Monocyclooctatetraene uranium amide compounds in the +4 and +5 oxidation states

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The compounds $M[U(cot)(NEt_2)_3]$ 1 (cot = η-C_8H_8, M = Li or K) were prepared by (a) reaction of $[U(NEt_2)_4]$ or $[U(NEt_2)_3][BPh_4]$ with $K_2(cot)$, (b) treatment of UCl_4 with $LiNEt_2$ and $K_2(cot)$ and (c) reaction of $[U(cot)_2]$ with $LiNEt_2$. The compound $[U(cot)(NEt_2)_2(thf)]$ 2 (thf = tetrahydrofuran) was synthesized by treating $[U(NEt_2)_2Cl_2]$ with $K_2(cot)$. Uranium(v) compounds were obtained by oxidation of 1 and 2. Treatment of 1 with $TlBPh_4$ afforded $[U(cot)(NEt_2)_3]$ which was transformed into $[U(cot)(OPr^i)_3]$ by alcoholysis. Complex 2 reacted with $AgBPh_4$ or $Tl(cp)$ (cp = η-C_5H_5) to give $[U(cot)(NEt_2)_2(thf)][BPh_4]$ and $[U(cot)(cp)(NEt_2)_2]$ respectively, the crystal structure of the first of which has been determined.

The chemistry of the monocyclooctatetraene uranium complexes has recently been developed as readily accessible precursors became available. The dichloride $[U(cot)Cl_2(thf)_2]$ (cot = η-C_8H_8, thf = tetrahydrofuran) was isolated by Streitwieser and co-workers[1] from the reaction of UCl_4 with cyclooctatetraene in the presence of sodium hydride, and was transformed into $[U(cot)(acac)_2]$ (acac = MeCO-CHCOMe) and $[U(cot)\{N(SiMe_3)_2\}_2]$.[2] In our laboratory, $[U(cot)I_2(thf)_2]$ was synthesized by treatment of bis(cyclooctatetraene)uranium with iodine[3] whereas $[U(cot)(BH_4)_2]$ was obtained by reaction of $U(BH_4)_4$ with $[U(cot)_2]$ or C_8H_8;[4] these complexes served to prepare a series of half-sandwich and mixed-ring uranium(iv) derivatives with alkyl,[5] alkoxide[6] and thiolate[7] ligands. In view of the special synthetic utility of the $M-NR_2$ functionality,[8] we wished to consider the behaviour of the mono(cyclooctatetraene)uranium dialkylamide complexes. In this paper, we report on the novel preparations of $K[U(cot)(NEt_2)_3]$ 1 and $[U(cot)(NEt_2)_2(thf)]$ 2. These were subjected to the classical reactions of amide compounds, i.e. substitution of the NR_2 group by means of a protic molecule and insertion of a dipolar double bond into the metal–nitrogen bond. However, the major interest of the amide ligand was its ability to stabilize some U(cot) complexes in the +5 oxidation state. Such organouranium(v) compounds are very rare, being limited to the cyclopentadienyl imido and oxo derivatives $[U(\eta$-$C_5H_4Me)_3(NR)]$ (R = $SiMe_3$ or Ph),[9] $[U\{\eta$-$C_5H_3(SiMe_3)_2$-1,3\}_2Cl(NSiMe_3)]$ [10] and $[U(\eta$-$C_5Me_5)_2(OC_6H_3Pr^i_2$-2,6)O]$.[11] Here we present the synthesis, characterization and some reactions of the neutral and cationic mono(cyclooctatetraene)-uranium(v) compounds $[U(cot)(NR_2)_3]$ (R = Me 3 or Et 4), $[U(cot)(NEt_2)_2(thf)][BPh_4]$ 5, $[U(cot)(cp)(NEt_2)_2]$ 6 (cp = η-C_5H_5) and $[U(cot)(OPr^i)_3]$ 7; we also describe the crystal structure of 5.[12]

Results and Discussion

Synthesis and reactions of $K[U(cot)(NEt_2)_3]$ 1 and $[U(cot)(NEt_2)_2(thf)]$ 2

We first tried to prepare compounds 1 and 2 by the methods which were successful for other mono(cyclooctatetraene)uranium compounds. No reaction occurred between $[U(NEt_2)_4]$ and $[U(cot)_2]$ or C_8H_8; metathesis of $[U(cot)X_2]$ (X = I or
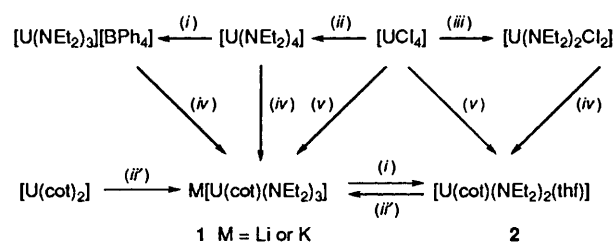
Scheme 1 Synthesis of the mono(cyclooctatetraene)uranium(iv) amide compounds 1 and 2. (i) $[NEt_3H][BPh_4]$; (ii) and (ii'), $LiNEt_2$; (iii) $[U(NEt_2)_4]$; (iv) $K_2(cot)$; (v) $LiNEt_2$ + $K_2(cot)$. All reactions in thf, except (ii) in diethyl ether

BH_4) with $LiNEt_2$ in diethyl ether or toluene gave green crystals of bis(cyclooctatetraene)uranium and unidentified products, similarly to what was observed when these precursors were treated with the less-hindered lithium alkyl or alkoxide reagents.[5,6] Other routes to complexes 1 and 2 had to be devised (Scheme 1). The anion $[U(cot)(NEt_2)_3]^-$ was readily formed in thf by the reactions of (a) UCl_4 with a 3:1 mixture of $LiNEt_2$ and $K_2(cot)$, (b) $[U(NEt_2)_4]$ with $K_2(cot)$ and (c) $[U(cot)_2]$ with 3 equivalents of $LiNEt_2$ (NMR experiments). Such a displacement of a cot ligand from bis(cyclooctatetraene)uranium leading to a monocot derivative was unprecedented; it was interesting to find that the tris(alkoxide) compound $Na[U(cot)(OPr^i)_3]$ could be similarly obtained by treating $[U(cot)_2]$ with $NaOPr^i$. The great stability of $[U(cot)(NEt_2)_3]^-$ and $[U(cot)(OPr^i)_3]^-$ with respect to $[U(cot)_2]$ is remarkable; in contrast, $Na[U(cot)(BH_4)_3]$[6] was immediately transformed into $[U(cot)_2]$ in the presence of $K_2(cot)$, and reactions of UX_4 (X = Cl or BH_4) with the cot dianion in thf also gave $[U(cot)_2]$ as the major identifiable product, without it being possible to isolate the monocyclooctatetraene intermediate.[1,4] This difference is obviously related to the greater steric hindrance and/or the better electron-donating ability of the NEt_2 and OPr^i ligands. An ochre powder of 1 was isolated in 80% yield from the reaction of $[U(NEt_2)_3][BPh_4]$[13] with 1 equivalent of $K_2(cot)$ in diethyl ether; this method was most practical as the product was easily extracted in thf from the insoluble salt $KBPh_4$. It was interesting that the cationic complex $[U(NEt_2)_3][BPh_4]$ reacted with 0.5 equivalents of $K_2(cot)$ in thf to give initially an intermediate the NMR spectrum of

Table 1 Analytical and ^{1}H NMR data for the complexes

Compound	Analyses[a]	Solvent	NMR data[b]
1 K[U(cot)(NEt$_2$)$_3$]	C, 39.75 (40.2); H, 6.2 (6.4); N, 6.8 (7.05)	[^{2}H$_8$]thf	0.22 (12 H, q, J 7, CH$_2$), −1.39 (18 H, t, J 7, Me), −15.84 (8 H, cot)
2 [U(cot)(NEt$_2$)$_2$(thf)]	C, 42.8 (43.0); H, 6.35 (6.5); N, 4.8 (5.0)	[^{2}H$_6$]Benzene	25.49 (8 H, CH$_2$), 4.78 (12 H, Me), −7.37 (4 H, H$_\beta$ of thf), −14.77 (4 H, H$_\alpha$ of thf), −29.20 (8 H, cot)
[U(cot)(NEt$_2$)$_2$]	C, 39.35 (39.5); H, 5.65 (5.8); N, 5.55 (5.75)	[^{2}H$_8$]Toluene	38.33 (8 H, s, $w_{\frac{1}{2}}$ 35, CH$_2$), −1.98 (12 H, Me), −35.18 (8 H, cot)
[U(cot)(O$_2$CNEt$_2$)$_2$]	C, 37.6 (37.65); H, 4.9 (4.9); N, 4.95 (4.9)	[^{2}H$_8$]thf	−10.21 (12 H, t, J 7, Me), −11.94 (8 H, q, J 7, CH$_2$), −21.06 (8 H, cot)
3 [U(cot)(NMe$_2$)$_3$]	C, 35.2 (35.45); H, 5.35 (5.5); N, 8.65 (8.85)	[^{2}H$_6$]Benzene	18.8 (18 H, s, $w_{\frac{1}{2}}$ 100, Me), −8.9 (8 H, $w_{\frac{1}{2}}$ 75, cot)
4 [U(cot)(NEt$_2$)$_3$]	C, 42.75 (43.0); H, 6.7 (6.85); N, 7.25 (7.5)	[^{2}H$_8$]Toluene	13.8 (12 H, $w_{\frac{1}{2}}$ 200, CH$_2$), 0.17 (18 H, $w_{\frac{1}{2}}$ 40, Me), −9.5 (8 H, $w_{\frac{1}{2}}$ 110, cot)
5 [U(cot)(NEt$_2$)$_2$(thf)][BPh$_4$]	C, 60.05 (60.2); H, 6.3 (6.45); N, 3.1 (3.2)	[^{2}H$_8$]thf	31.2 (8 H, s, $w_{\frac{1}{2}}$ 360, CH$_2$), 6.44 (20 H, Ph), 3.8 (12 H, s, $w_{\frac{1}{2}}$ 60, Me), −15.3 (8 H, $w_{\frac{1}{2}}$ 170, cot)
6 [U(cot)(cp)(NEt$_2$)$_2$]	C, 45.35 (45.75); H, 5.8 (6.05); N, 4.85 (5.1)	[^{2}H$_6$]Benzene	22.5 (8 H, s, $w_{\frac{1}{2}}$ 370, CH$_2$), 0.3 (12 H, s, $w_{\frac{1}{2}}$ 120, Me), −3.2 (5 H, s, $w_{\frac{1}{2}}$ 95, cp), −12.5 (8 H, s, $w_{\frac{1}{2}}$ 120, cot)
7 [U(cot)(OPr^i)$_3$]	C, 39.1 (39.3); H, 5.45 (5.65)	[^{2}H$_6$]Benzene	14.8 (3 H, s, $w_{\frac{1}{2}}$ 110, CHMe$_2$), 1.84 (18 H, CHMe_2), −6.6 (8 H, s, $w_{\frac{1}{2}}$ 90, cot)

[a] Analytical data given as: found (required) in %. [b] At 30 °C; data given as chemical shift (δ) (relative integral, multiplicity, coupling constant or half-height width in Hz, assignment); when not specified, the signal is a singlet with $w_{\frac{1}{2}} = 10$–30 Hz.

which exhibited three resonances at δ 6.30, 1.50 and −22.46 with relative intensities 24:36:8; these signals were assigned to [(Et$_2$N)$_3$U(cot)U(NEt$_2$)$_3$], the amide analogue of [(H$_4$B)$_3$-U(cot)U(BH$_4$)$_3$] which was observed during the synthesis of [U(cot)(BH$_4$)$_2$].[4] The cot-bridged bimetallic compound [(Et$_2$N)$_3$U(cot)U(NEt$_2$)$_3$], which was also obtained by mixing 1 and [U(NEt$_2$)$_3$][BPh$_4$], was not stable in solution and after 3 h at 20 °C was totally transformed into an equimolar mixture of 2 and [U(NEt$_2$)$_4$].

Reaction of the chloroamide complex [U(NEt$_2$)$_2$Cl$_2$][13] with 1 equivalent of K$_2$(cot) in thf afforded [U(cot)(NEt$_2$)$_2$(thf)] 2 which, after extraction in diethyl ether, was isolated as a maroon oily material in almost quantitative yield. The trimethylsilyl amide analogue [U(cot){N(SiMe$_3$)$_2$}$_2$][2] was similarly prepared in 83% yield from [U{N(SiMe$_3$)$_2$}$_2$Cl$_2$]. Compound 2 was alternatively obtained by treatment of UCl$_4$ with 2 equivalents of LiNEt$_2$ in thf, followed by addition of K$_2$(cot) (NMR experiment). Not surprisingly, 2 reacted with LiNEt$_2$ to give the anion [U(cot)(NEt$_2$)$_3$]$^-$ but, like this latter, 2 was not transformed into [U(cot)$_2$] in the presence of K$_2$(cot). However, spin-saturation-transfer experiments[14] revealed that the cot ligand of 2 was rapidly exchanging with the free cyclo-octatetraene dianion; such a substitution was not observed with 1 but it was previously shown that some [M(η-C$_8$H$_7$R)$_2$] complexes (M = Th or U) could undergo rapid ligand exchange with the dianions [C$_8$H$_7$R']$^{2-}$.[15]

Complex 2 showed no tendency to dissociate its thf ligand under vacuum and, in refluxing toluene solution, it slowly decomposed into [U(cot)$_2$] and other unidentified products. This stability of 2 is in contrast to the reluctance of the alkoxide and thiolate analogues [U(cot)(ER)$_2$] (E = O or S) to form adducts with tetrahydrofuran and which exist as dimers in this solvent; here again, the distinct behaviour of 2 should be accounted for by the steric and electronic characteristics of the amide ligand. Nevertheless, we have previously reported that a brown powder of the thf-free compound [U(cot)(NEt$_2$)$_2$] can be prepared from UCl$_4$, by successive treatment with LiNEt$_2$ and K$_2$(cot) in diethyl ether.[12,16] The ^{1}H NMR spectra of [U(cot)(NEt$_2$)$_2$] in [^{2}H$_8$]toluene at +30 °C exhibited a high-field signal attributed to the cot ligand and two low-field resonances corresponding to equivalent NEt$_2$ groups (Table 1), but at −60 °C the cot signal was split into two peaks at δ −50.8 and −53.2 (intensity ratio ca. 4:3) whereas the amide signals

were too broad and complicated to be accurately assigned. By analogy with [{U(cot)(μ-OEt)(OEt)}$_2$],[6] these results suggested that [U(cot)(NEt$_2$)$_2$] would exist in aromatic solvents in the form of the two equilibrating cis and trans dimeric isomers [{U(cot)(μ-NEt$_2$)(NEt$_2$)}$_2$]. Owing to the low yield of the synthesis of [U(cot)(NEt$_2$)$_2$], which at best never exceeded 40%, and the concomitant formation of [U(cot)$_2$], we gave up this route to the U(cot) amide complexes.

Some reactions of complexes 1 and 2 have been examined. Protonation of 2 by means of [NEt$_3$H][BPh$_4$], giving the cationic compound [U(cot)(NEt$_2$)(thf)$_2$][BPh$_4$], was previously reported;[12,16] a similar reaction of 1 afforded 2 in almost quantitative yield. Treatment of metal amides with acidic proton substrates was used classically to prepare a series of neutral substitution products[8] and the monocot complexes [U(cot)X$_2$] (X = acac, OPr^i, SPr^i, Cl or cp) were thus synthesized in good yields (>95% according to NMR spectroscopy) by treating 2 with Hacac, Pr^{i}OH, Pr^{i}SH, [NEt$_3$H]Cl and C$_5$H$_6$ respectively. In the presence of propan-2-ol, the tris(amide) anion [U(cot)(NEt$_2$)$_3$]$^-$ was cleanly converted into the alkoxide analogue [U(cot)(OPr^i)$_3$]$^-$, and its treatment with cyclopentadiene gave a mixture of the mixed-ring derivatives [U(cot)(cp)(NEt$_2$)] and [U(cot)(cp)(NEt$_2$)$_2$]$^-$; this anion was alternatively obtained by treating 2 with Na(cp) (NMR experiment). Insertion of CO$_2$ into the U–N bonds of 1 or 2 led to the formation of the bis(carbamate) derivative [U(cot)(O$_2$CNEt$_2$)$_2$] which was isolated as orange micro-crystals in 62% yield.

After [U(cot)Cl$_2$(thf)$_2$], [U(cot)I$_2$(thf)$_2$] and [U(cot)-(BH$_4$)$_2$], complexes 1 and 2 thus proved to be valuable precursors to mono(cyclooctatetraene)uranium(IV) derivatives. An additional and remarkable feature of 1 and 2 was revealed by their oxidation to uranium(V) compounds.

Synthesis of the mono(cyclooctatetraene)uranium(V) compounds

A yellow solution of the anionic compound K[U(cot)(NEt$_2$)$_3$] 1 in thf immediately darkened upon addition of TlBPh$_4$ or AgX (X = I or BPh$_4$) and a black metallic powder precipitated; after usual work-up, dark red microcrystals of the organouranium(V) product [U(cot)(NEt$_2$)$_3$] 4 were obtained in 98% yield (Scheme 2). The complexes [U(cot)(NR$_2$)$_3$] (R = Me 3 or Et 4) can be
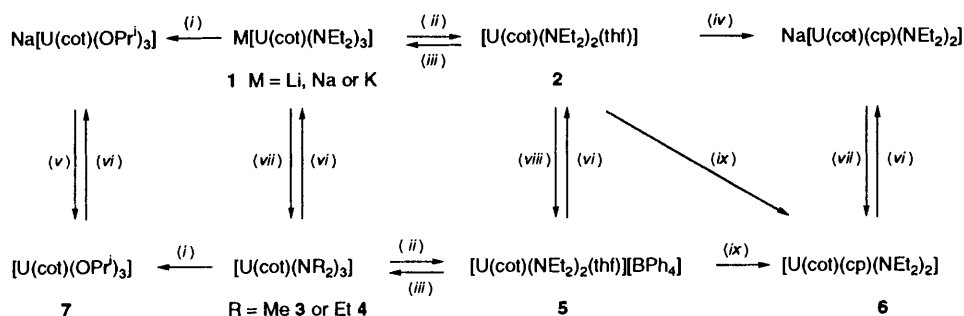
Scheme 2 Synthesis of the mono(cyclooctatetraene)uranium(v) complexes 3–7. (*i*) Pr^{i}OH; (*ii*) [NEt$_3$H][BPh$_4$]; (*iii*) LiNEt$_2$; (*iv*), Na(cp); (*v*) AgI; (*vi*) Na–Hg; (*vii*) TlBPh$_4$; (*viii*) AgBPh$_4$; (*ix*), Tl(cp). All reactions in thf

synthesized directly from UCl$_4$ by using a one-pot procedure (see Experimental section). The neutral bis(amide) **2** did not react with TlBPh$_4$ but in the presence of the more oxidizing reagent AgBPh$_4$ it was transformed into [U(cot)(NEt$_2$)$_2$-(thf)][BPh$_4$] **5**, the first cationic uranium(v) complex to have been characterized. The latter was, however, best prepared by protonolysis of **4** with [NEt$_3$H][BPh$_4$] and was isolated as a dark brown microcrystalline powder in 76% yield. These two reactions of uranium amide compounds with AgBPh$_4$ and [NEt$_3$H][BPh$_4$] constitute new efficient routes to cationic derivatives and have been used for preparing a series of complexes in the +4 and +5 oxidation states.[13,16,17]

Whereas compound **2** was inert towards TlBPh$_4$, its treatment with Tl(cp) in tetrahydrofuran readily afforded the mixed-ring uranium(v) compound [U(cot)(cp)(NEt$_2$)$_2$] **6**, with precipitation of metallic thallium; after filtration and evaporation, the dark red product was extracted with pentane and crystallized from this solvent (44% yield). It was then likely that this reaction, which represents a unique example of oxidation with Tl(cp), did not involve the uranium(v) cation [U(cot)(NEt$_2$)$_2$(thf)]$^+$ but proceeded by initial addition of cp$^-$ to **2**, giving the anion [U(cot)(cp)(NEt$_2$)$_2$]$^-$, followed by oxidation with Tl^I; as expected, the anion [U(cot)(cp)(NEt$_2$)$_2$]$^-$ was transformed into **6** in the presence of TlBPh$_4$. This oxidation was reversible and **6**, as well as **4** and **5**, was converted back into its uranium(iv) counterpart by reduction with sodium amalgam.

Complexes **3–6** are the first organouranium(v) compounds to have been synthesized by oxidation of uranium(iv) precursors, in contrast to the few cyclopentadienyl imido and oxo derivatives, which were obtained by treatment of uranium(iii) complexes with organic azides or pyridine *N*-oxide.$^{9-11}$ The factors, steric and electronic, which determine the stability of the uranium(v) complexes are not well understood; **3** and **4** were relatively stable in benzene at 60 °C, being slowly decomposed into unidentified products (*ca.* 5% after 2 h), but under the same conditions cleavage of a U–NEt$_2$ bond of **5** and **6** occurred readily, giving [U(cot)(NEt$_2$)(thf)$_2$]-[BPh$_4$]^{12,16} and [U(cot)(cp)(NEt$_2$)]^{16} (100 and 30% in 2 h, respectively).

Attempts to prepare new organouranium(v) derivatives from compounds **4** and **5** showed a mitigated success. By treatment with anionic species **5** was always partially reduced into a mixture of uranium(iv) products containing **2** as the major component; **4** and **6**, expected respectively from the reactions with LiNEt$_2$ and Tl(cp), were obtained in *ca.* 40% yield. The mono(cyclooctatetraene)uranium(iv) compounds [U(cot)X$_2$] were formed when **4** was treated with CO$_2$ or with most of the proton acidic substrates; none of the complexes [U(cot)(NEt$_2$)$_{3-n}$X$_n$] (X = O$_2$CNEt$_2$, acac or SPr^i) could be detected by NMR spectroscopy. No reaction was observed between **4** and cyclopentadiene at 20 and at 60 °C, formation of [U(cot)(cp)(NEt$_2$)] should result from thermal decomposition of **6**. At least, the only unequivocal synthesis of an uranium(v)
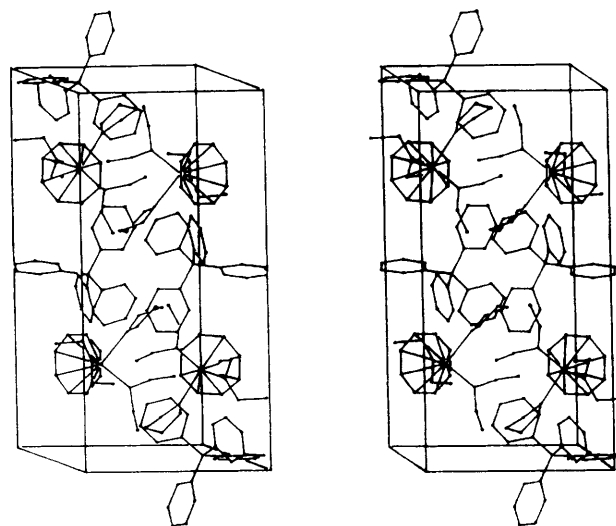
Fig. 1 Stereoview of the unit cell of [U(cot)(NEt$_2$)$_2$(thf)][BPh$_4$]

compound from **4** was provided by its alcoholysis with Pr^{i}OH which took place at room temperature and afforded [U(cot)(OPr^i)$_3$] **7** in 93% yield. This dark red oily tris(alkoxide), which was alternatively prepared by oxidation of the anion [U(cot)(OPr^i)$_3$]$^-$, was particularly stable since a benzene solution did not show any sign of decomposition after 20 h at 70 °C.

The new complexes have been characterized by their elemental analyses and their ^{1}H NMR spectra (Table 1); the crystal structure of **5** is presented below.

Crystal structure of [U(cot)(NEt$_2$)$_2$(thf)][BPh$_4$] 5

The crystals of compound **5** are composed of discrete cation–anion pairs; a stereoview of the unit cell is shown in Fig. 1. The BPh$_4$ anion displays the usual geometry; an ORTEP^{18} drawing of the cation is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The cation adopts a distorted-tetrahedral configuration, if the cot ligand is considered to occupy a single site of co-ordination; the angles N(1)–U–N(2), N(1)–U–O and N(2)–U–O are respectively 99.4(3), 90.9(3) and 84.7(2)° and the angles Cot–U–N(1), Cot–U–N(2) and Cot–U–O (Cot is the centroid of the ring) are 125.3(3), 123.5(3) and 122.3(3)°. The U–N distances, which average 2.116(8) Å, are shorter than those measured in the other two structurally characterized amide cations of uranium(v), 2.30(5) Å in [U(η-C$_5$Me$_5$)(NMe$_2$)$_3$(thf)]$^+$ and 2.164(3) Å in [U(η-C$_5$Me$_5$)$_2$(NEt$_2$)$_2$]$^+$;^{17} these are, however, in the range of U^{IV}–N bond lengths for terminally co-ordinated amide groups.^{13} As usual for transition-metal and uranium amides, each nitrogen atom lies in the plane (within ± 0.02 Å) defined by the metal and the two α-carbons, suggesting the presence
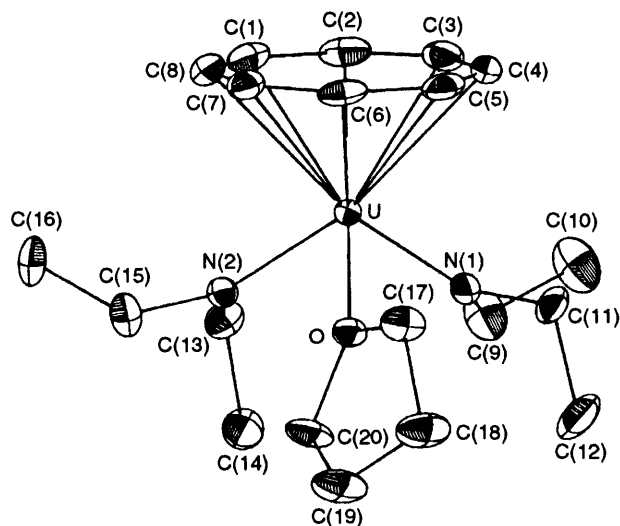
Fig. 2 Perspective view of the cation [U(cot)(NEt₂)₂(thf)]⁺, with 25% probability thermal ellipsoids

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **5**

U–N(1)	2.121(7)	U–N(2)	2.110(7)
U–O	2.465(6)	U–Cot *	1.96(2)
U–C(1)	2.67(1)	U–C(2)	2.66(1)
U–C(3)	2.66(1)	U–C(4)	2.69(1)
U–C(5)	2.68(1)	U–C(6)	2.69(1)
U–C(7)	2.71(1)	U–C(8)	2.71(1)
Cot–U–N(1)	125.3(3)	Cot–U–N(2)	123.5(3)
Cot–U–O	122.3(2)	N(1)–U–N(2)	99.4(3)
N(1)–U–O	90.9(3)	N(2)–U–O	84.7(2)

* Cot is the centroid of the cyclooctatetraene ring.

of a π interaction between the U and N atoms. The co-ordination of thf is unexceptional, with a value of 2.465(6) Å for the U–O distance. The cyclooctatetraene ring is planar within ± 0.01 Å and the U atom is 1.96(2) Å from this plane; the mean U–C bond distance, 2.68(2) Å, is identical to that invariably found in the U^{IV}(cot) complexes.[1-7] The values of the U–N and U–C bond distances, which are not significantly different from those determined in uranium(IV) complexes, confirm that these structural parameters cannot be used with confidence for predicting the metal oxidation state.[19]

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 glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ¹H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The salts [NEt₃H][BPh₄], TlBPh₄ and AgBPh₄ were precipitated in water by mixing NaBPh₄ and [NEt₃H]Cl, TlNO₃ and AgNO₃, respectively. The compounds [U(NEt₂)₄],[20] UCl₄,[21] [U(NEt₂)₂Cl₂],[13] [U{N(SiMe₃)₂}₂-Cl₂][22] and [U(NEt₂)₃][BPh₄][12,13] were prepared by published methods.

M[U(cot)(NEt₂)₃] 1 (M = Li or K)

(*a*) A round-bottom flask (50 cm³) was charged with [U(NEt₂)₃][BPh₄] (500 mg, 0.65 mmol) and K₂(cot) (118 mg, 0.65 mmol) and diethyl ether (25 cm³) was condensed into it at − 78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C, evaporated to dryness and the residue extracted with thf (30 cm³). After evaporation, the ochre powder of compound 1 was washed with toluene (20 cm³) and dried under vacuum (307 mg, 80%).

(*b*) An NMR tube was charged with UCl₄ (10 mg, 0.026 mmol), LiNEt₂ (6.2 mg, 0.079 mmol) and K₂(cot) (4.8 mg, 0.026 mmol) in [²H₈]thf (0.4 cm³). The tube was immersed for 10 min in an ultrasound bath (60 W, 40 kHz). The spectrum of the orange solution showed that the anion [U(cot)(NEt₂)₃]⁻ was formed in almost quantitative yield.

(*c*) An NMR tube was charged with U(NEt₂)₄ (10 mg, 0.019 mmol) and K₂(cot) (3.5 mg, 0.019 mmol) in [²H₈]thf (0.4 cm³); after 2 h at 70 °C the spectrum showed the formation of compounds 1 and 2 in the ratio 80:20. The solvent was evaporated off and the residue washed with toluene; after redissolution in [²H₈]thf the spectrum showed only the presence of 1.

(*d*) An NMR tube was charged with [U(cot)₂] (10 mg, 0.022 mmol) and LiNEt₂ (5.2 mg, 0.066 mmol) in [²H₈]thf (0.4 cm³); after 10 h at 20 °C the spectrum showed the quantitative formation of an equimolar mixture of Li[U(cot)(NEt₂)₃] and Li₂(cot).

(*e*) An NMR tube was charged with compound 2 (12.2 mg, 0.022 mmol) and LiNEt₂ (1.7 mg, 0.022 mmol) in [²H₈]thf (0.4 cm³); the spectrum showed the immediate and quantitative formation of Li[U(cot)(NEt₂)₃].

Formation of Na[U(cot)(OPrⁱ)₃] from [U(cot)₂]

An NMR tube was charged with [U(cot)₂] (6.7 mg, 0.015 mmol) and NaOPrⁱ (3.7 mg, 0.045 mmol) in [²H₈]thf (0.4 cm³). After 10 h at 20 °C the spectrum showed the quantitative formation of an equimolar mixture of Na₂(cot) and Na[U(cot)(OPrⁱ)₃]: δ(30 °C) −2.36 (18 H, d, *J* 6 Hz, CH*Me*₂), −5.66 (3 H, C*H*Me₂), and −23.28 (8 H, cot).

Formation and rearrangement of [(Et₂N)₃U(cot)U(NEt₂)₃]

An NMR tube was charged with [U(NEt₂)₃][BPh₄] (9.3 mg, 0.012 mmol) and K₂(cot) (1.1 mg, 0.006 mmol) or compound 1 (7.1 mg, 0.012 mmol) in [²H₈]thf (0.4 cm³). After 30 min at 20 °C the spectrum showed the signals of 2, [U(NEt₂)₄] and other resonances which were attributed to [(Et₂N)₃U(cot)U-(NEt₂)₃]: δ(30 °C) 6.30 (24 H, *w*₁ 50, CH₂), 1.50 (36 H, Me), and −22.46 (8 H, cot). These compounds were in the proportions 15:15:70 but after 3 h at 20 °C the cot-bridged complex had been totally transformed into an equimolar mixture of 2 and [U(NEt₂)₄].

[U(cot)(NEt₂)₂(thf)] 2

(*a*) A round-bottom flask (50 cm³) was charged with [U(NEt₂)₂Cl₂] (200 mg, 0.44 mmol) and K₂(cot) (80.5 mg, 0.44 mmol) and thf (25 cm³) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 15 min at 20 °C; the orange solution was filtered and evaporated to dryness and the residue extracted in diethyl ether (30 cm³). After evaporation compound 2 was obtained as a maroon oily material (234 mg, 95%).

(*b*) An NMR tube was charged with UCl₄ (10 mg, 0.026 mmol) and LiNEt₂ (4.2 mg, 0.053 mmol) in [²H₈]thf (0.4 cm³); after 30 min at 20 °C, K₂(cot) (4.8 mg, 0.026 mmol) was added to the green solution which turned orange immediately. The solvent was evaporated off and after drying under vacuum for 20 h the residue was extracted in [²H₈]toluene (0.4 cm³); the

spectrum showed the unique formation of [U(cot)(NEt₂)₂-(OC₄D₈)].

[U(cot){N(SiMe₃)₂}₂]

A round-bottom flask (50 cm³) was charged with [U{N(Si-Me₃)₂}₂Cl₂] (850 mg, 1.35 mmol) and K₂(cot) (246 mg, 1.35 mmol) and diethyl ether (30 cm³) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 90 min at 20 °C; the red solution was filtered and evaporated, and the residue extracted with pentane (30 cm³). After evaporation, [U(cot){N(SiMe₃)₂}₂]² was isolated as a bright orange microcrystalline powder (745 mg, 83%).

Reactions of M[U(cot)(NEt₂)₃] 1 (M = Na or K) with proton acidic substrates

(a) With [NEt₃H]X (X = Cl or BPh₄). An NMR tube was charged with compound 1 (12.3 mg, 0.020 mmol) and [NEt₃H]Cl (2.8 mg, 0.020 mmol) or [NEt₃H][BPh₄] (8.4 mg, 0.020 mmol) in [²H₈]thf (0.4 cm³). After 10 min at 20 °C the spectrum showed that 1 was transformed into 2, with a trace of [U(cot)₂].

(b) With PrⁱOH. An NMR tube was charged with Na[U(cot)(NEt₂)₃] (prepared by Na–Hg reduction of compound 4 (10.5 mg, 0.018 mmol) in [²H₈]thf (0.4 cm³) and PrⁱOH (4.1 mm³, 0.054 mmol) introduced via a microsyringe. The orange solution turned yellow immediately and the spectrum showed that Na[U(cot)(NEt₂)₃] was totally transformed into Na[U(cot)(OPrⁱ)₃], with liberation of NEt₂H.

(c) With cyclopentadiene. An NMR tube was charged with compound 1 (8.7 mg, 0.014 mmol) in [²H₈]thf (0.4 cm³) and freshly distilled C₅H₆ (1.2 mm³, 0.014 mmol) was introduced via a microsyringe. After 10 min at 20 °C the spectrum of the red solution showed that 1 was transformed into a 75:25 mixture of [U(cot)(cp)(NEt₂)][13] and K[U(cot)(cp)(NEt₂)₂].

Reactions of compound 2 with proton acidic substrates

(a) With Hacac. An NMR tube was charged with compound 2 (5.1 mg, 0.009 mmol) in [²H₈]thf (0.4 cm³) and Hacac (2.1 mm³, 0.020 mmol) introduced via a microsyringe. The yellow solution turned red immediately and the spectrum showed that 2 was totally transformed into [U(cot)(acac)₂].[1,5]

(b) With PrⁱOH and PrⁱSH. An NMR tube was charged with compound 2 (5.7 mg, 0.010 mmol) in [²H₆]benzene (0.4 cm³) and PrⁱOH (1.6 mm³, 0.020 mmol) or PrⁱSH (1.8 mm³, 0.020 mmol) was introduced via a microsyringe. The yellow solution turned green immediately and the spectrum showed that the amide complex was totally transformed into [U(cot)(EPrⁱ)₂] (E = O or S).[6,7]

(c) With [NEt₃H]Cl. An NMR tube was charged with compound 2 (5.1 mg, 0.009 mmol) and [NEt₃H]Cl (1.4 mg, 0.010 mmol) in [²H₈]thf (0.4 cm³). The yellow solution turned green immediately and the spectrum showed that 2 was transformed into a 10:90 mixture of [U(cot)Cl₂(OC₄D₈)₂][1] and [U(cot)(NEt₂)Cl(OC₄D₈)ₓ]: δ(30 °C) 103.5 (4 H, CH₂), 34.11 (6 H, Me) and −30.11 (8 H, cot). Further addition of [NEt₃H]Cl (1.4 mg) led to the complete formation of the dichloride.

(d) With cyclopentadiene. An NMR tube was charged with compound 2 (7.5 mg, 0.013 mmol) in [²H₈]thf (0.4 cm³) and freshly distilled C₅H₆ (1.1 mm³, 0.013 mmol) was introduced via a microsyringe. After 24 h at 20 °C the spectrum showed that 2 was totally transformed into [U(cot)(cp)(NEt₂)].[16] Further addition of cyclopentadiene (1.1 mm³) led to

[U(cot)(cp)₂] which was partially deposited as red crystals: δ(30 °C) −2.06 (10 H, cp) and −37.83 (8 H, cot).

[U(cot)(O₂CNEt₂)₂]

(a) An NMR tube was charged with compound 1 (6.3 mg, 0.010 mmol) in [²H₈]thf (0.4 cm³) and was pressurized with CO₂ (1 atm, ca. 101 325 Pa); after 15 min at 20 °C the spectrum showed that 1 was totally transformed into [U(cot)(O₂CNEt₂)₂]. The solution deposited orange crystals after a few hours.

(b) A round-bottom flask (50 cm³) was charged with compound 2 (390 mg, 0.70 mmol) and diethyl ether (30 cm³) was condensed into it at −78 °C under vacuum; the flask was then pressurized with CO₂ (1 atm). The yellow solution turned red immediately and deposited orange crystals. More crystals were obtained by cooling at −78 °C; these were filtered off and dried under vacuum (250 mg, 62%).

[U(cot)(NMe₂)₃] 3 and [U(cot)(NEt₂)₃] 4

(a) A round-bottom flask (50 cm³) was charged with UCl₄ (472 mg, 1.24 mmol) and LiNMe₂ (193 mg, 3.78 mmol) and thf (20 cm³) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 5 h at 20 °C and K₂(cot) (227 mg, 1.24 mmol) was added; the orange solution turned yellow. After 90 min, addition of TlBPh₄ (650 mg, 1.24 mmol) led to the immediate precipitation of a black metallic powder in a dark red solution. After 90 min the solvent was evaporated off, the residue extracted with pentane (4 × 20 cm³) and the black microcrystalline powder of compound 3 was isolated after evaporation (484 mg, 82%). Molecular weight by osmometry: 510 (calc.: 474).

(b) Compound 4 was prepared as described for 3, by using UCl₄ (708 mg, 1.86 mmol), LiNEt₂ (447 mg, 5.65 mmol), K₂(cot) (340 mg, 1.86 mmol) and TlBPh₄ (977 mg, 1.86 mmol). The yield was 95%.

(c) A round-bottom flask (50 cm³) was charged with compound 1 (500 mg, 0.84 mmol) and TlBPh₄ (876 mg, 1.67 mmol) and thf (30 cm³) was condensed into it at −78 °C under

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for [U(cot)(NEt$_2$)$_2$(thf)][BPh$_4$] **5**

Atom	x	y	z	Atom	x	y	z
U	0.139 35(3)	0.128 24(2)	0.276 82(1)	C(22)	0.812 9(9)	0.067 0(6)	0.017 7(5)
O	0.273 1(5)	0.092 7(3)	0.365 6(3)	C(23)	0.857(1)	−0.006 4(6)	0.040 8(5)
N(1)	0.279 8(7)	0.090 7(4)	0.216 1(3)	C(24)	0.836 8(9)	−0.027 3(6)	0.102 0(5)
N(2)	0.051 4(7)	0.018 6(4)	0.292 9(3)	C(25)	0.768 3(8)	0.023 7(6)	0.138 8(5)
C(1)	−0.090 3(9)	0.177 5(6)	0.245 4(5)	C(26)	0.725 7(8)	0.097 6(5)	0.115 1(4)
C(2)	−0.014(1)	0.198 4(6)	0.196 5(5)	C(27)	0.615 7(8)	0.257 2(5)	0.072 4(4)
C(3)	0.100(1)	0.239 3(6)	0.192 4(5)	C(28)	0.661 6(8)	0.285 3(5)	0.128 9(4)
C(4)	0.187(1)	0.274 4(6)	0.234 3(6)	C(29)	0.586 8(9)	0.328 6(5)	0.169 6(4)
C(5)	0.191 9(9)	0.280 5(6)	0.299 8(6)	C(30)	0.462 1(8)	0.345 9(5)	0.153 4(4)
C(6)	0.111(1)	0.256 7(6)	0.347 7(5)	C(31)	0.414 5(9)	0.318 5(6)	0.098 2(5)
C(7)	−0.005 5(9)	0.217 9(6)	0.349 7(5)	C(32)	0.488 8(8)	0.274 0(5)	0.057 8(4)
C(8)	−0.087 2(9)	0.186 4(6)	0.308 3(5)	C(33)	0.640 4(8)	0.192 7(5)	−0.040 2(4)
C(9)	0.278(1)	0.045 2(7)	0.156 7(5)	C(34)	0.673 4(8)	0.231 2(6)	−0.093 8(4)
C(10)	0.318(1)	0.093 3(8)	0.102 8(5)	C(35)	0.615(1)	0.213 2(7)	−0.151 0(5)
C(11)	0.401 8(8)	0.129 1(7)	0.232 2(4)	C(36)	0.520 9(9)	0.157 6(7)	−0.154 6(5)
C(12)	0.508(1)	0.067(1)	0.246 1(6)	C(37)	0.484 0(8)	0.118 6(7)	−0.101 2(5)
C(13)	0.032 8(9)	−0.032 7(6)	0.239 5(5)	C(38)	0.543 6(8)	0.135 6(6)	−0.044 6(4)
C(14)	0.119(1)	−0.104 3(6)	0.240 2(6)	C(39)	0.835 3(7)	0.263 8(5)	0.019 0(4)
C(15)	−0.009 8(9)	−0.010 5(7)	0.349 3(5)	C(40)	0.959 3(8)	0.234 0(6)	0.025 0(4)
C(16)	−0.155(1)	−0.018 7(8)	0.342 7(6)	C(41)	1.064 7(9)	0.284 7(7)	0.019 1(4)
C(17)	0.355 6(9)	0.146 1(6)	0.402 6(5)	C(42)	1.047 4(9)	0.364 9(7)	0.006 1(4)
C(18)	0.458(1)	0.091 2(7)	0.426 9(6)	C(43)	0.925 8(9)	0.395 4(6)	−0.000 6(4)
C(19)	0.398(1)	0.014 5(7)	0.433 9(5)	C(44)	0.882 5(9)	0.344 7(5)	0.006 5(4)
C(20)	0.298(1)	0.009 4(6)	0.383 4(5)	B	0.709 7(9)	0.207 9(6)	0.026 7(5)
C(21)	0.748 9(7)	0.121 4(6)	0.055 2(4)				

vacuum. The reaction mixture was stirred for 15 min at 20 °C; a black metallic powder precipitated in a dark red solution. After evaporation to dryness, the residue was extracted with pentane (30 cm^3); the solvent was evaporated, leaving a black microcrystalline powder of **4** (458 mg, 98%).

[U(cot)(NEt$_2$)$_2$(thf)][BPh$_4$] 5

(*a*) A round-bottom flask (50 cm^3) was charged with compound **4** (300 mg, 0.54 mmol) and [NEt$_3$H][BPh$_4$] (219 mg, 0.52 mmol) and thf (20 cm^3) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 30 min at 20 °C, filtered, reduced in volume to 10 cm^3 and pentane (30 cm^3) added under vacuum at −60 °C. The dark brown powder which precipitated was filtered off and was once again recrystallized from thf–pentane. The powder was washed with toluene (2 × 20 cm^3) and dried under vacuum (346 mg, 76%).

(*b*) An NMR tube was charged with compound **2** (12.1 mg, 0.022 mmol) and AgBPh$_4$ (12.6 mg, 0.030 mmol) in [^{2}H$_8$]thf (0.4 cm^3). The orange solution turned dark brown immediately and a black metallic powder precipitated; the spectrum showed that the reaction gave a mixture of **5** (65%), [U(cot)(NEt$_2$)-(thf)$_2$][BPh$_4$][12,16] (10%) and [U(NEt$_2$)$_3$][BPh$_4$] (25%).

[U(cot)(cp)(NEt$_2$)$_2$] 6

(*a*) A round-bottom flask (50 cm^3) was charged with compound **2** (570 mg, 1.02 mmol) and Tl(cp) (275 mg, 1.02 mmol) and thf (20 cm^3) was condensed into it at −78 °C under vacuum. The flask was immersed in an ultrasound bath for 40 min at 20 °C; the solution turned dark red and a black metallic powder precipitated. The solvent was evaporated off and the residue extracted with pentane (20 cm^3). Upon cooling at −78 °C the pentane solution deposited a dark red powder which was filtered off and dried under vacuum (250 mg, 44%).

(*b*) An NMR tube was charged with compound **2** (6.0 mg, 0.011 mmol) and Na(cp) (1.0 mg, 0.011 mmol) in [^{2}H$_8$]thf (0.4 cm^3). The spectrum at 30 °C exhibited broad resonances but well resolved signals were visible at −25 °C, corresponding to **2**, Na(cp) and Na[U(cot)(cp)(NEt$_2$)$_2$]: δ 22.19 and 12.97 (4 H + 4 H, CH$_2$), 2.86 (12 H, Me), −28.29 (8 H, cot) and −28.83 (5 H, cp). These three compounds, in relative proportions 20:20:60, were in equilibrium, as demonstrated by

spin-saturation-transfer experiments.[14] Addition of TlBPh$_4$ (5.9 mg, 0.011 mmol) led to the immediate formation of **6**, with precipitation of metallic thallium.

Reactions of compound 5 with LiNEt$_2$ and Tl(cp)

(*a*) An NMR tube was charged with compound **5** (7.8 mg, 0.0089 mmol) and LiNEt$_2$ (0.7 mg, 0.0089 mmol) in [^{2}H$_8$]thf (0.4 cm^3). After 10 min at 20 °C the spectrum showed, in the paramagnetic region, the signals of **4** (46%), **2** (37%) and [U(NEt$_2$)$_3$][BPh$_4$] (17%) and in the diamagnetic region those of free cyclooctatetraene.

(*b*) An NMR tube was charged with compound **5** (7.1 mg, 0.0081 mmol) and Tl(cp) (2.2 mg, 0.0081 mmol) in [^{2}H$_8$]thf (0.4 cm^3). After 10 min at 20 °C the spectrum showed, in the paramagnetic region, the signals of **6** (38%), **2** (23%), [U(cp)$_2$(NEt$_2$)$_2$] (30%) and [U(cot)(cp)(NEt$_2$)] (9%) and the resonances of free NEt$_2$H and C$_8$H$_8$ were visible in the diamagnetic region.

[U(cot)(OPr^i)$_3$] 7

(*a*) Isopropyl alcohol (55 mm^3, 0.71 mmol) was added dropwise to a round-bottom flask (25 cm^3) containing a solution of compound **4** (128 mg, 0.23 mmol) in thf (15 cm^3). After 30 min at 20 °C the solvent was evaporated off and the residue extracted with pentane (15 cm^3). After evaporation, **7** was obtained as a dark red oily material (111 mg, 93%).

(*b*) An NMR tube was charged with Na[U(cot)(OPr^i)$_3$] (prepared by Na–Hg reduction of **7**) (10 mg, 0.018 mmol) in [^{2}H$_8$]thf (0.4 cm^3) and AgI (4.7 mg, 0.020 mmol). The yellow solution turned red immediately and the spectrum showed that Na[U(cot)(OPr^i)$_3$] was totally transformed into **7**.

Sodium amalgam reduction of compounds 4–7

In a typical experiment, an NMR tube, charged with the uranium(v) compound (*ca.* 10 mg) and the stoichiometric quantity of 2% Na–Hg in [^{2}H$_8$]thf (0.4 cm^3), was immersed in an ultrasound bath. After 10 min at 20 °C the spectrum showed that the complex was completely reduced to its uranium(iv) counterpart; addition of TlBPh$_4$ or AgX (X = I or BPh$_4$) gave back the uranium(v) compound.

Thermal stability of compounds 3–7

In a typical experiment, an NMR tube, charged with the uranium(v) compound (ca. 10 mg) in [$^2H_6$]benzene (0.4 cm^3) was heated at 60 °C; after 2 h, 5% of **3** or **4** were decomposed into unidentified products, **5** was totally transformed into [U(cot)(NEt$_2$)(thf)$_2$][BPh$_4$] and 30% of **6** was reduced to [U(cot)(cp)(NEt$_2$)].[16] The tris(alkoxide) **7** was much more stable, not being decomposed after 20 h at 70 °C.

Crystal structure determination of complex 5

Well shaped parallelepiped crystals were obtained from thf–pentane. A single crystal was introduced into a thin-walled Lindeman glass tube in a glove-box. Data were collected on an Enraf-Nonius diffractometer equipped with a graphite mono-chromator [λ(Mo-Kα) = 0.700 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 every hour; a decay was observed (2% in 67 h) and linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[23] The structure was solved by the heavy-atom method and refined by full-matrix least squares on F with anisotropic thermal parameters. The hydrogen atoms were not introduced. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MOLEN system and unit weights were applied.[24] Analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion.[25] Crystallographic data are given in Table 3 and final positional parameters in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1

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