Synthesis and Some Reactions of Tris(cyclopentadienyl)-uranium(IV) Hydrides; Crystal Structure of $[U(C_5H_4Bu^t)_3H]$†

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The uranium(IV) hydrides $[U(C_5H_4R)_3H]$ (R = $SiMe_3$ **1** or Bu^t **2**), which are thermally very stable, were isolated from the reactions of the corresponding chlorides with $KBEt_3H$. The hydridic character of **1** and **2** was demonstrated by their reactions with chloroform and alcohols, and by treatment with NEt_3HBPh_4, which gives the cationic complexes $[U(C_5H_4R)_3][BPh_4]$. The crystal structure of **2** has been determined.

The only organometallic uranium(IV) hydride which has been so far reported is the bis(pentamethylcyclopentadienyl)-compound $[\{U(C_5Me_5)_2H_2\}_2]$;[1] this only exists under a dihydrogen atmosphere and is otherwise transformed, by easy and reversible loss of H_2, into the uranium(III) hydride $[U(C_5Me_5)_2H]$.[2] In contrast, the thorium derivative $[\{Th(C_5Me_5)_2H_2\}_2]$[1] and the uranium alkoxy hydrides $[U(C_5Me_5)_2H(OR)]$ (R = $CHBu^t_2$ or $SiMe_2Bu^t$)[3] are resistant to dihydrogen elimination. The distinct behaviour of these complexes has been explained by the stabilization of their +4 oxidation state: thorium(IV) compounds are effectively much less easily reduced than their uranium analogues and hard ligands such as alkoxides should stabilize higher valences. On the other hand, despite many efforts, the tris(cyclopentadienyl)uranium hydride $[U(C_5H_5)_3H]$ has never been isolated or even observed,[4] a fact that has been accounted for by the ready accessibility of the trivalent complex $[U(C_5H_5)_3]$.

We found that the tris(cyclopentadienyl)uranium(IV) hydride $[U(C_5H_4SiMe_3)_3H]$ **1** could be easily obtained from the parent chloride $[U(C_5H_4SiMe_3)_3Cl]$.[5] In order to determine the origin of the remarkable stability of **1** we have changed the electron-withdrawing substituent $SiMe_3$ to the electron donating group CMe_3 and thus isolated the corresponding hydride $[U(C_5H_4Bu^t)_3H]$ **2**, which is as stable as **1**. Here we report the synthesis, characterization and some reactions of these uranium(IV) hydrides, and also describe the crystal structure of **2**.

Results and Discussion

Synthesis.—The tris(cyclopentadienyl)uranium chlorides $[U(C_5H_4R)_3Cl]$ (R = $SiMe_3$[6] or Bu^t[7]) reacted with $KBEt_3H$ in tetrahydrofuran (thf) to give, after 1 h at 20 °C, the hydrides **1** and **2** which were isolated as green crystals in almost quantitative yields. Similar reaction with $LiBEt_3D$ afforded the deuteride analogue of **1**. The NMR spectra of **1** and **2** (Table 1) are quite similar and exhibit a low-field signal at δ 290.5 and 276.1, respectively, corresponding to the hydride ligand. These narrow resonances ($w_{\frac{1}{2}}$ = 10 and 30 Hz) could be easily detected, in contrast to those of other uranium hydrides.[1,8] In the IR spectra the bands centred at 1395 **1** and 1410 cm^{-1} **2** are assigned to the terminal U–H stretching mode; this frequency was shifted to 1015 cm^{-1} in the spectrum of $[U(C_5H_4SiMe_3)_3D]$ (ν_H/ν_D = 1.37).

Table 1 Analytical and ^1H NMR data

Compound	Analyses[a]	NMR data[b]
1 $[U(C_5H_4SiMe_3)_3H]$	C 43.95 (44.3) H 5.95 (6.15) U 36.85 (36.6)	290.50 (1 H, s, $w_{\frac{1}{2}}$ 10 Hz, U–H), 26.71 and −12.57 (6 H + 6 H, CH), −12.74 (27 H, Me)
2 $[U(C_5H_4Bu^t)_3H]$	C 53.55 (53.8) H 6.55 (6.65)	276.10 (1 H, s, $w_{\frac{1}{2}}$ 30 Hz, U–H), 27.17 and −18.63 (6 H + 6 H, CH), −12.54 (27 H, Me)
$[U(C_5H_4SiMe_3)_3(OEt)]$	C 44.65 (44.95) H 6.25 (6.35) Si 11.85 (12.1)	64.69 (2 H, CH_2), 19.54 (3 H, Me), −0.27 (27 H, $SiMe_3$), −12.37 and −22.40 (6 H + 6 H, CH)
$[U(C_5H_4SiMe_3)_3(OPr^i)]$	C 45.4 (45.75) H 6.35 (6.5) Si 11.55 (11.85)	74.52 (1 H, OC*H*Me_2), 23.12 (6 H, OCH*Me*$_2$), −0.06 (27 H, $SiMe_3$), −17.51 and −22.06 (6 H + 6 H, CH)
3 $[U(C_5H_4SiMe_3)_3][BPh_4]$	C 59.2 (59.5) H 6.3 (6.1) B 1.25 (1.15) Si 8.5 (8.7)	6.52 (20 H, m, Ph), 0.71 and −2.71 (6 H + 6 H, CH), −3.52 (27 H, Me)
4 $[U(C_5H_4Bu^t)_3][BPh_4]$	C 66.45 (66.5) H 6.55 (6.4) B 1.1 (1.2)	6.57 (20 H, m, Ph), 2.08 and −0.72 (6 H + 6 H, CH), −5.47 (27 H, Me)

[a] Analytical data given as: found (required) in %. [b] At 30 °C, in $[^2H_8]$toluene except for complexes **1**, **3** and **4** in $[^2H_8]$tetrahydrofuran. Data given as chemical shift (δ) (relative integral, multiplicity, assignment); when not specified, the signal is a singlet with $w_{\frac{1}{2}}$ = 10–30 Hz.

The hydridic character of complexes **1** and **2** was demonstrated by their reactions with chloroform and alcohols which led to the formation of the corresponding chlorides and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

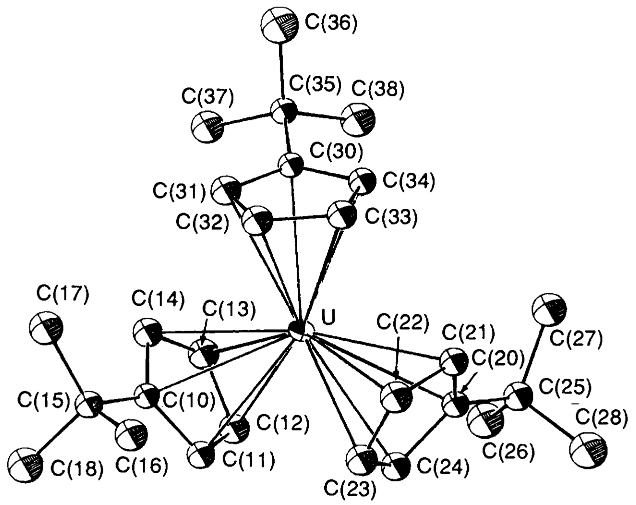

Fig. 1 Perspective view of [U($C_5H_4Bu^t$)$_3$H]

alkoxides [equations (1) and (2)]. Protonation of **1** and **2** by

$$[U(C_5H_4R)_3H] \xrightarrow{CHCl_3} [U(C_5H_4R)_3Cl] \quad (1)$$
$$R = SiMe_3 \text{ or } Bu^t$$

$$[U(C_5H_4SiMe_3)_3H] \xrightarrow{R'OH} [U(C_5H_4SiMe_3)_3(OR')] \quad (2)$$
$$R' = Et \text{ or } OPr^i$$

NEt_3HBPh_4 in thf induced the immediate evolution of dihydrogen and the cationic complexes [U(C_5H_4R)$_3$][BPh_4] (R = $SiMe_3$ **3** or Bu^t **4**), obtained in almost quantitative yield, were isolated as ochre crystals. Cationic metallocenes of the type [U(C_5H_5)$_3$][BPh_4] have already been reported.[9] Compounds **3** and **4** were transformed back into **1** and **2** by treatment with $KBEt_3H$ and were converted into the trivalent metallocenes [U(C_5H_4R)$_3$] (R = $SiMe_3$ **5**[6] or Bu^t **6**[10]) by sodium amalgam reduction (NMR experiments).

Stability of the Hydrides [U(C_5H_4R)$_3$H].—Ultraviolet irradiation of complexes **1** and **2** in toluene led, after 3 h at 20 °C, to the quantitative formation of **5** and **6**, respectively [equation (3)]. Such photochemical reaction of organo-

$$2[U(C_5H_4R)_3H] \xrightarrow{h\nu} 2[U(C_5H_4R)_3] + H_2 \quad (3)$$
$$R = SiMe_3\ \mathbf{5} \text{ or } Bu^t\ \mathbf{6}$$

transition-metal monohydrides, which presumably involves homolytic cleavage of the metal–hydrogen bond, is not common.[11]

The hydrides **1** and **2** were found to be thermally very resistant in solution or in the solid state; they did not decompose when heated at 100 °C in toluene for several days. This behaviour is in striking contrast to that of the putative hydride [U(C_5H_5)$_3$H] which has never been observed, presumably because of its rapid transformation into [U(C_5H_5)$_3$]. It has been argued, from thermochemical considerations, that bimolecular elimination of H_2 from such hydrides [equation (3)] should be sufficiently close to thermoneutrality to be entropically driven, as well as driven by typical work-up procedures.[12] We initially suggested that the remarkable thermal stability of **1** was due to the electron-attracting property of the $SiMe_3$ ring substituent which would stabilize the +4 oxidation state of this complex.[5] This suggestion is clearly invalidated by the results reported here, since the electron-withdrawing abilities of the cyclopentadienyl substituents follow the order $SiMe_3 > H > CMe_3$. It seems now evident that steric factors are responsible for the stability of **1** and **2**; the bulkiness of the substituted cyclopentadienyl ligands should impede the collision between two molecules and the formation of the dimeric intermediate [{U(C_5H_4R)$_3$H}$_2$] which would be the key step in the bimolecular hydrogen elimination. In this context, it is interesting that the dimeric dihydride [{U(C_5Me_5)$_2H_2$}$_2$][1] easily eliminates H_2 whereas the alkoxy hydrides [U(C_5Me_5)$_2$H(OR)][3] are monomeric and stable; it is possible that, as in the case of **1** and **2**, this stability has its origin in kinetic factors, the bulky alkoxide groups (R = $CHBu^t_2$ or $SiMe_2Bu^t$) preventing any bimolecular process. The distinct electronic effects of the various cyclopentadienyl substituents could be, however, easily detected. The reduction potentials of the chlorides [U(C_5H_4R)$_3$Cl] are respectively −1.83, −1.87 and −2.02 V (*vs.* ferrocene–ferrocenium) for R = $SiMe_3$, H and Bu^t.[13] On the other hand, the co-ordination ability of the trivalent metallocene [U($C_5H_4SiMe_3$)$_3$] **5** is quite different from that of its *tert*-butyl analogue **6**; the latter, which is more electron rich, gave a much more labile adduct with tetrahydrofuran (thf). Nevertheless, these electronic effects, although non-negligible, do not play a predominant role in the stabilization of the hydrides **1** and **2**.

Crystal Structure of [U($C_5H_4Bu^t$)$_3$H].—An ORTEP drawing[14] of complex **2** is shown in Fig. 1; selected bond distances and angles are listed in Table 2. The structure consists of discrete neutral molecules in which the uranium atom is bonded to three *tert*-butylcyclopentadienyl ligands in a pentahapto fashion; the hydride ligand was not located. It is noteworthy that, within the experimental errors, the geometrical parameters of the U($C_5H_4XMe_3$)$_3$ fragment (X = Si or C) are quite similar in the series of the crystallographically characterized complexes listed in Table 3. It has been already pointed out that the stereochemistry of the trigonal-planar compound [U($C_5H_4SiMe_3$)$_3$] changes very slightly upon co-ordination with ethyl isocyanide.[15] It is peculiar that this geometry is also adopted by the uranium(IV) complexes **2** and [{U($C_5H_4SiMe_3$)$_3$}$_2$(μ-O)]. In the binuclear oxo-bridged compound[16] the small contraction of the (ring centroid)–U–(ring centroid) angle certainly reflects the steric repulsion between the cyclopentadienyl ligands of the two organometallic units, but the U–C(ring centroid) distance is similar to that found in the other derivatives. This situation is in marked contrast to that encountered within the series of complexes [U(C_5H_5)$_3$X], [U(C_5H_5)$_3$X]$^-$ and [U(C_5H_5)$_3$L],[17] (X = Cl, F or Bu^n; L = thf) where the U–C(ring centroid) distances of the uranium(III) derivatives, typically equal to 2.55 Å, are generally longer, by 0.1 Å, than those of the uranium(IV) compounds; this variation corresponds to the difference between the ionic radii of U^{IV} and U^{III}. The invariance of the U–C bond lengths in the substituted tris(cyclopentadienyl)uranium complexes should be accounted for by the steric hindrance of the ligands which cannot come in closer contact with the metal centre. These steric factors should also be responsible for the positions of the Si or C atoms of the XMe_3 substituents which are invariably out of the cyclopentadienyl ring planes, by an average distance of 0.25 Å in **2**. This distance is similar in [U($C_5H_4SiMe_3$)$_3$] (0.21 Å) and is equal to 0.60 Å in the more congested binuclear oxo complex.

Experimental

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a dry-box. Solvents were thoroughly dried and deoxygenated by the standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy.

Elemental analyses and molecular weight determinations were carried out by Analytische Laboratorien at Engelskirchen (Germany). The IR spectra were recorded on a Perkin-Elmer

Table 2 Selected bond distances (Å) and angles (°)* with estimated standard deviations for $[\mathrm{U(C_5H_4Bu^t)_3H}]$

Uranium environment					
U–C(10)	2.796(6)	U–C(20)	2.833(7)	U–C(30)	2.829(7)
U–C(11)	2.768(7)	U–C(21)	2.767(7)	U–C(31)	2.764(7)
U–C(12)	2.727(8)	U–C(22)	2.707(8)	U–C(32)	2.729(7)
U–C(13)	2.741(8)	U–C(23)	2.710(7)	U–C(33)	2.731(8)
U–C(14)	2.790(7)	U–C(24)	2.769(7)	U–C(34)	2.790(7)
U–Cp1	2.476(7)	U–Cp2	2.477(7)	U–Cp3	2.484(7)
Cp1–U–Cp2	117.9(2)	Cp1–U–Cp3	123.0(2)	Cp2–U–Cp3	117.4(2)
Cyclopentadienyl ligand					
$\langle \mathrm{C{-}C} \rangle_{\mathrm{cp}}$	1.41(2)	$\langle \mathrm{C{-}C{-}C} \rangle_{\mathrm{cp}}$	108(2)		
$\langle \mathrm{C_{cp}{-}C_{tert}} \rangle$	1.52(1)	$\langle \mathrm{C_{cp}{-}C_{tert}{-}C_{Me}} \rangle$	109(2)		
$\langle \mathrm{C_{tert}{-}C_{Me}} \rangle$	1.52(2)				

* Cp1 is the centroid of the cyclopentadienyl ring 1, *etc.*

Table 3 Geometrical parameters of the $\mathrm{U(C_5H_4R)_3}$ fragment (R = $\mathrm{SiMe_3}$ or $\mathrm{Bu^t}$) in some uranium-(III) and -(IV) complexes*

	$[\mathrm{U(C_5H_4SiMe_3)_3}]$[13]	$[\mathrm{U(C_5H_4SiMe_3)_3(CNEt)}]$[15]	$[\{\mathrm{U(C_5H_4SiMe_3)_3}\}_2(\mu\text{-}\mathrm{O})]$[16]	$[\mathrm{U(C_5H_4Bu^t)_3H}]$
⟨U–C⟩	2.78(4)	2.81(3)	2.80(1)	2.76(1)
⟨U–Cp⟩	2.51(3)	2.53	2.53(1)	2.48(1)
⟨Cp–U–Cp⟩	119(2)	119	117.2(5)	119(4)

* Distances in Å and angles in °; Cp is the centroid of the cyclopentadienyl ligand.

782 instrument in Nujol mulls, ^{1}H NMR spectra on a Bruker W 60 (FT) instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). These data are presented in Table 1. The compounds $\mathrm{KBEt_3H}$ and $\mathrm{LiBEt_3D}$ (Aldrich) were used without purification, $\mathrm{NEt_3HBPh_4}$ was made by mixing $\mathrm{NEt_3HCl}$ and $\mathrm{NaBPh_4}$ in water and $[\mathrm{U(C_5H_4SiMe_3)_3Cl}]$[6] and $[\mathrm{U(C_5H_4Bu^t)_3Cl}]$[7] were prepared according to published methods.

$[\mathrm{U(C_5H_4SiMe_3)_3H}]$ **1**.—A round bottom flask (50 cm^3) was charged with $[\mathrm{U(C_5H_4SiMe_3)_3Cl}]$ (2.0 g, 2.9 mmol) in thf or toluene (20 cm^3) and $\mathrm{KBEt_3H}$ (3.5 cm^3 of a 1 mol dm^{-3} solution in thf, 3.5 mmol) was added *via* a syringe. The orange solution immediately turned green and the reaction mixture was stirred at 20 °C for 1 h. The solvent was evaporated off and the residue extracted in pentane (20 cm^3). After evaporation to dryness, the product **1** was isolated as a green microcrystalline powder (1.88 g, 98%). Similar reaction of $[\mathrm{U(C_5H_4SiMe_3)_3Cl}]$ with $\mathrm{LiBEt_3D}$ gave the deuteride $[\mathrm{U(C_5H_4SiMe_3)_3D}]$. Molecular weight by osmometry: 687 (theoretical 651).

$[\mathrm{U(C_5H_4Bu^t)_3H}]$ **2**.—The preparation of complex **2** was similar to that of **1**. Reaction of $[\mathrm{U(C_5H_4Bu^t)_3Cl}]$ (2.18 g, 3.42 mmol) with $\mathrm{KBEt_3H}$ (4 cm^3 of a 1 mol dm^{-3} solution in thf) afforded yellow-green crystals of **2** (1.80 g, 87%). Molecular weight by osmometry: 622 (theoretical 602).

Reactions of Complexes **1** *and* **2** *with Chloroform*.—An NMR tube was charged with complex **1** or **2** (*ca.* 5 mg) in [^{2}H$_8$]thf (0.5 cm^3) and $\mathrm{CHCl_3}$ (50 µl) was added *via* a gas-tight syringe. After 2 h at 20 °C the NMR spectrum showed quantitative formation of the corresponding chlorides $[\mathrm{U(C_5H_4XMe_3)_3Cl}]$ (X = Si or C).

$[\mathrm{U(C_5H_4SiMe_3)_3(OEt)}]$.—(*a*) A round bottom flask (50 cm^3) was charged with $[\mathrm{U(C_5H_4SiMe_3)_3Cl}]$ (200 mg, 0.29 mmol) and NaOEt (27 mg, 0.4 mmol) and thf (20 cm^3) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 45 min at 70 °C. The solvent was evaporated off and the residue extracted in pentane (15 cm^3). After evaporation to dryness the product was isolated as yellow needles (165 mg, 81%).

(*b*) An NMR tube was charged with complex **1** (10 mg, 0.015 mmol) in [^{2}H$_6$]benzene (0.5 cm^3) and ethanol (1 µl, 0.015 mmol) was introduced *via* a gas-tight microsyringe. Gas was immediately evolved. The NMR spectrum showed quantitative formation of the ethoxide compound.

$[\mathrm{U(C_5H_4SiMe_3)_3(OPr^i)}]$.—A round bottom flask (50 cm^3) was charged with complex **1** (150 mg, 0.23 mmol) and toluene (15 cm^3) was condensed into it under vacuum at −78 °C. Isopropyl alcohol (17.6 µl, 0.23 mmol) was added *via* a syringe. Gas was immediately evolved. The solvent was evaporated off and the residue extracted in pentane (10 cm^3). After evaporation to dryness, the product was isolated as yellow needles (130 mg, 80%).

$[\mathrm{U(C_5H_4SiMe_3)_3}][\mathrm{BPh_4}]$ **3**.—A round bottom flask (25 cm^3) was charged with complex **1** (150 mg, 0.23 mmol) and $\mathrm{NEt_3HBPh_4}$ (96 mg, 0.23 mmol) and thf (15 cm^3) was condensed into it under vacuum at −78 °C. Upon heating at room temperature, the yellow-green solution turned red and gas was evolved. The solvent was evaporated off, leaving an ochre powder which was washed with pentane (20 cm^3) and dried under vacuum (190 mg, 85%).

$[\mathrm{U(C_5H_4Bu^t)_3}][\mathrm{BPh_4}]$ **4**.—The preparation of complex **4** was similar to that of **3**. The reaction of **2** (300 mg, 0.50 mmol) with $\mathrm{NEt_3HBPh_4}$ (209 mg, 0.50 mmol) gave an ochre microcrystalline powder of **4** (440 mg, 96%).

Reactions of Complexes **3** *and* **4**.—*With* $\mathrm{KBEt_3H}$. An NMR tube was charged with complex **3** or **4** (*ca.* 10 mg) in [^{2}H$_8$]thf (0.5 cm^3). The compound $\mathrm{KBEt_3H}$ (13 µl of a 1 mol dm^{-3} solution in thf) was added *via* a gas-tight microsyringe. The NMR spectra showed the quantitative formation of **1** and **2** respectively.

With sodium amalgam. An NMR tube was charged with complex **3** or **4** (*ca.* 10 mg) and 2% Na(Hg) (60 mg) in [^{2}H$_8$]thf (0.5 cm^3) and was immersed for 5 min in an ultrasound bath (60 W, 40 kHz). The NMR spectra showed the quantitative formation of **5** and **6** respectively.

Photolysis of Complexes **1** *and* **2**.—In an NMR tube a solution of complex **1** and **2** (*ca.* 10 mg) in [^{2}H$_8$]toluene (0.4 cm^3) was irradiated by a mercury UV lamp (450 W). After 3 h

Table 4 Crystallographic data and experimental details

Crystal data	
Crystal dimensions (mm)	0.60 × 0.25 × 0.15
Colour	Yellow-green
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.804(3)
b/Å	16.871(3)
c/Å	14.155(6)
β/°	107.00(3)
U/Å^3	2467(2)
Z	4
D_c/g cm^{-3}	1.622
μ(Mo-Kα)/cm^{-1}	62.47
F(000)	1176
Data collection	
θ limits (°)	1, 20
Scan type	ω, 2θ
Scan width	0.8 + 0.35 tan θ
Range absol. transmittance	0.897–1.077
Range hkl	−10 to 10, 0–16, 0–13
Reflections collected	
total	2543
unique	2307
with $I > 3\sigma(I)$	1506
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.026
$R' = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w(\|F_o\|^2)]^{\frac{1}{2}}$	0.031 (w = 1)
Maximum shift/e.s.d.	0.01
Maximum residual (e Å^{-3})	< 1

Table 5 Fractional atomic coordinates with e.s.d.s for $[U(C_5H_4Bu^t)_3H]$

Atom	x	y	z
U	0.231 77(4)	0.243 15(3)	−0.005 85(3)
C(10)	0.257(1)	0.078 4(6)	−0.010 4(9)
C(11)	0.196(1)	0.094 6(7)	0.065 1(9)
C(12)	0.283(1)	0.133 1(8)	0.142(1)
C(13)	0.401(1)	0.142 4(8)	0.120(1)
C(14)	0.386(1)	0.107 6(8)	0.026(1)
C(15)	0.202(1)	0.027 8(8)	−0.101(1)
C(16)	0.065(1)	0.052 0(9)	−0.158(1)
C(17)	0.283(1)	0.029 0(9)	−0.172(1)
C(18)	0.199(1)	−0.057 9(9)	−0.065(1)
C(20)	0.083(1)	0.338 4(7)	0.085 3(9)
C(21)	0.050(1)	0.360 7(8)	−0.015(1)
C(22)	−0.015(1)	0.296 7(8)	−0.075(1)
C(23)	−0.022(1)	0.234 4(9)	−0.014 6(9)
C(24)	0.038(1)	0.257 2(8)	0.085 0(9)
C(25)	0.132(1)	0.392 8(8)	0.175(1)
C(26)	0.209(1)	0.349(1)	0.265(1)
C(27)	0.213(1)	0.460 9(9)	0.151(1)
C(28)	0.011(1)	0.427(1)	0.194(1)
C(30)	0.429(1)	0.314 9(7)	−0.070 8(9)
C(31)	0.381(1)	0.249 2(9)	−0.134 7(9)
C(32)	0.253(1)	0.264 1(9)	−0.191 7(9)
C(33)	0.220(1)	0.339 3(8)	−0.163(1)
C(34)	0.325(1)	0.370 0(8)	−0.091 6(9)
C(35)	0.570(1)	0.331 9(7)	−0.016 9(9)
C(36)	0.630(1)	0.371(1)	−0.091(1)
C(37)	0.646(1)	0.256 9(9)	0.023(1)
C(38)	0.581(1)	0.388 4(9)	0.072(1)

the NMR spectra showed the quantitative formation of **5** and **6** respectively.

Relative Stabilities of the Tetrahydrofuran Adducts of Complexes **5** *and* **6**.—(*a*) An NMR tube was charged with complex **5** (13.6 mg, 0.02 mmol) in [$^2H_6$]benzene (0.5 cm^3): δ −18.70 (27 H, Me), −19.22 and 9.23 (6 H + 6 H, CH). Tetrahydrofuran (1.5 μl, 0.02 mmol) was introduced into the tube *via* a gas-tight microsyringe. The NMR spectrum showed that the thf molecule was well co-ordinated to **5**, since the corresponding signals are substantially shifted towards the high-field region: δ −6.40 (27 H, Me), −7.31 and −16.95 (6 H + 6 H, CH), −16.18 (4 H, H_α of thf) and −3.03 (4 H, H_β of thf). The spectrum of **5** in [$^2H_8$]thf has been recorded: δ −3.72 (27 H, Me), −5.83 and −16.43 (6 H + 6 H, CH).

(*b*) An NMR tube was charged with complex **6** (12.0 mg, 0.02 mmol) in [$^2H_6$]benzene (0.5 cm^3): δ −20.85 (27 H, Me), −24.04 and 9.00 (6 H + 6 H, CH). Tetrahydrofuran (1.5 μl, 0.02 mmol) was introduced into the tube. The resonances corresponding to **6** were slightly affected and the thf signals were not very much shifted from their diamagnetic positions: δ −20.69 (27 H, Me), −24.06 and 8.88 (6 H + 6 H, CH) 3.32 (4 H, Hα of thf), 1.37 (4 H, Hβ of thf). The spectrum of **6** in [$^2H_8$]thf has been recorded: δ −8.66 (27 H, Me), −22.08 and −1.27 (6 H + 6 H, CH). These results indicated that thf is much less strongly co-ordinated to **6** than to **5**.

Crystal Structure Determination.—The hydride **2** was recrystallized from pentane at −80 °C. A selected single crystal was introduced into a thin-walled Lindeman glass tube in a glove-box. Data were collected at room temperature on an Enraf-Nonius diffractometer equipped with a graphite monochromator (λ = 0.710 73 Å). The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour; the decay of 39.8% in 33 h was linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[18] The structure was solved by the heavy-atom method and refined by full-matrix least squares on F. Only the uranium atom was refined anisotropically. Hydrogen atoms of the $C_5H_4Bu^t$ groups were included in the refinement at calculated positions on the basis of sp^2 and sp^3 geometries with C–H 0.95 Å and fixed isotropic thermal parameters equal to 6 Å^2; they were not refined but constrained to ride on their C atoms. The hydride ligand was not found. All calculations were performed on a Micro Vax II computer with the Enraf-Nonius Structure Determination Package.[19] Analytical scattering factors for neutral atoms[20] were corrected for both Δ*f*′ and Δ*f*″ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 4, final positional parameters in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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