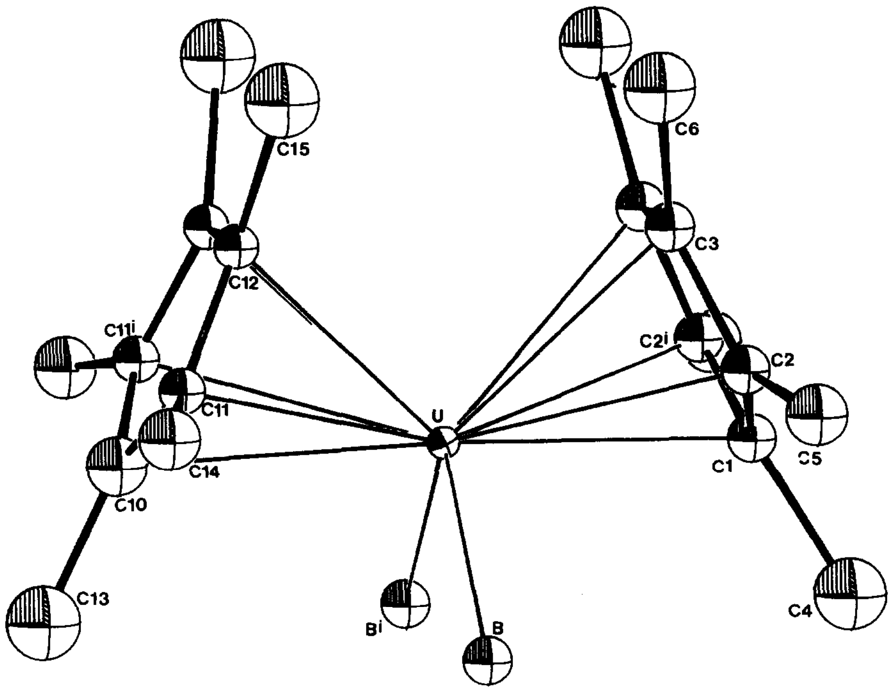


Fig. 2. ORTEP drawing of [U(cp*)$_2$(BH$_4$)$_2$]. (i) atoms are related by the mirror plane.

The reaction pathway depicted by eqn. (5) is similar to that observed for the synthesis of the anions $[U(C_5H_5)_3(R)]^-$ from the corresponding U^{IV} complexes $[U(C_5H_5)_3(R)]$ [18].

Equimolar mixtures of $[U(cp^*)_2(X)_2]$ and $[U(tmp)_2(X)_2]$ (X = Cl, BH_4, or Me) were treated in THF by 0.5 equiv of Na(Hg). In each case, only the phospholyl anionic complex was formed, the cyclopentadienyl compound remaining unaffected. Conversely, oxidation of a 1 : 1 mixture of $[U(tmp)_2(BH_4)_2]^-$ and $[U(cp^*)_2(BH_4)_2]^-$ or $[U(cp^*)(tmp)(BH_4)_2]^-$ with $TlBPh_4$ (0.5 equiv) gave **6** or **7**, without modifying the bis(phospholyl) anion. These results are consistent with the redox potentials of the borohydride complexes **4**, **7** and **6** which are −1.49, −1.66 and −1.83 V (*vs.* ferrocene–ferricinium) [17], and reflect the more electron-donating capacity of the cp*.

Finally, the individual character and special interest of the tmp ligand were revealed by it being possibly to obtain tris(phospholyl)uranium complexes [4], although no tris(pentamethylcyclopentadienyl)actinide analogue has so far been isolated. The synthesis and properties of $[U(tmp)_3(Cl)]$ and its derivatives will be presented in detail in a separate paper; the facile access to $[U(tmp)_3(X)]$ complexes should be a function of the limited electron-donating ability of tetramethylphospholyl.

3. Experimental section

3.1. General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (Germany). ^1H NMR spectra were recorded on a Bruker W 60 (FT) instrument. Deuterated solvents were dried over Na–K alloy. The chemical shifts are relative to tetramethylsilane ($\delta = 0$). The spectra of the U^{IV} complexes are given in Table 1.

All experiments were carried out under argon (less than 5 ppm O_2 and water) in Schlenk type glassware in a high vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and were distilled immediately before use. UCl_4 [19], $U(BH_4)_4$ [20], Ktmp [5], $[U(cp^*)_2(Cl)_2]$ [3], $[U(cp^*)_2(Me)_2]$ [3], $[U(tmp)(BH_4)_3]$ [5], $[U(tmp)_2(BH_4)_2]$ [5] were prepared by published methods.

3.2. Syntheses

3.2.1. $[U(tmp)(Cl)_3(DME)]$ (1a)

(a) A 50 ml round bottomed flask was charged with UCl_4 (317.8 mg, 0.84 mmol) and Ktmp (149.1 mg, 0.84 mmol) in toluene (20 ml) and DME (90 μl, 0.84 mmol) was added via a gas-tight microsyringe. The reaction mixture was stirred for 12 h at 20°C. The solvent was evaporated off, and the residue was dried under vacuum for 10 h and then extracted in toluene (2 × 10 ml). After evaporation, the red product was isolated as a red microcrystalline powder (268 mg, 56%). Analysis Found: C, 25.05; H, 3.97; P, 5.28. $C_{12}H_{22}Cl_3O_2PU$ calcd.: C, 25.12; H, 3.87; P, 5.40%.

(b) A 50 ml round bottomed flask was charged with UCl_4 (246.6 mg, 0.649 mmol), **2** (381.5 mg, 0.649 mmol) and DME (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2 h at 20°C and after evaporation to dryness, **1a** was obtained as an orange microcrystalline powder (715 mg, 96%).

3.2.2. $[U(tmp)(Cl)_3(THF)_2]$ (1b)

(a) An NMR tube was charged with UCl_4 (17.4 mg, 0.046 mmol) and **2** (26.9 mg, 0.046 mmol) in THF-d_8 (0.4 ml). After 15 min, the spectrum showed two signals of equal intensity at 7.07 (d, $J = 10$ Hz) and 1.11 ppm, attributed to the phospholyls of **1b**.

(b) The complex was prepared on a preparative scale in a manner similar with that for **1a**, from UCl_4 (152.4 mg, 0.40 mmol), Ktmp (71.0 mg, 0.40 mmol) and THF (66 μl, 0.81 mmol). The sticky product (168 mg) was not pure; the NMR spectrum in toluene-d_8 exhibited a broad signal centred at 1.5 ppm (10% of the total integration), which was not assigned. The compound could not be purified by crystallization.

3.2.3. $[U(tmp)_2(Cl)_2]$ (2)

A 100 ml round bottomed flask was charged with UCl_4 (950.7 mg, 2.50 mmol) and Ktmp (441.9 mg, 2.48 mmol), and toluene (40 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 1.5 h at 20°C. After filtration, the solvent was evaporated off, leaving a brown microcrystalline powder of **2** (423 mg, 29%). Analysis Found: C, 32.45; H, 4.13; Cl, 12.29; P, 10.44. $C_{16}H_{24}Cl_2P_2U$ calcd.: C, 32.72; H, 4.12; Cl, 12.07; P, 10.55%.

3.2.4. $[U(cp^*)(BH_4)_3]$ (5)

A 50 ml round bottomed flask was charged with $U(BH_4)_4$ (734.8 mg, 2.47 mmol) and Kcp* (432.0 mg, 2.48 mmol), and toluene (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (3 × 20 ml). The solution was evaporated to 10 ml and, on cooling to −78°C, deposited red crystals of **5** which were filtered off and dried under vacuum (847 mg, 82%). The analytical sample was prepared by sublimation (10^{-2} mm Hg, 20°C). Analysis Found: C, 28.41; H, 6.31; B, 7.75. $C_{10}H_{27}B_3U$ calcd.: C, 28.75; H, 6.47; B, 7.76%.

3.2.5. [U(cp)$_2$(BH$_4$)$_2$] (6)*

(a) A 100 ml round bottomed flask was charged with U(BH$_4$)$_4$ (1711 mg, 5.75 mmol) and Kcp* (2023 mg, 11.62 mmol), and toluene (50 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (3 × 25 ml). The solution was evaporated to 20 ml and, on cooling to −78°C, deposited red crystals of **6** which were filtered off and dried under vacuum (1790 mg, 58%). Analysis Found: C, 44.42; H, 6.96; B, 3.94. $C_{20}H_{38}B_2U$ calcd.: C, 44.64; H, 7.12; B, 4.01%.

(b) An NMR tube was charged with [U(cp*)$_2$(Cl)$_2$] (19.8 mg, 0.034 mmol) and NaBH$_4$ (4.0 mg, 0.105 mmol) in THF-d_8 (0.4 ml). After 48 h at 65°C, the spectrum showed that the dichloride was totally transformed into **6**. Similarly, **2** was converted into **4**.

3.2.6. [U(cp)(tmp)(BH$_4$)$_2$] (7)*

A 50 ml round bottomed flask was charged with **5** (524.0 mg, 1.25 mmol) and Ktmp (225.4 mg, 1.26 mmol), and toluene (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (3 × 15 ml). The solution was evaporated to 10 ml and, on cooling to −78°C, deposited red crystals of **7** which were filtered off and dried under vacuum (613 mg, 90%). Analysis Found: C, 39.54; H, 6.53; P, 5.56. $C_{18}H_{35}B_2PU$ calcd.: C, 39.88; H, 6.51; P, 5.71%.

3.2.7. [U(tmp)(CH$_2$Ph)$_3$] (8)

A 50 ml round bottomed flask was charged with [U(tmp)(BH$_4$)$_3$] (125.8 mg, 0.30 mmol) and LiCH$_2$Ph (88.3 mg, 0.90 mmol), and toluene (10 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 1 h at 20°C. The solvent was evaporated off and the residue was extracted with pentane (2 × 10 ml). The solution was evaporated to dryness, leaving a red microcrystalline powder of **8** (82 mg, 43%). Analysis Found: C, 53.26; H, 5.08; P, 5.00. $C_{29}H_{33}PU$ calcd.: C, 53.54; H, 5.11; P, 4.76%.

3.2.8. [U(tmp)$_2$(R)$_2$] (9, R = Me; 10, R = CH$_2$SiMe$_3$) and [U(cp)(tmp)(R)$_2$] (11, R = Me; 12, R = CH$_2$SiMe$_3$)*

(a) A 100 ml round bottomed flask was charged with **4** (1066 mg, 1.96 mmol) and LiMe (97.1 mg, 4.42 mmol), and toluene (50 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2 days at 20°C. The solvent was evaporated off and the residue was extracted with pentane (3 × 25 ml). The solution was evaporated to 20 ml and, on cooling to −78°C, deposited red crystals of **9** which were filtered off and dried under vacuum (814 mg, 76%). Analysis Found: C, 39.31; H, 5.36; P, 11.47. $C_{18}H_{30}P_2U$ calcd.: C, 39.57; H, 5.53; P, 11.34%.

(b) Complex **10** was prepared in 81% yield by the same procedure, from **4** (570.2 mg, 1.05 mmol) and LiCH$_2$SiMe$_3$ (206.9 mg, 2.20 mmol).

(c) Complex **11** was prepared in 76% yield by the same procedure, from **7** (412.6 mg, 0.76 mmol) and LiMe (39.1 mg, 1.78 mmol). Analysis Found: C, 44.04; H, 5.97; P, 5.87. $C_{20}H_{33}PU$ calcd.: C, 44.28; H, 6.13; P, 5.71%.

(d) Complex **12** was prepared in 53% yield by the same procedure, from **7** (163.2 mg, 0.30 mmol) and LiCH$_2$SiMe$_3$ (71.1 mg, 0.76 mmol). Analysis Found: C, 44.40; H, 6.89; P, 4.58. $C_{26}H_{49}PSi_2U$ calcd.: C, 45.47; H, 7.19; P, 4.51%.

These four reactions were monitored by NMR spectroscopy; the spectra showed the intermediate formation of the mixed alkyl borohydride complexes [U(tmp)$_2$(BH$_4$)(R)] and [U(cp*)(tmp)(BH$_4$)(R)]. An NMR tube was charged with **4** (12.4 mg, 0.023 mmol) and LiMe (0.5 mg, 0.023 mmol) in toluene-d_8 (0.4 ml); after 6 h at 20°C, the spectrum showed the signals corresponding to a mixture of **4** (12%), **9** (12%) and [U(tmp)$_2$(BH$_4$)(Me)] (76%). The latter was slowly transformed into [{U(tmp)$_2$(BH$_4$)}$_2$] (complete conversion after 15 days at room temperature).

3.2.9. [U(tmp)$_2$(OR)$_2$] (14, R = Et; R = ^{i}Pr and ^{t}Bu)

(a) A 50 ml round bottomed flask was charged with **4** (419.7 mg, 0.77 mmol) and NaOEt (136.2 mg, 2.0 mmol), and diethyl ether (20 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 4 h at −78°C and 12 h at room temperature. The solvent was evaporated off and the residue was extracted with pentane (2 × 15 ml). The solution was evaporated to dryness, leaving a brown microcrystalline powder of **14** (357.2 mg, 76%). Analysis Found: C, 39.33; H, 5.51; P, 10.07. $C_{20}H_{34}O_2P_2U$ calcd.: C, 39.61; H, 5.65; P, 10.21%.

(b) An NMR tube was charged with **4** (*ca.* 10 mg) and NaO^{i}Pr or NaO^{t}Bu (2 equiv) in toluene-d_8 (0.4 ml). After 48 h at 20°C, the spectra showed the quantitative formation of the corresponding bis(alkoxide) complexes.

3.2.10. [U(cp)$_2$(BH$_4$)] (15)*

A 100 ml round bottomed flask was charged with **6** (820.2 mg, 1.52 mmol) and [U(cp*)$_2$(Me)$_2$] (817.9 mg, 1.52 mmol), and toluene (50 ml) was condensed into it under vacuum at −78°C. Dihydrogen (1 atm) was introduced and the reaction mixture was stirred for 24 h at 20°C. The solvent was evaporated off and the green microcrystalline powder was washed with pentane (3 × 15 ml) and dried under vacuum (1193 mg, 75%). Analysis Found: C, 45.61; H, 6.37; B, 2.25. $C_{20}H_{34}BU$ calcd.: C, 45.90; H, 6.55; B, 2.07%. δ (THF-d_8, 30°C): −2.52 (30H, $w_{1/2} = 40$ Hz, cp*), −56.9 (4H, $w_{1/2} = 400$ Hz, BH_4). After evaporation of a THF solution of **15**, the adduct $[U(cp^*)_2(BH_4)(THF)]$ was obtained as a green powder. δ(benzene-d_6): 60.1 (4H, $w_{1/2} = 380$ Hz, BH_4), −2.44 (30H, cp*), −14.1 and −41.6 (4H + 4H, $w_{1/2} = 190$ Hz, THF).

3.3. Ligand exchange reactions

(a) An NMR tube was charged with $[U(cp^*)_2(Me)_2]$ or $[U(tmp)_2(Me)_2]$ (*ca.* 10 mg) and 1 equivalent of $[U(cp^*)_2(X)_2]$ or $[U(tmp)_2(X)_2]$ (X = Cl or BH_4) in toluene-d_8 (0.4 ml). After 1 h at 20°C, the spectra showed that these equimolar mixtures were almost totally transformed into $[U(cp^*)_2(Me)(Cl)]$ (85%), $[U(cp^*)_2(Me)(BH_4)]$ (90%), $[U(tmp)_2(Me)(Cl)]$ (80%), and $[U(tmp)_2(Me)(BH_4)]$ (76%). The distribution reaction between $[U(cp^*)_2(Me)_2]$ and $[U(cp^*)_2(Cl)_2]$ has been described previously [3].

(b) In similar experiments, an equimolar mixture of **2** and **10** was partially transformed into $[U(tmp)_2(CH_2SiMe_3)(Cl)]$ (33% after 24 h at 20°C) and a 1:1 mixture of **4** and **10** was partially converted after 3 days at 30°C into $[U(tmp)_2(CH_2SiMe_3)(BH_4)]$ (30%) and $[U(tmp)_2(BH_4)]$ (25%); after 6 days, only these two products were present, in proportions of 20:80.

3.4. Reactions of $[U(tmp)_2(Me)_2]$ (9) with H_2, Me_2CO, and ^tBuOH

(a) An NMR tube was charged with **9** (10 mg, 0.018 mmol) and DMPE (3.1 μl, 0.018 mmol), and benzene-d_6 (0.4 ml) was condensed into it under vacuum at −78°C. Dihydrogen (1 atm.) was introduced and after 24 h at 30°C the spectrum showed the total transformation of **9** into $[U(tmp)_2(DMPE)(H)]$. This hydride complex **13** was also obtained by hydrogenolysis of **10** under the same conditions. δ(benzene-d_6, 30°C): 856 (1H, $w_{1/2} = 240$ Hz, U–H), −1.93, −25.47, −33.11 and −39.44 (6H × 4, tmp), −5.82 (12H, P–Me), −9.87 and −15.16 (2H + 2H, CH_2).

(b) An NMR tube was charged with **9** (9.3 mg, 0.017 mmol) and acetone (2.5 μl, 0.034 mmol) or tertiary-butyl alcohol (3.2 μl, 0.034 mmol) in toluene-d_8 (0.4 ml). The spectrum showed the immediate and quantitative formation of $[U(tmp)_2(O^tBu)_2]$.

3.5. Reduction of the complexes $[U(cp^*)(BH_4)_3]$, $[U(\eta^5\text{-}L)_2(Cl)_2]$, $[U(\eta^5\text{-}L)_2(BH_4)_2]$ (L = cp*, tmp), and $[U(cp^*)(tmp)(BH_4)_2]$

(a) A 50 ml round bottomed flask was charged with **5** (51.5 mg, 0.123 mmol) and 2% Na(Hg) (201.8 mg, 0.175 mmol of Na), and THF (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 2.5 h, filtered and after evaporation to dryness, a red powder of $Na[U(cp^*)(BH_4)_3]$ was obtained (44 mg, 81%). Analysis Found: C, 27.05; H, 5.98; B, 7.16. $C_{10}H_{27}B_3NaU$ calcd.: C, 27.25; H, 6.17, B, 7.36%.

(b) An NMR tube, charged with **2** (10.2 mg, 0.017 mmol) and 2% Na(Hg) (20.4 mg, 0.018 mmol of Na) in THF-d_8 (0.4 ml), was immersed in an ultrasound bath (60 W, 40 kHz). After 20 min, the spectrum exhibited two signals of equal intensity at 3.90 and −21.23 ppm, corresponding to the methyl groups of the anion $[U(tmp)_2(Cl)_2]^-$.

(c) An NMR tube charged with **2** (9.4 mg, 0.016 mmol), $[U(cp^*)_2(Cl)_2]$ (9.3 mg, 0.016 mmol) and 2% Na(Hg) (18.5 mg, 0.016 mmol of Na) in THF-d_8 (0.4 ml) was immersed in an ultrasound bath. After 15 min, the spectrum showed that **2** was reduced to the corresponding anion whereas $[U(cp^*)_2(Cl)_2]$ remained unchanged.

(d) An NMR tube charged with **6** (5.1 mg, 0.009 mmol) and 2% Na(Hg) (17.0 mg, 0.015 mmol of Na) in THF-d_8 (0.4 ml) was immersed in an ultrasound bath and after 10 min, the spectrum showed the signals corresponding to $[U(cp^*)_2(BH_4)_2]^-$; δ (THF-d_8, 30°C): 33.5 (8H, $w_{1/2} = 240$ Hz, BH_4), −2.01 (30H, cp*).

(e) An NMR tube was charged with **4** (8.9 mg, 0.016 mmol), **6** (8.8 mg, 0.016 mmol) and 2% Na(Hg) (18.8 mg, 0.016 mmol of Na) in THF-d_8 (0.4 ml) and was immersed in an ultrasound bath. After 15 min, the spectrum showed that **4** had been reduced to the corresponding anion [5], whereas **6** remained unchanged.

(f) A 50 ml round bottomed flask was charged with **7** (137.0 mg, 0.25 mmol) and 2% Na(Hg) (638 mg, 0.56 mmol of Na), and THF (25 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 24 h, filtered, and after evaporation to dryness a red powder of $[Na(THF)_2][U(cp^*)(tmp)(BH_4)_2]$ was obtained (137 mg, 76%). Analysis Found: C, 44.23; H, 7.16; B, 3.00; Na, 3.13; P, 4.61. $C_{26}H_{51}B_2NaO_2PU$ calcd.: C, 44.07; H, 7.25, B, 3.05; Na, 3.24; P, 4.35%. δ(THF-d_8, 30°C): 48.9 (8H, $w_{1/2} = 320$ Hz, BH_4), 14.62 and −20.37 (6H + 6H, tmp), −2.59 (15H, cp*).

3.6. Reduction of the alkyl complexes $[U(\eta^5\text{-}L)_2(R)_2]$ (L = cp* or tmp)

(a) An NMR tube charged with the dialkyl compound (*ca.* 10 mg) and 1 equiv of 2% Na(Hg) in THF-d_8 (0.4 ml) was immersed in an ultrasound bath. After 30 min, the spectrum showed the formation of the corresponding anion. δ(THF-d_8, 30°C). $[U(cp^*)_2(Me)_2]^-$: −11.55 (30H, cp*), −73.1 (6H, $w_{1/2} = 80$ Hz, Me); $[U(cp^{*})_2(CH_2SiMe_3)_2]^{-}$: −6.32 (30H, cp*), −6.98 (18H, Me), −69.9 (6H, $w_{1/2}$ = 110 Hz, CH_2); $[U(tmp)_2(Me)_2]^{-}$: −7.46 and −28.57 (12H + 12H, tmp), −35.8 (6H, $w_{1/2}$ = 55 Hz, Me); $[U(tmp)_2(CH_2SiMe_3)_2]^{-}$: −1.86 (18H, Me), −4.38 and −22.57 (12H + 12H, tmp), −33.04 (4H, $w_{1/2}$ = 50 Hz, CH_2).

(b) An NMR tube was charged with $[U(cp^{*})_2(Me)_2]$ (15.2 mg, 0.028 mmol) and LiMe (0.7 mg, 0.032 mmol), and THF-d_8 (0.4 ml) was condensed under vacuum at −78°C. After 20 min at 30°C, the spectrum showed that 85% of $[U(cp^{*})_2(Me)_2]$ was transformed into $[U(cp^{*})_2(Me)_3]^{-}$. δ(THF-d_8, 30°C): 223.9 (6H, $w_{1/2}$ = 220 Hz, axial Me), −6.85 (30H, $w_{1/2}$ = 150 Hz, cp*), −172.3 (3H, $w_{1/2}$ = 40 Hz, equatorial Me). After 3 days at 20°C, formation of the anion $[U(cp^{*})_2(Me)_2]^{-}$ was complete.

(c) An NMR tube was charged with **9** (14.7 mg, 0.027 mmol) and LiMe (0.6 mg, 0.027 mmol), and THF-d_8 (0.4 ml) was condensed under vacuum at −78°C. After 10 min at −78°C, the spectrum exhibited, in addition to the signals corresponding to the equilibrium mixture of **9** and $[U(tmp)_2(Me)_2]^{-}$, resonances attributed to $[U(tmp)_2(Me)_3]^{-}$. δ(THF-d_8, −100°C): 420.5 (6H, $w_{1/2}$ = 600 Hz, axial Me), 15.0 (12H, $w_{1/2}$ = 280 Hz, tmp), −27.89 (12H, $w_{1/2}$ = 160 Hz, tmp), −259.1 (3H, $w_{1/2}$ = 250 Hz, equatorial Me). After 24 h at 20°C, formation of the anion $[U(tmp)_2(Me)_2]^{-}$ was complete.

(d) An NMR tube, charged with **9** (7.4 mg, 0.013 mmol), $[U(cp^{*})_2(Me)_2]$ (7.3 mg, 0.013 mmol) and 2% Na(Hg) (15.6 mg, 0.013 mmol) in THF-d_8 (0.4 ml), was immersed in an ultrasound bath. After 5 min, the

TABLE 3. Crystallographic data and experimental details for compounds **1a** and **6**

	$[U(tmp)(Cl)_3(DME)]$ (**1a**)	$[U(cp^{*})_2(BH_4)_2]$ (**6**)
Crystal data		
Crystal dimensions (mm)	0.40 × 0.30 × 0.250	0.40 × 0.20 × 0.10
Colour	red	red
M	573.67	538.18
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	Cm
a (Å)	13.840(3)	8.187(6)
b (Å)	13.876(6)	15.172(8)
c (Å)	9.661(3)	9.717(4)
β (°)	–	114.82(5)
V (Å³)	1855(2)	1096(1)
Z	4	2
D_{calc} (g cm^{-3})	2.054	1.631
μ(Mo Kα) (cm^{-1})	88.14	70.23
Data collection		
θ limits (°)	1,22	1,20
Scan type	ω–2θ	ω–2θ
Scan width	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
Range abs. trans.	0.75, 0.999	0.778, 1.412
Range h	0, −14	0, 7
k	0, 14	0, 14
l	0, 10	−9, 9
Reflections collected total	1406	624
unique	1324	591
with $I > 3\sigma(I)$	1098	591
Refinement on F		
$R(F) = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.024	0.035
$Rw(F) = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w(\|F_o\|)^2]^{1/2}$	0.028	0.043
variables	112	52
$\Delta\rho_{max}$ (e/Å³)	0.585	0.762
$\Delta\rho_{min}$ (e/Å³)	−0.545	−0.596
$(\Delta/\sigma)_{max}$	0.05	0.05
S	2.79	3.08

spectrum showed the formation of the anion $[U(tmp)_2(Me)_2]^-$ whereas $[U(cp^\star)_2(Me)_2]$ remained unchanged.

3.7. X-Ray crystal structure determinations

Crystals of **1a** and **6** were obtained by crystallization from cold pentane (−78°C). A single crystal was introduced into a thin-walled Lindemann glass tube in a glove box. Data were collected at room temperature on an Enraf-Nonius diffractometer equipped with a graphite monochromator ($\lambda = 0.71073$ Å). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour: a decay was observed (6% in 21 h for **1a** and 5% in 11 h for **6**) and was linearly corrected. The data were corrected for Lorentz polarization effects and absorption [21 for **1a**, 22 for **6**]. The structure was solved by the heavy-atom method and refined by full matrix least-squares on F with anisotropic thermal parameters for non B and C atoms. In **6**, the U atom lies on the mirror plane which contains the C(1), C(4), C(10) and C(13) atoms of the cp* ligands; the uranium and two boron atoms constitute a pseudo plane of symmetry of the molecule. The absolute configuration was determined for **1a** ($R_F = 0.024$ and 0.044) whereas there was no significant difference between the two enantiomers of **6**. All calculations were performed on a Vax 4200 computer with the Enraf-Nonius MOLEN system [23]. Analytical scattering factors for neutral atoms [24] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3; final positional and thermal parameters are listed in Tables 4 and 5 for **1a** and **6** respectively, and full lists are available from the Cambridge Crystallographic Data Centre.

TABLE 4. Fractional atomic coordinates, equivalent or isotropic thermal parameter and their esds for compound **1a**

Atom	x	y	z	B (Å^2)
U	0.98478(3)	0.93711(3)	0.99387(6)	2.154(8) [a]
Cl(1)	0.9002(3)	1.1040(3)	0.9995(7)	4.28(8) [a]
Cl(2)	1.0754(3)	0.9912(3)	0.7699(4)	4.3(1) [a]
Cl(3)	0.8469(3)	0.8521(3)	1.1301(5)	4.2(1) [a]
P	1.1294(3)	0.8531(3)	1.1790(5)	3.70(9) [a]
O(1)	1.0099(8)	0.7770(7)	0.876(1)	3.9(2) [a]
O(2)	0.8637(7)	0.9013(8)	0.812(1)	3.9(2) [a]
C(1)	1.053(1)	0.933(1)	1.271(1)	3.1(3)
C(2)	1.065(1)	1.029(1)	1.230(2)	3.1(3)
C(3)	1.135(1)	1.040(1)	1.122(2)	3.2(3)
C(4)	1.176(1)	0.951(1)	1.085(2)	3.2(3)
C(5)	0.993(1)	0.901(1)	1.394(2)	5.0(4)
C(6)	1.015(1)	1.112(1)	1.305(2)	4.3(3)
C(7)	1.168(1)	1.136(1)	1.069(2)	4.7(4)
C(8)	1.260(1)	0.939(1)	0.984(2)	4.8(3)
C(9)	1.099(1)	0.726(1)	0.855(2)	5.1(4)
C(10)	0.953(2)	0.758(2)	0.751(3)	8.1(6)
C(11)	0.862(1)	0.803(2)	0.755(2)	6.0(5)
C(12)	0.773(2)	0.952(2)	0.791(3)	9.1(7)

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

TABLE 5. Fractional atomic coordinates, equivalent or isotropic thermal parameters and their esds for compound **6**

Atom	x	y	z	B (Å^2)
U	0.000	0.000	0.000	2.08(2) [a]
C(1)	−0.153(4)	0.000	−0.307(3)	3.0(7)
C(2)	−0.059(3)	0.073(2)	−0.276(2)	4.1(5)
C(3)	0.123(3)	0.046(2)	−0.209(2)	4.0(5)
C(4)	−0.376(7)	0.000	−0.395(5)	8(1)
C(5)	−0.101(4)	0.171(2)	−0.313(3)	5.5(6)
C(6)	0.296(4)	0.103(2)	−0.187(3)	7.4(8)
C(10)	0.148(6)	0.000	0.314(5)	7(1)
C(11)	0.219(3)	0.074(2)	0.276(2)	3.2(5)
C(12)	0.330(3)	0.048(1)	0.214(2)	3.2(5)
C(13)	0.022(7)	0.000	0.393(5)	8(1)
C(14)	0.215(4)	0.167(2)	0.319(3)	5.7(7)
C(15)	0.482(5)	0.103	0.184(4)	8.3(9)
B	−0.200(4)	0.132(2)	0.000(3)	3.9(6)

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

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