

*Journal of Organometallic Chemistry*, 440 (1992) 53–65  
 Elsevier Sequoia S.A., Lausanne  
 JOM 22890

## Anionic triscyclopentadienyluranium(III) hydrides

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(Received April 8, 1992)

### Abstract

Addition of  $H^-$  to  $[(C_5H_4R)_3U]$  ( $R = H, Me, SiMe_3,$  or  $^tBu$ ) or sodium amalgam reduction of the  $U^{IV}$  hydrides  $[(C_5H_4R)_3UH]$  ( $R = SiMe_3,$  or  $^tBu$ ) afforded the hydrido-bridged anions  $[(C_5H_4R)_3UHU(C_5H_4R)_3]^-$  ( $R = H$  or  $Me$ ) or the monomeric anions  $[(C_5H_4R)_3UH]^-$  ( $R = SiMe_3$  or  $^tBu$ ). Crystals of  $[Na(18-crown-6)(THF)_2][(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]$  were obtained from an equimolar mixture of  $[Na(18-crown-6)][(C_5H_4SiMe_3)_3UH]$  and  $[(C_5H_4SiMe_3)_3U]$  and their structure determined.

### Introduction

Organometallic hydrides of the actinides are very rare [1] and the only complex in the +III oxidation state is  $[(C_5Me_5)_2UH(Me_2PCH_2CH_2PMe_2)]$ , which was obtained by hydrogenolysis of  $[(C_5Me_5)_2UMe_2]$  in the presence of 1,2 bis(dimethylphosphino)ethane [2]. We found that anionic triscyclopentadienyluranium(III) hydrides could be prepared either by reaction of sodium hydride with the trivalent metallocenes  $[(C_5H_4R)_3U(THF)]$  ( $R = H$  or  $Me$ ; THF = tetrahydrofuran) and  $[(C_5H_4R)_3U]$  ( $R = SiMe_3$  or  $^tBu$ ) or by sodium amalgam reduction of the corresponding uranium(IV) hydrides  $[(C_5H_4R)_3UH]$  ( $R = SiMe_3$  or  $^tBu$ ) [3]. In this paper are presented the synthesis and characterization of this series of complexes, composed of the dinuclear derivatives  $[M][(C_5H_4R)_3UHU(C_5H_4R)_3]$  [ $M = Na(THF)_2$  and  $R = H$  (I) or  $Me$  (II);  $M = Na(18-crown-6)$  and  $R = H$  (III)] and the monomeric compounds  $[Na(18-crown-6)][(C_5H_4R)_3UH]$  [ $R = SiMe_3$  (IV) or  $^tBu$  (V)]; the marked influence of the ring substituent on the structure and stability of these triscyclopentadienyluranium hydrides is discussed along with the crystal structure of  $[Na(18-crown-6)(THF)_2][(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]$ , which was isolated from an equimolar mixture of IV and  $[(C_5H_4SiMe_3)_3U]$ .

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## Results and discussion

*The cyclopentadienyl and methylocyclopentadienyl derivatives: the hydrido-bridged dinuclear complexes*  $[\text{Na}(\text{THF})_2][(\text{C}_5\text{H}_4\text{R})_3\text{UHU}(\text{C}_5\text{H}_4\text{R})_3]$  ( $\text{R} = \text{H}$  or  $\text{Me}$ )

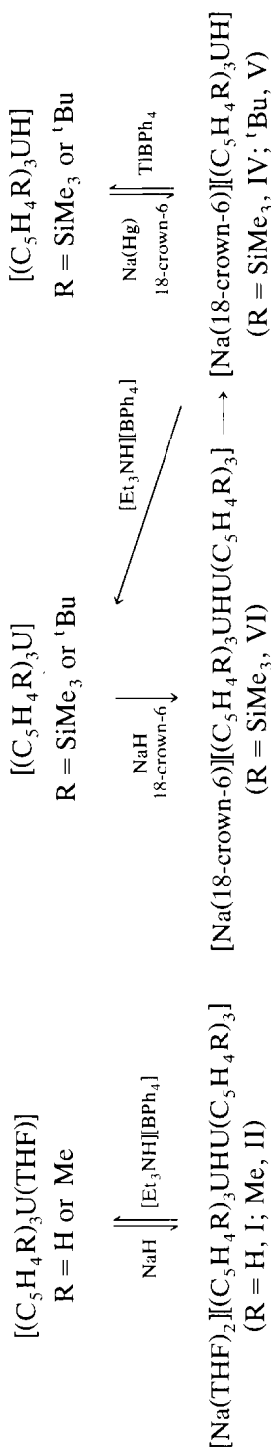
The complexes  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}(\text{THF})]$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) reacted in THF with an excess of sodium hydride to give the bridged anionic monohydrides  $[\text{Na}(\text{THF})_2][(\text{C}_5\text{H}_4\text{R})_3\text{UHU}(\text{C}_5\text{H}_4\text{R})_3]$  [ $\text{R} = \text{H}$  (I) or  $\text{Me}$  (II)] in *ca.* 70% yield (Scheme 1). The analogous lutetium compound  $[\text{Na}(\text{THF})_6][(\text{C}_5\text{H}_5)_3\text{LuHLu}(\text{C}_5\text{H}_5)_3]$  had been similarly prepared from  $[(\text{C}_5\text{H}_5)_3\text{Lu}(\text{THF})]$  [4]. Complexes I and II were obtained alternatively by reduction of  $[(\text{C}_5\text{H}_4\text{R})_3\text{UCl}]$  with an excess of sodium hydride, and treatment of the compounds  $[(\text{C}_5\text{H}_5)_3\text{UX}]$  ( $\text{X} = \text{BH}_4$  or alkyl) with NaH also afforded the hydride I. It was found by NMR spectroscopy that the first step of these reactions is reduction of  $[(\text{C}_5\text{H}_5)_3\text{UX}]$  to the corresponding anion  $[(\text{C}_5\text{H}_5)_3\text{UX}]^-$ . A THF solution of I, in the presence of 18-crown-6 ether, deposited red crystals of  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_5)_3\text{UHU}(\text{C}_5\text{H}_5)_3]$  (III). These bridged hydrides were characterized by their NMR spectra (Table 1) which exhibited a signal at 293.1 ppm (I and III) or 302.2 ppm (II); in contrast to the U–H resonances of most of the other known uranium hydrides [1], those of I and II, as well as those of the other hydrides reported here, could be easily detected. The U–H IR frequencies were too weak to be detected.

When treated with  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  in THF, I and II were quantitatively transformed into  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}(\text{THF})]$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) with evolution of dihydrogen. Prolonged reactions of I and II with an excess of NaH at 80°C did not lead to the clean formation of the anion  $[(\text{C}_5\text{H}_4\text{R})_3\text{UH}]^-$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) but gave unidentified degradation products.

*The trimethylsilyl- and t-butyl-cyclopentadienyl derivatives: the monomeric hydrides*  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{R})_3\text{UH}]$  ( $\text{R} = \text{SiMe}_3$  or  $^t\text{Bu}$ ) and the hydrido-bridged complex  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UHU}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$

Treatment of  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}]$  ( $\text{R} = \text{SiMe}_3$  or  $^t\text{Bu}$ ) with sodium hydride in THF afforded the anionic complexes  $[\text{Na}(\text{THF})_n][(\text{C}_5\text{H}_4\text{R})_3\text{UH}]$  which were found to be stable in solution only in the presence of an excess of NaH. After addition of 18-crown-6 ether, the red crystalline compounds  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{R})_3\text{UH}]$  ( $\text{R} = \text{SiMe}_3$ , IV or  $^t\text{Bu}$ , V) were isolated in almost quantitative yield. These uranium(III) hydrides were also formed in THF by treating  $[(\text{C}_5\text{H}_4\text{R})_3\text{UCl}]$  or  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}][\text{BPh}_4]$  ( $\text{R} = \text{SiMe}_3$  or  $^t\text{Bu}$ ) with an excess of NaH in the presence of the crown ether. Complexes IV and V were obtained alternatively in almost quantitative yield by  $\text{Na}(\text{Hg})$  reduction of the  $\text{U}^{\text{IV}}$  hydrides  $[(\text{C}_5\text{H}_4\text{R})_3\text{UH}]$  ( $\text{R} = \text{SiMe}_3$  or  $^t\text{Bu}$ ). Thus was prepared the deuteride analogue of IV. In its IR spectrum, a band at  $1020\text{ cm}^{-1}$  was assigned to the terminal U–D stretching mode; this corresponding band is at  $1405\text{ cm}^{-1}$  in the spectrum of IV ( $\nu_{\text{H}}/\nu_{\text{D}} = 1.38$ ). The NMR spectra of IV and V (Table 1) exhibited signals at 547.1 and 521.3 ppm, respectively, assigned to the hydride ligand; these proton isotropic shifts are, to our knowledge, the largest ever observed.

It was clear that the dinuclear species  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{R})_3\text{UHU}(\text{C}_5\text{H}_4\text{R})_3]$  ( $\text{R} = \text{SiMe}_3$  or  $^t\text{Bu}$ ), the analogues of III, could be intermediates in the synthesis of the monomeric complexes IV and V. NMR experiments revealed the presence of  $[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UHU}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$  (VI) during the



Scheme 1

Table I

<sup>1</sup>H NMR spectra of the complexes <sup>a</sup>

Compound	Cyclopentadienyl	Hydride
[Na(THF) <sub>2</sub> ][(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> UHU(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> ] (I)	- 21.90 (30H)	293.1 (11H, 55)
[Na(THF) <sub>2</sub> ][(C <sub>5</sub> H <sub>4</sub> Me) <sub>3</sub> UHU(C <sub>5</sub> H <sub>3</sub> Me) <sub>3</sub> ] (II)	- 15.93 and - 20.84 (12H + 12H, CH)	302.2 (11H, 50)
[Na(18-crown-6)][(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> UHU(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> ] (III)	- 21.90 (30H)	293.1 (11H, 50)
[Na(18-crown-6)][(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>3</sub> UH] (IV)	0.45 and - 19.68 (6H + 6H, CH)	547.1 (11H, 220)
[Na(18-crown-6)][(C <sub>5</sub> H <sub>4</sub> <sup>t</sup> Bu) <sub>3</sub> UH] (V)	- 7.42 (27H, CH <sub>3</sub> ) - 0.38 and - 29.49 (6H + 6H, CH)	521.3 (11H, 160)
[Na(18-crown-6)][(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>3</sub> UHU(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>3</sub> ] (VI) <sup>b</sup>	- 5.53 (27H, CH <sub>3</sub> ) - 6.10 (54H) - 15.12 and - 18.95 (12H + 12H, CH)	319.2 (11H, 170)
[Na(18-crown-6)][(C <sub>5</sub> H <sub>4</sub> SiMe <sub>3</sub> ) <sub>3</sub> UCl] (VII)	- 3.05 and - 19.34 (6H + 6H, CH) - 3.60 (27H, CH <sub>3</sub> )	

<sup>a</sup> At 30°C, in THF-*d*<sub>6</sub>. δ relative to TMS (intensity, half height width in Hz); when not specified, the signal is a singlet with  $w_{1/2} = 10-30$  Hz. The spectra, except those of I and II, also exhibit a singlet (24H) corresponding to the crown ether, located between 3.2 and 3.7 ppm. <sup>b</sup> The complex is in equilibrium with IV and [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] (see text).

formation of IV, but the analogue in the *t*-butylcyclopentadienyl series was not observed. Crystals of VI · 2THF were obtained by slow diffusion of pentane into a THF solution of an equimolar mixture of IV and [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] (*vide infra*). The NMR spectrum of these crystals in THF-*d*<sub>6</sub> showed that VI was dissociated into its components to the extent of 75%. As expected, addition of NaH to this equilibrium mixture led to the quantitative formation of the anion [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UH]<sup>-</sup>. Rapid exchange of the hydride ligand was found to occur between V and [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>U] but the dinuclear species [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>UHU(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>], which is presumably the intermediate of this exchange, could not be characterized by NMR spectroscopy.

Protonation of IV by [Et<sub>3</sub>NH][BPh<sub>4</sub>] gave [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U], with evolution of dihydrogen, whereas its oxidation to [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UH] was easily performed using TIBPh<sub>4</sub>. The NMR spectra of solutions containing mixtures of IV or V and the related U<sup>IV</sup> hydrides [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>UH] (R = SiMe<sub>3</sub> or <sup>t</sup>Bu) exhibited single averaged resonances corresponding to the cyclopentadienyl and hydride ligands of these complexes, revealing rapid and reversible electron-transfer between the U<sup>III</sup> and U<sup>IV</sup> centres. Similar behaviour of the redox systems [(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UX]/[(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UX]<sup>-</sup> has already been noted [5]. Reaction of IV with *n*-butyl chloride afforded the red crystalline [Na(18-crown-6)][(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] (VII) which was prepared alternatively in 80% yield by treating [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] with sodium amalgam in the presence of 18-crown-6 ether.

*Relative stabilities of the anionic triscyclopentadienyl uranium (III) hydrides*

Recently we described the synthesis of the organouranium(IV) hydrides  $[(C_5H_4SiMe_3)_3UH]$  and  $[(C_5H_4^tBu)_3UH]$  [6] which exhibited a remarkable thermal stability, in contrast to  $[(C_5H_5)_3UH]$  and  $[(C_5H_4Me)_3UH]$  which could never be isolated, because of their rapid transformation into  $[(C_5H_4R)_3U(THF)]$  ( $R = H$  or  $Me$ ). This striking difference was accounted for by the bulk of the  $SiMe_3$  and  $^tBu$  substituents preventing the formation of the dimeric species  $\{[(C_5H_4R)_3UH]_2\}$ , the key intermediate in the bimolecular dihydrogen elimination. On the other hand, it has already been noted that the  $U^{III}$  metallocenes  $[(C_5H_4R)_3U]$  could exist if  $R = SiMe_3$  or  $^tBu$ , but could only be isolated as adducts  $[(C_5H_4R)_3UL]$  when  $R = H$  or  $Me$  [7]. This distinctive behaviour is also determined by steric factors, since the electron-withdrawing capacities of the cyclopentadienyl substituents follow the order  $SiMe_3 > H > Me > ^tBu$ . Steric effects should also explain why the reaction of  $[(C_5H_4R)_3U]$  with  $NaH$  gave either the hydrido-bridged anions  $[(C_5H_4R)_3UHU(C_5H_4R)_3]^-$  ( $R = H$  or  $Me$ ) or the monomeric anions  $[(C_5H_4R)_3UH]^-$  ( $R = SiMe_3$  or  $^tBu$ ). It is clear that the steric repulsions induced by the bulky  $SiMe_3$  and  $^tBu$  groups would destabilize the dinuclear species. Electronic effects are, however, not negligible and we have shown that THF coordinates much more strongly to  $[(C_5H_4SiMe_3)_3U]$  than to the more electron rich  $[(C_5H_4^tBu)_3U]$  [6]. The same effects should be responsible for the instability of the anion  $[(C_5H_4^tBu)_3UHU(C_5H_4^tBu)_3]^-$ , whereas the trimethylsilyl analogue VI is only partially dissociated in solution.

*X-ray crystal structures*

We have attempted to determine the crystal structure of the monohydride  $[K(18-crown-6)][(C_5H_4^tBu)_3UH]$ , obtained by addition of  $KH$  to  $[(C_5H_4^tBu)_3U]$  in the presence of the crown ether. Crystals were grown by slow diffusion of pentane into a solution of the complex in THF and were found to be monoclinic, belonging to space group  $P2_1/a$  with  $a = 26.767(4)$  Å,  $b = 16.482(2)$  Å,  $c = 24.653(3)$  Å,  $\beta = 94.80(1)^\circ$  and  $Z = 4$ . X-Ray diffraction analysis revealed that the crystals were in fact  $[K(18-crown-6)][(\mu-C_5H_4^tBu)\{K(18-crown-6)\}_2][(C_5H_4^tBu)_3UH]_2$ . Unfortunately, the structure could not be solved with good accuracy, presumably because of a disorder problem concerning the C atoms of the crown ethers, and will not be presented here in detail. The unit cell packing diagram (Fig. 1) shows that two independent anions  $(C_5H_4^tBu)_3UH^-$  are accompanied by one cation  $[K(18-crown-6)]^+$  and one cation  $[(\mu-C_5H_4^tBu)\{K(18-crown-6)\}_2]^+$ . Another example of a cyclopentadienyl group sandwiched between two alkali metals was recently provided by the crystal structure of  $[(\mu-C_5H_4Me)\{Li(tmed)_2\}_2][(C_5H_4Me)_3U]_2(\mu-Me)[Li(tmed)_2]$  ( $tmed = Me_2NCH_2CH_2NMe_2$ ) [8].

The crystal structure of I consists of infinite puckered chains of  $(C_5H_5)_3UHU(C_5H_5)_3$  and  $Na(THF)_2$  fragments linked by  $Na-C_5H_5$  bonds [3]. The bridging hydride ligand was found to occupy statistically two positions symmetrical with respect to the inversion centre ( $U-H = 2$  Å,  $U^i-H = 2.4$  Å and  $U-H-U^i = 160^\circ$ ). Such bent  $M-H-M$  structures were invariably found in the series of the bridged monohydride transition metal complexes; this geometry has been explained by backbonding from  $M$  ( $d\pi$ ) to the  $M-H \sigma^*$  orbital [9]. The crystallographic data for  $[Na(18-crown-6)(THF)_2][(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]$  appear in Tables 2–4. The structure is composed of discrete anion-cation

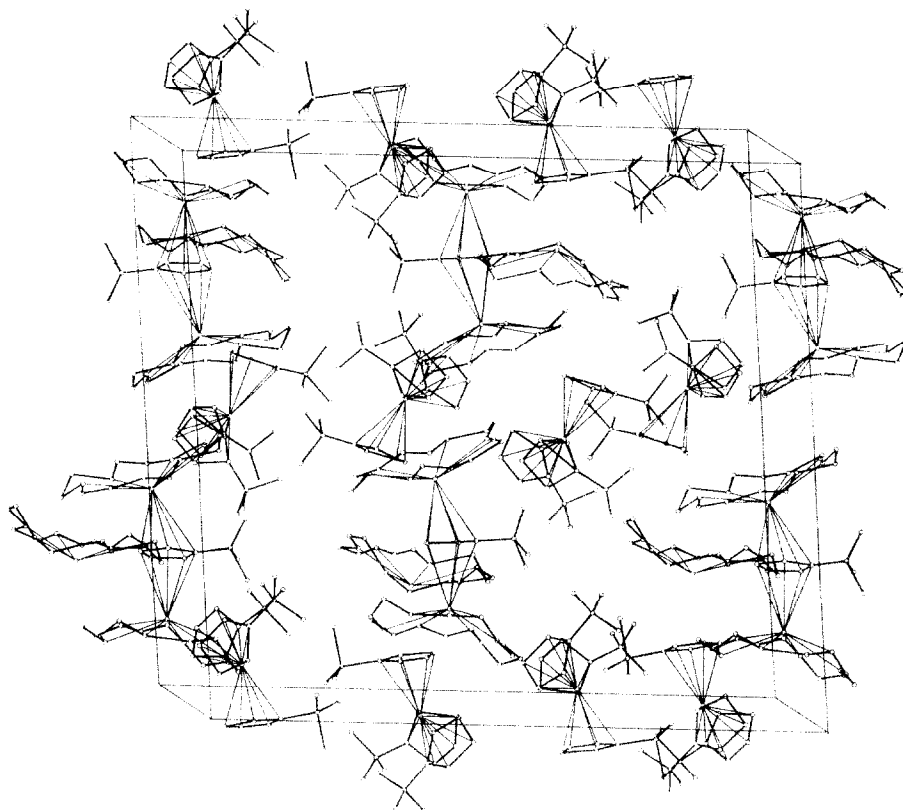


Fig. 1. Unit cell packing diagram of  $[\text{K}(18\text{-crown-}6)][(\mu\text{-C}_5\text{H}_4^t\text{Bu})(\text{K}(18\text{-crown-}6))_2][(\text{C}_5\text{H}_4^t\text{Bu})_3\text{UH}]_2$ .

pairs; ORTEP drawings [10] of the anion are shown in Figs. 2 and 3. This dinuclear fragment has a diad axis; the bridging hydride was not located. The  $\text{U}\text{-U}'$  distance is  $4.4638(4)$  Å and is quite similar to that determined in **1** ( $4.403(2)$  Å). The structural parameters of the  $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}$  moiety are unexceptional: the

Table 2

Selected bond distances (Å) and angles (°) in the anion  $[(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UHU}(\text{C}_5\text{H}_4\text{SiMe}_3)_3]$

<i>Uranium environment</i>					
$\text{U}\text{-C}(20)$	2.853(5)	$\text{U}\text{-C}(30)$	2.873(5)	$\text{U}\text{-C}(40)$	2.892(5)
$\text{U}\text{-C}(21)$	2.822(5)	$\text{U}\text{-C}(31)$	2.825(5)	$\text{U}\text{-C}(41)$	2.861(5)
$\text{U}\text{-C}(22)$	2.835(5)	$\text{U}\text{-C}(32)$	2.810(5)	$\text{U}\text{-C}(42)$	2.789(4)
$\text{U}\text{-C}(23)$	2.844(4)	$\text{U}\text{-C}(33)$	2.819(5)	$\text{U}\text{-C}(43)$	2.812(5)
$\text{U}\text{-C}(24)$	2.865(5)	$\text{U}\text{-C}(34)$	2.848(5)	$\text{U}\text{-C}(44)$	2.863(5)
$\text{U}\text{-U}'^a$	2.570(5)	$\text{U}\text{-3}$	2.557(5)	$\text{U}\text{-4}$	2.569(5)
$\text{U}\text{-U}'$	4.4638(4)				
$2\text{-U}\text{-3}$	118.5(2)	$2\text{-U}\text{-4}$	120.1(2)	$3\text{-U}\text{-4}$	118.49(2)
<i>Cyclopentadienyl ligands</i> <sup>b</sup>					
$\langle\text{C}\text{-C}\rangle_{\text{Cp}}$	1.43(3)	$\langle\text{Si}\text{-C}_{\text{Me}}\rangle$	1.90(2)	$\langle\text{Si}\text{-C}_{\text{Cp}}\rangle$	1.84(2)
$\langle\text{C}\text{-C}\text{-C}\rangle_{\text{Cp}}$	108(2)	$\langle\text{C}_{\text{Cp}}\text{-Si}\text{-C}_{\text{Me}}\rangle$	109(4)		

<sup>a</sup> 2, 3, 4 are the centroids of the cyclopentadienyl rings. <sup>b</sup>  $\text{C}_{\text{Cp}}$ : Carbon of a cyclopentadienyl ring.  $\text{C}_{\text{Me}}$ : Carbon of a methyl group.

Table 3

## Crystallographic data and experimental details for compound VI·2THF

Crystal dimensions (mm)	0.40 × 0.40 × 0.30
Colour	red
Crystal system	monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	30.246(6)
<i>b</i> (Å)	11.737(7)
<i>c</i> (Å)	25.997(10)
$\beta$ (°)	116.53(2)
<i>V</i> (Å <sup>3</sup> )	8256(8)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	0.697
$\mu$ (Mo– <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	19.238
$\theta$ limits (°)	1, 20
Scan type	$\omega$ , 2 $\theta$
Scan width	0.8 + 0.35 tan $\theta$
Range abs. trans.	0.808, 0.999
Range <i>h</i>	0, 29
<i>k</i>	0, 11
<i>l</i>	–24, 24
Reflections collected	
total	4215
unique	3762
with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	2632
Final values	
$R(F) = \Sigma \ F_o\  -  F_c  / \Sigma \ F_o\ $	0.038
$R_w(F) = [\Sigma w \ F_o\  -  F_c\ ^2 / \Sigma w ( F_o )^2]^{1/2}$	0.047
Max shift/esd	0.01
Max residual (e/Å <sup>3</sup> )	< 1

Cp'(centroid)–U–Cp'(centroid) angle average 119(1)° (Cp' = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>) and the U–C bond lengths range from 2.789(4) to 2.892(5) Å (mean 2.84(5) Å); the average U–Cp'(centroid) distance is 2.56(9) Å. The cyclopentadienyl rings are planar to within  $\pm 0.008(14)$  Å and the silicon atom of the trimethylsilyl substituent is out of the Cp' ring plane, pointing away from the U atom, by 0.49(9) Å. The centroids of the three cyclopentadienyl ligands of each Cp'<sub>3</sub>U fragment form parallel and staggered equilateral triangles; this is the best geometry to minimize steric interactions between these bulky ligands.

The structure of the cation [Na(18-crown-6)(THF)<sub>2</sub>]<sup>+</sup> is classical and quite similar to that in the complex [Na(18-crown-6)(THF)<sub>2</sub>][(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>UClU(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>] [5]. The Na atom lies on an inversion centre and its coordination environment is a hexagonal bipyramid; the six oxygen atoms of the crown ether lie in the equatorial plane (the mean Na–O distance is 2.79(6) Å) and the apices are occupied by the two THF ligands at 2.357(4) Å.

## Experimental

### General methods

Microanalyses were performed by Analytische Laboratorien at Engelskirchen (Germany). Infra red spectra were recorded in nujol mulls on a Perkin Elmer 782

Table 4

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their esd's for compound VI·2THF

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> ) <sup>a</sup>
U	0.41760(2)	0.04597(5)	0.20352(2)	3.48(1)★
Si(2)	0.3261(2)	-0.1156(4)	0.0448(2)	5.7(1)★
Si(3)	0.3216(2)	0.3442(4)	0.1422(2)	5.6(1)★
Si(4)	0.3182(2)	-0.0948(5)	0.2687(2)	6.1(1)★
Na	0.000	0.000	0.000	7.3(3)★
O(1)	-0.0155(5)	-0.226(1)	0.0101(6)	11.5(5)★
O(4)	0.0978(4)	0.084(1)	0.0463(5)	10.3(5)★
O(7)	0.0811(5)	-0.151(1)	0.0360(6)	10.4(5)★
O(10)	-0.0137(4)	-0.028(1)	-0.0958(4)	9.9(4)★
C(2)	-0.0633(8)	-0.272(2)	-0.0259(9)	11.4(7)
C(3)	-0.1026(8)	-0.192(2)	-0.0256(9)	10.3(7)
C(5)	0.1347(7)	0.009(2)	0.0485(8)	9.9(6)
C(6)	0.1281(8)	-0.100(2)	0.0716(9)	10.2(6)
C(8)	0.0710(9)	-0.250(2)	0.059(1)	12.7(8)
C(9)	0.0244(9)	-0.301(2)	0.013(1)	12.9(8)
C(11)	0.0253(7)	-0.014(3)	-0.1104(8)	15(1)★
C(12)	0.0035(6)	-0.050(2)	-0.1722(7)	10.4(6)★
C(13)	-0.0492(7)	-0.050(2)	-0.1929(7)	9.1(6)★
C(14)	-0.0577(8)	-0.048(4)	-0.1454(8)	18(1)★
C(20)	0.3777(5)	-0.020(1)	0.0856(6)	4.9(3)
C(21)	0.3747(5)	0.103(1)	0.0857(5)	4.2(3)
C(22)	0.4241(5)	0.148(1)	0.1083(6)	4.5(3)
C(23)	0.4572(5)	0.056(1)	0.1229(5)	4.6(3)
C(24)	0.4303(4)	-0.046(1)	0.1089(5)	4.4(3)
C(25)	0.3456(6)	-0.268(2)	0.0626(7)	6.4(4)
C(26)	0.3055(6)	-0.092(2)	-0.0352(7)	7.6(5)
C(27)	0.2707(6)	-0.082(2)	0.0596(7)	7.5(5)
C(30)	0.3711(5)	0.262(1)	0.1981(6)	5.1(4)
C(31)	0.3662(5)	0.196(1)	0.2427(6)	5.3(4)
C(32)	0.4152(5)	0.184(1)	0.2906(6)	4.9(4)
C(33)	0.4499(5)	0.238(1)	0.2764(5)	4.8(3)
C(34)	0.4240(5)	0.286(1)	0.2212(6)	5.4(4)
C(35)	0.3069(6)	0.468(2)	0.1785(7)	7.7(5)
C(36)	0.2633(6)	0.256(2)	0.1029(7)	7.2(5)
C(37)	0.3417(6)	0.403(2)	0.0881(7)	6.7(4)
C(40)	0.3725(5)	-0.108(1)	0.2532(6)	4.7(3)
C(41)	0.3717(5)	-0.167(1)	0.2047(5)	4.4(3)
C(42)	0.4211(5)	-0.191(1)	0.2140(5)	3.9(3)
C(43)	0.4527(5)	-0.150(1)	0.2721(6)	5.1(4)
C(44)	0.4240(5)	-0.099(1)	0.2953(6)	5.0(4)
C(45)	0.2612(6)	-0.037(2)	0.2038(7)	8.2(5)
C(46)	0.3029(7)	-0.248(2)	0.2851(8)	9.5(6)
C(47)	0.3341(6)	-0.000(2)	0.3338(7)	7.3(5)

<sup>a</sup>  $B_{eq} = 4/3 \sum_i \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ .

instrument and NMR spectra on a Bruker W 60 (FT) spectrometer. Deuterated solvents were dried over Na/K alloy. Chemical shifts are given as  $\delta$  values relative to tetramethylsilane. The <sup>1</sup>H NMR spectra and the analytical data are given in Tables 1 and 5.



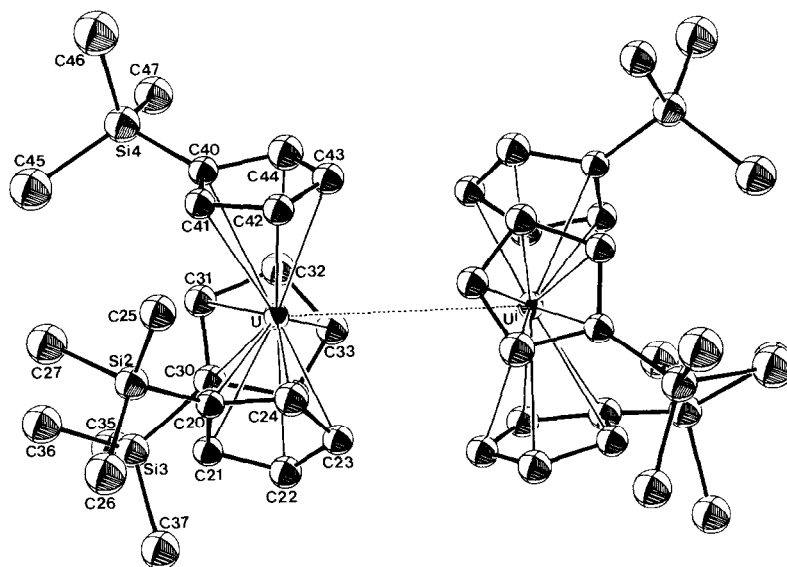


Fig. 2. ORTEP drawing of the anion  $[(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]^-$ . *i* indicates the symmetry operation  $1-x, y, 1/2-z$ .

All experiments were carried out under argon ( $< 5$  ppm oxygen and water) in Schlenk type glassware on a high-vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately

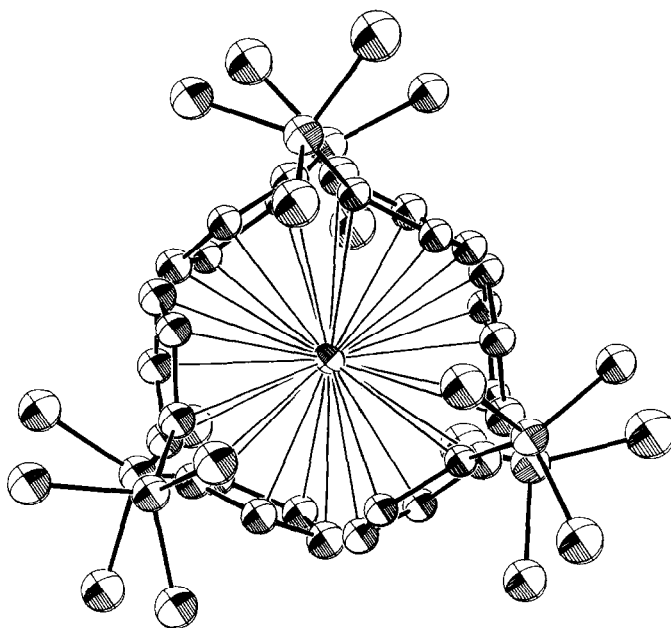


Fig. 3. ORTEP drawing of  $[(C_5H_4SiMe_3)_3UHU(C_5H_4SiMe_3)_3]^-$ . View along the  $U-U'$  axis.

Table 5  
Elemental analyses

Compound	Analyses (found (calcd), %)		
	C	H	Na
$[\text{Na}(\text{THF})_2][(\text{C}_5\text{H}_4\text{Me})_3\text{UHU}(\text{C}_5\text{H}_4\text{Me}_3)]$ (II)	46.94 (47.23)	5.12 (5.28)	2.24 (2.06)
$[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_5)_3\text{UHU}(\text{C}_5\text{H}_5)_3]$ (III)	43.30 (43.67)	4.84 (4.80)	1.96 (1.99)
$[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UH}]$ (IV)	45.73 (46.09)	6.71 (6.87)	2.53 (2.45)
$[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4^t\text{Bu})_3\text{UH}]$ (V)	52.30 (52.63)	7.08 (7.25)	2.66 (2.58)
$[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UCl}]$ (VII) <sup>a</sup>	44.29 (44.45)	6.41 (6.53)	2.27 (2.36)

<sup>a</sup> Cl: 3.50 (3.64).

before use. NaH and <sup>n</sup>BuCl (Aldrich) were used without purification; NaD (20% in oil, Strem) was washed with toluene and dried under vacuum.  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  and  $\text{TIBPh}_3$  were precipitated in water from equimolar mixtures of  $\text{NaBPh}_4$  and  $\text{Et}_3\text{NHCl}$  or  $\text{TINO}_3$  and after filtration, were dried under vacuum. 18-crown-6 ether (Janssen) was dried under vacuum after evaporation from toluene. The chlorides  $[(\text{C}_5\text{H}_4\text{R})_3\text{UCl}]$  (R = H [11], Me,  $\text{SiMe}_3$  or <sup>t</sup>Bu [12]), the hydrides  $[(\text{C}_5\text{H}_4\text{R})_3\text{UH}]$  (R =  $\text{SiMe}_3$  or <sup>t</sup>Bu [6]),  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}]$  (R =  $\text{SiMe}_3$  [13] or <sup>t</sup>Bu [14]), and  $[(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})]$  [5], the cationic complexes  $[(\text{C}_5\text{H}_4\text{R})_3\text{U}][\text{BPh}_4]$  [6], and the compounds  $[(\text{C}_5\text{H}_5)_3\text{UX}]$  (X =  $\text{BH}_4$  [15] or alkyl [16]) were prepared by published methods.  $[(\text{C}_5\text{H}_4\text{Me})_3\text{U}(\text{THF})]$  [13] was synthesized in a manner similar to that of  $[(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})]$ , by Na(Hg) reduction of  $[(\text{C}_5\text{H}_4\text{Me})_3\text{UCl}]$  and was identified by its NMR spectrum.

$[\text{Na}(\text{THF})_2][(\text{C}_5\text{H}_5)_3\text{UHU}(\text{C}_5\text{H}_5)_3]$  (I). (a) from  $[(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})]$ . A 50 ml round bottom flask was charged with  $[(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})]$  (100 mg) and NaH (15 mg) and THF (20 ml) was condensed into it at  $-78^\circ\text{C}$  under vacuum. After stirring for 48 h at  $20^\circ\text{C}$ , the suspension was filtered and evaporated, leaving red microcrystals of I (78 mg, 75%).

(b) from  $[(\text{C}_5\text{H}_5)_3\text{UCl}]$ . A 50 ml round bottom flask was charged with  $[(\text{C}_5\text{H}_5)_3\text{UCl}]$  (1.0 g) and NaH (140 mg) and THF (25 ml) was condensed into it at  $-78^\circ\text{C}$  under vacuum. The reaction mixture was stirred for 48 h at  $20^\circ\text{C}$ ; the solution was filtered and evaporated, leaving a red powder of I (810 mg, 73%) which was recrystallized from THF-pentane.

$[\text{Na}(\text{THF})_2][(\text{C}_5\text{H}_4\text{Me})_3\text{UHU}(\text{C}_5\text{H}_4\text{Me}_3)]$  (II). Preparation of II was similar to that of I. Yields: 65% from  $[(\text{C}_5\text{H}_4\text{Me})_3\text{U}(\text{THF})]$ ; 70% from  $(\text{C}_5\text{H}_4\text{Me})_3\text{UCl}$ .

#### Reactions of $[(\text{C}_5\text{H}_5)_3\text{UX}]$ (X = $\text{BH}_4$ , Me, or <sup>n</sup>Bu) with NaH

An NMR tube, charged with  $[(\text{C}_5\text{H}_5)_3\text{UX}]$  (ca. 10 mg) and an excess of NaH (10 equiv.) in  $\text{THF-}d_6$  (0.4 ml) was immersed in the ultrasound bath. After 1 day, the <sup>1</sup>H NMR spectrum showed resonances of I and others corresponding to a mixture of  $[(\text{C}_5\text{H}_5)_3\text{UX}]$  and  $[(\text{C}_5\text{H}_5)_3\text{UX}]^-$ . Formation of I was complete after 2–3 days.

$[\text{Na}(18\text{-crown-6})][(\text{C}_5\text{H}_5)_3\text{UHU}(\text{C}_5\text{H}_5)_3]$  (III). A tube was charged with I (100 mg) and 18-crown-6 ether (25.5 mg) in THF (10 ml). By cooling to  $-30^\circ\text{C}$ , the

solution deposited red crystals of III (50 mg) which were filtered off and dried under vacuum.

*Reactions of I with [Et<sub>3</sub>NH][BPh<sub>4</sub>]*

An NMR tube was charged with I (10 mg) and [Et<sub>3</sub>NH][BPh<sub>4</sub>] (4 mg) in THF-*d*<sub>8</sub> (0.4 ml). Evolution of dihydrogen was immediately observed and the NMR spectrum showed the quantitative formation of [(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>U(THF)].

*Reactions of [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>U] (R = SiMe<sub>3</sub> or <sup>t</sup>Bu) with NaH*

(a) An NMR tube was charged with [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] (10 mg) and NaH (3 mg) in THF-*d*<sub>8</sub> (0.4 ml) and was immersed in an ultrasound bath (60 W, 40 kHz). After 10 min, the NMR spectrum showed signals corresponding to [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UH]<sup>-</sup> (δ: 451.7 (1H), -0.8 and -18.3 (6H + 6H), -7.0 (27H)) and to [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U]<sub>2</sub>(μ-H)<sup>-</sup> (δ: 320 (1H), -6.2 (54H), -15.4 and -19.5 (12H + 12H)); other small peaks, the intensity of which represented *ca.* 15% of the total, were not identified. After 90 min, the dinuclear species was totally transformed into the monomeric anion. Addition of 18-crown-6 ether (4 mg) led to the immediate formation of IV (hydride resonance at 547.1 ppm).

(b) An NMR tube was charged with [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>U] (10 mg) and NaH (5 mg) in THF-*d*<sub>8</sub> (0.4 ml) and was immersed in the ultrasound bath. After 20 min, the monohydride anion (C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>UH<sup>-</sup> was formed (δ: 431.0 (1H), -0.4 and -27.8 (6H + 6H), -6.3 (27H)). The spectra recorded during the course of the reaction showed that the resonances of the cyclopentadienyl ligands of the neutral species shifted progressively towards positions corresponding to the monohydride anion. After addition of 18-crown-6 ether (4.0 mg), the signal at 431 ppm was replaced by a peak at 521.3 ppm, corresponding to the hydride ligand of V.

*[Na(18-crown-6)][(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UH] (IV) and its deuteride analogue. (a) from [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U].* A 50 ml round bottom flask was charged with [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] (200 mg), 18-crown-6 ether (81.3 mg) and NaH (55 mg); THF (20 ml) was condensed into it at -78°C under vacuum. The mixture was stirred for 3 days at 20°C. After filtration, the solvent was evaporated off and the red sticky oil of IV solidified when dried under vacuum (285 mg, 98%). This reaction was monitored by NMR spectroscopy and the transient formation of the hydrido-bridged intermediate VI was observed. IR: 1405 cm<sup>-1</sup> (ν(U-H)).

*(b) from [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UD].* A 50 ml round bottom flask was charged with [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UD] (50 mg), 18-crown-6 ether (20.3 mg) and 2% Na(Hg) (900 mg); THF (20 ml) was condensed into it at -78°C under vacuum. The reaction mixture was stirred for 10 h at 20°C; the solution was filtered and evaporated to dryness, leaving a red powder of the deuteride analogue of IV (70 mg, 97%). IR: 1020 cm<sup>-1</sup> (ν(U-D)).

*[Na(18-crown-6)][(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>UH] (V). (a) from [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>U].* A round bottom flask was charged with [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>U] (300 mg), NaH (60 mg) and 18-crown-6 ether (131.8 mg); THF (20 ml) was condensed into it at -78°C under vacuum. The reaction mixture was stirred for 30 h at 20°C. The solution was filtered and its volume was reduced to 5 ml; addition of pentane (20 ml) precipitated a red powder, V, which was filtered off and dried under vacuum (373 mg, 84%).

*(b) from [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>UH].* An NMR tube was charged with [(C<sub>5</sub>H<sub>4</sub><sup>t</sup>Bu)<sub>3</sub>UH] (10 mg), 18-crown-6 ether (4.4 mg) and Na(Hg) (96 mg) in THF-*d*<sub>8</sub> (0.4 ml). The

tube was immersed in the ultrasound bath for 1 h and the spectrum showed the quantitative formation of V.

*Reactions of [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>UCl] or [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>U][BPh<sub>4</sub>] (R = SiMe<sub>3</sub> or <sup>t</sup>Bu) with NaH*

An NMR tube was charged with [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>UCl] or [(C<sub>5</sub>H<sub>4</sub>R)<sub>3</sub>U][BPh<sub>4</sub>] (*ca.* 10 mg), one equivalent of 18-crown-6 ether and NaH (*ca.* 2 mg) in THF-*d*<sub>8</sub> (0.4 ml). The tube was immersed in the ultrasound bath and after 6 h, the spectrum showed the formation of IV or V. The chloride [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] was first reduced to [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] and the dinuclear compound VI was observed as an intermediate.

*[Na(18-crown-6)(THF)<sub>2</sub>][(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UHU(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>] (VI).* Crystals of this complex were obtained by slow diffusion of pentane (15 ml) into a solution of [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U] (30 mg) and I (43 mg) in THF (5 ml). The NMR spectrum in THF-*d*<sub>8</sub> showed that 75% of this compound was dissociated into IV and [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U].

*Reactions of IV with [Et<sub>3</sub>NH][BPh<sub>4</sub>], TIBPh<sub>4</sub> and <sup>n</sup>BuCl*

(a) An NMR tube was charged with IV (10 mg) and [Et<sub>3</sub>NH][BPh<sub>4</sub>] (4.5 mg) in THF-*d*<sub>8</sub> (0.4 ml). Bubbles immediately appeared and the NMR spectrum showed the quantitative formation of [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>U].

(b) An NMR tube was charged with IV (6 mg) and TIBPh<sub>4</sub> (5 mg) in THF-*d*<sub>8</sub> (0.4 ml). Immediate precipitation of black TI was observed and the NMR spectrum showed the quantitative formation of [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UH].

(c) An NMR tube was charged with IV (10 mg) and BuCl (1.2 μl) in THF-*d*<sub>8</sub> (0.4 ml). After 1.5 h, the NMR spectrum showed the quantitative formation of VII.

*[Na(18-crown-6)][(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] (VII).* A 50 ml round bottom flask was charged with [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] (152 mg), 18-crown-6 ether (58.6 mg) and 2% Na(Hg) (1.28 g); THF (20 ml) was condensed into it at -78°C under vacuum. The mixture was stirred at 20°C for 10 h. THF was evaporated off and the residue was extracted in toluene; the oil, obtained after evaporation of the aromatic solvent, was washed with pentane and, by drying under vacuum, was transformed into a red powder which was recrystallized from THF-pentane (171 mg, 80%). An NMR tube was charged with VII (10 mg) and TIBPh<sub>4</sub> (6 mg) in THF-*d*<sub>8</sub> (0.4 ml). Immediate precipitation of black TI was observed and the NMR spectrum showed the formation of [(C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub>UCl] in quantitative yield.

*X-Ray crystal structure of VI · 2THF*

A selected single crystal was introduced into a thin walled Lindeman glass tube in the glove box. Data were collected at room temperature on an Enraf-Nonius diffractometer equipped with a graphite monochromator ( $\lambda = 0.71073 \text{ \AA}$ ). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with  $\theta$  between 8 and 12°. Three standard reflections were measured after each hour: a decay of 18.4% in 43 hours was linearly corrected. The data were corrected for Lorentz polarization effects and absorption [17]. The structure was solved by the heavy-atom method and refined by full matrix least-squares on F; U, O, Si and C atoms of the THF ligands were refined anisotropically. The bridging hydride was not found. All calculations were performed on a MicroVax II computer with the Enraf-Nonius Structure Determination Package [18]. Analytical

scattering factors for neutral atoms [19] were corrected for both  $\Delta f'$  and  $\Delta f''$  components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3. Selected bond distances and angles are listed in Table 2 and final positional and thermal parameters in Table 4. Full lists of structure factors, atomic coordinates, thermal parameters etc. are available from the authors.

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