Synthesis, Crystal Structure and Dynamic Behaviour in Solution of Monocyclooctatetraene Uranium Alkoxides *

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Treatment of [U(cot)$(BH_4)_2$] (cot = η-C_8H_8) with ROH (R = Et, Pr^i or Bu^t) led to successive formation of the alkoxide derivatives [U(cot)(BH_4)(OR)] **4** and [U(cot)$(OR)_2$] **5**. Their structure and dynamic behaviour in solution have been studied by NMR spectroscopy; complexes **4** are monomeric in tetrahydrofuran whereas **5** are dimeric in this solvent and monomeric in pyridine. Rapid stereoselective exchange occurs between the terminal propoxide ligands of [{U(cot)(OPr^i)(μ-OPr^i)}$_2$] and free Pr^iOH. The crystal structures of [{U(cot)(BH_4)(μ-OEt)}$_2$] and [{U(cot)(OPr^i)(μ-OPr^i)}$_2$] have been determined.

The synthesis of uranocene [U$(cot)_2$] (cot = η-C_8H_8 = cyclooctatetraene) was a milestone in the history of organoactinide chemistry,[1] but the reactivity of this sandwich compound has proven to be rather limited,[2] and less co-ordinatively saturated monocyclooctatetraene complexes were highly desirable. Readily available precursors to such compounds have recently been synthesised: [U(cot)$X_2$$(thf)_2$] (X = Cl[3] or I;[4] thf = tetrahydrofuran) and [U(cot)$(BH_4)_2$];[5] they all gave adducts with Lewis bases, [U(cot)$Cl_2$$(PMe_3)$], [U(cot)$Cl_2$$(py)_2$][3] (py = pyridine), [U(cot)I_2{OP$(NMe_2)_3$}][4] and [U(cot)$(BH_4)_2$L][5] (L = thf, PPh_3 or $OPPh_3$), and yielded a series of derivatives by metathesis of the halide or tetrahydroborate ligands, [U(cot)$(MeCOCHCOMe)_2$],[3,4] [U(cot){N$(SiMe_3)_2$}$_2$],[6] [U(cot)(η-C_5Me_5)I][4] and [U(cot)(η-C_5H_5)(BH_4)L][5] (L = thf or $OPPh_3$). However, the reactions of [U(cot)$Cl_2$$(thf)_2$] with alkali-metal alkoxides failed to produce any tractable half-sandwich compounds, a fact that has been explained by the steric unsaturation of the expected products.[3]

We found that the mixed alkoxide–tetrahydroborate and bis(alkoxide) compounds [U(cot)(BH_4)(OR)] and [U(cot)$(OR)_2$] (R = Et, Pr^i or Bu^t) could be successively obtained by alcoholysis of [U(cot)$(BH_4)_2$]; this latter, when treated with NaOEt, led to the formation of the addition product of general formula NaU(cot)$(BH_4)_2$(OEt).[7] Here we report the synthesis of these complexes and present the NMR spectra which provide information on their structure and dynamic behaviour in solution; we also describe the X-ray crystal structures of [{U(cot)(BH_4)(μ-OEt)}$_2$] and [{U(cot)(OPr^i)(μ-OPr^i)}$_2$].

Results and Discussion

Syntheses.—We first tried to prepare the monocyclooctatetraeneuranium bis(alkoxide) complexes [U(cot)$(OR)_2$] by treatment of [U(cot)$(BH_4)_2$] **1** with 2 equivalents of alkali-metal alkoxides. The reaction of **1** with NaOEt in toluene gave a mixture of NaU(cot)$(BH_4)_2$(OEt) **2**, [U(cot)(BH_4)(OEt)] and NaU(cot)$(BH_4)_3$ in relative proportions of 55, 35 and 10% (according to NMR spectroscopy). The orange crystalline compound **2** was subsequently obtained in 69% yield from an equimolar mixture of [U(cot)(BH_4)(OEt)] and $NaBH_4$ in tetrahydrofuran, whereas addition of KBH_4 to **1** in the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) led to the formation of [K(18-crown-6)][U(cot)$(BH_4)_3$] **3**, which was isolated as dark red crystals in 53% yield. These reactions of **1** were not surprising in view of its propensity to form a series of adducts [U(cot)$(BH_4)_2$L] with various Lewis bases.[5] It seems likely that [U(cot)$Cl_2$$(thf)_2$] should also react with metal alkoxides MOR to give initially the species MU(cot)Cl_2(OR), but the latter, which have not been observed, should rapidly rearrange into a mixture of products containing the cyclooctatetraene dianion and an array of mixed uranium(IV) chloro alkoxides.[3] Thus it appeared that the formation of MU(cot)X_2(OR) intermediates during the attempted preparation of the complexes [U(cot)$(OR)_2$], by treatment of [U(cot)X_2] precursors with metal alkoxides, should be a handicap. This difficulty could be avoided by using the alcoholysis reaction (1), in which the BH_4 ligand is irreversibly transformed into hydrogen and alkoxyboranes.

$$[\mathrm{U}]\text{–}\mathrm{BH_4} + n\mathrm{ROH} \longrightarrow [\mathrm{U}]\text{–}\mathrm{OR} + n\mathrm{H_2} + \mathrm{BH_{4-n}(OR)_{n-1}} \quad (1)$$
$$n \leqslant 4$$

Treatment of complex **1** with 3 equivalents of ethanol in tetrahydrofuran led to the formation of the mixed alkoxide–tetrahydroborate compound [U(cot)(BH_4)(OEt)] **4a** which has been isolated as red crystals in 52% yield. Complex **4a** reacted further with ethanol (3.5 equivalents) to give the orange bis(alkoxide) derivative [U(cot)$(OEt)_2$] **5a** which crystallized from pentane (72% yield). Similar alcoholysis reactions with Pr^iOH (3 equivalents) and Bu^tOH (1 equivalent) afforded the complexes [U(cot)(BH_4)(OR)] (R = Pr^i **4b** or Bu^t **4c**) and [U(cot)$(OR)_2$] (R = Pr^i **5b** or Bu^t **5c**). In contrast to the ethoxide and isopropoxide complexes, the butoxide derivatives **4c** and **5c** slowly decomposed in toluene solution and could not be isolated analytically pure by crystallization (see the NMR studies and the Experimental section). The mixed alkoxide–tetrahydroborates **4** were also formed immediately and quantitatively by comproportionation of **1** and **5** in thf (NMR experiments). For this reason, compounds **4** could be easily obtained in good yield from the reaction of **1** with ROH, even if the transformation **4** to **5** proceeded at a comparable rate.

Compounds **2**–**5** have been characterized by their elemental analyses and ^1H NMR spectra (Table 1), **4c** and **5c** only by

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

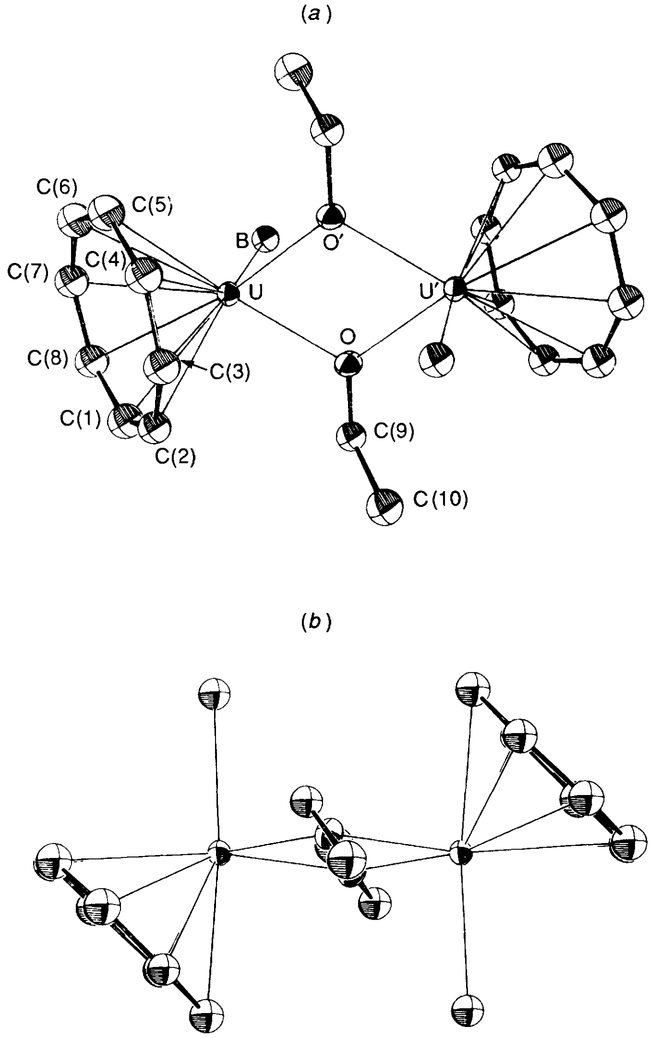

Fig. 1 (*a*) Perspective view of $[\{U(cot)(BH_4)(\mu\text{-}OEt)\}_2]$; primed atoms are related by a centre of symmetry. (*b*) View parallel to the planes of the cot ligands

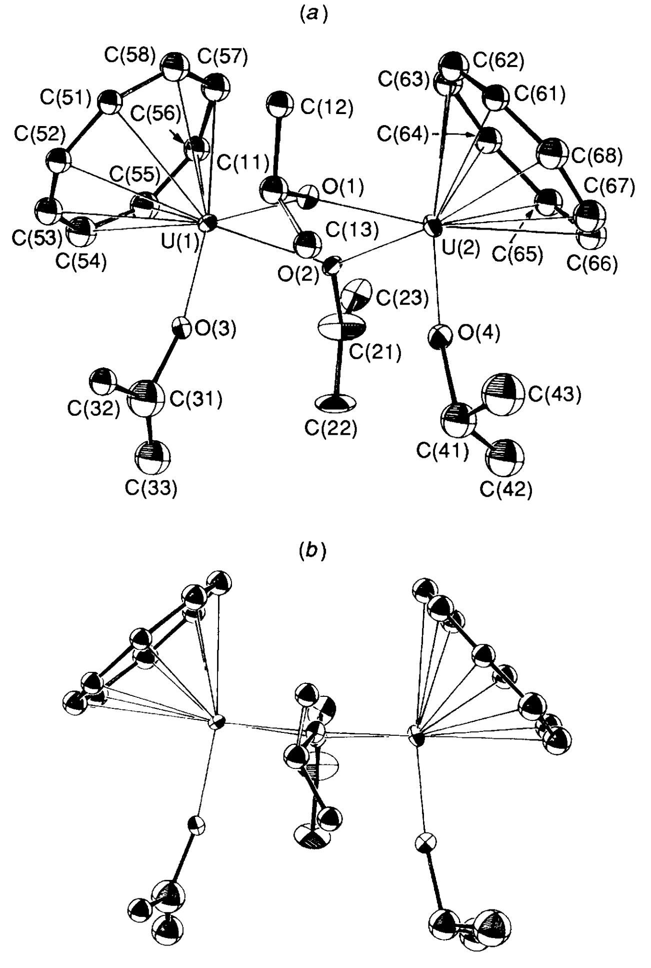

Fig. 2 Perspective view of $[\{U(cot)(OPr^i)(\mu\text{-}OPr^i)\}_2]$. (*b*) View parallel to the planes of the cot ligands

their NMR spectra. The crystal structures of dimeric **4a** and **5b** have been determined.

Crystal Structures of $[\{U(cot)(BH_4)(\mu\text{-}OEt)\}_2]$ *and* $[\{U(cot)(OPr^i)(\mu\text{-}OPr^i)\}_2]$.—The ORTEP drawings are shown in Figs. 1 and 2 and selected bond distances and angles are listed in Table 2. Complexes **4a** and **5b** are dimeric in the solid state and each structure is built up of two monomeric units which are bridged by two alkoxide groups. The configuration of the dinuclear molecules is edge-sharing bitetrahedral, considering the cyclooctatetraenes as monodentate ligands. The cot ligation is unexceptional, being identical to that found in uranocene[8] and other monocyclooctatetraeneuranium(IV) compounds.[3,5] The four-membered $(UO)_2$ rings are planar and form lozenges in which the mean U–O distance is 2.30(1) Å and the mean U–O–U and O–U–O angles are respectively 111(1) and 69(1)°. This geometry, which appears to be general for such doubly bridged uranium alkoxides, has been encountered in the uranium(V) isopropoxide $[\{U(OPr^i)_4(\mu\text{-}OPr^i)\}_2]$[9] and the mixed alkoxide–allyl complex $[\{U(\eta\text{-}C_3H_5)_2(OPr^i)(\mu\text{-}OPr^i)\}_2]$.[10] The bridging oxygen atoms are sp^2 hybridized since they are bonded to their adjacent carbon atoms and to the metallic centres with a planar co-ordination. The two planar cot rings are parallel and placed on opposite sides of the $(UO)_2$ plane in $[\{U(cot)(BH_4)(\mu\text{-}OEt)\}_2]$, whereas in $[\{U(cot)(OPr^i)(\mu\text{-}OPr^i)\}_2]$ they are respectively in *cis* positions and orthogonal, the angle between their mean planes being 89.5(7)° [Figs. 1(*b*) and 2(*b*)]. The reasons for this difference of stereochemistry are not obvious. The alkoxide–tetrahydroborate complex possesses a crystallographically imposed centre of symmetry which is located at the middle of the U–U′ segment. In both compounds the plane defined by the U atoms, the cot centroids and the boron or the terminal oxygen atoms is a pseudo-mirror plane which is perpendicular to the $(UO)_2$ plane. The short U–B distance is characteristic of a tridentate BH_4 ligand.[11] The quasi-linear co-ordination of the terminal oxygen atoms O(3) and O(4), and the short U–O(3) and U–O(4) distances, are classical and reflect sp hybridization and $O_\pi \rightarrow U$ dative bonds.[9,12]

NMR Studies; Structure and Dynamic Behaviour of the Complexes in Solution.—The ^1H NMR data for the complexes are reported in Table 2.

The mixed alkoxide–tetrahydroborate complexes $[U(cot)(BH_4)(OR)]$ **4**. The NMR spectrum of $[U(cot)(BH_4)(OPr^i)]$ **4b** in thf exhibits, at δ −88.34, a quartet which corresponds to the tetrahydroborate ligand, and the other signals which are easily assigned to the cot and OPr^i groups are visible at lower field. The spectrum in toluene is drastically different, with the tetrahydroborate signal occurring at δ +72.29, while the resonances corresponding to the isopropoxide ligand are in the high-field region. This spectrum also shows a series of small peaks which contribute to 20% of the total integration, and which could not be assigned; these paramagnetic signals are not due to the presence of impurities or decomposition products since after evaporation of toluene, the residue was totally soluble in thf and its NMR spectrum was identical to that of an

Table 1 Proton NMR spectra of the complexes[a]

Compound	Solvent	cot ligand[b]	Alkoxide ligand	BH_4 ligand
2 $NaU(cot)(BH_4)_2(OEt)$	$[^2H_8]$thf	−28.72	140.52 (2 H), 50.31 (3 H)	−67.6 (8 H, br, $w_{\frac{1}{2}}$ 400)
3 $[K(18\text{-crown-}6)][U(cot)(BH_4)_3]$	$[^2H_8]$thf	−24.09	*c*	56.74 (12 H, q, *J* 80)
4a $[U(cot)(BH_4)(OEt)]$	$[^2H_8]$thf	−30.25	147.63 (2 H), 52.48 (3 H)	−84.8 (4 H, br q, $w_{\frac{1}{2}}$ 280)
4b $[U(cot)(BH_4)(OPr^i)]$	$[^2H_8]$thf	−30.63	151.44 (1 H), 54.38 (6 H)	−88.34 (4 H, q, *J* 85)
	$[^2H_8]$Toluene[d]	−33.19	−15.73 (6 H, d, *J* 6), −46.34 (1 H)	72.29 (4 H, q, *J* 85)
4c $[U(cot)(BH_4)(OBu^t)]$	$[^2H_8]$thf	−30.64	54.68 (9 H)	−88.84 (4 H, q, *J* 85)
	$[^2H_8]$Toluene[d]	−32.70	54.75 (9 H)	−126 (4 H, br, $w_{\frac{1}{2}}$ 1100)
5a $[U(cot)(OEt)_2]$	$[^2H_8]$thf[e]	−27.8 (br, $w_{\frac{1}{2}}$ 330)	110 (2 H, br, $w_{\frac{1}{2}}$ 330), 36 (3 H, br, $w_{\frac{1}{2}}$ 400), −36 (3 H, br, $w_{\frac{1}{2}}$ 250), −75 (2 H, br, $w_{\frac{1}{2}}$ 490)	
	$[^2H_5]$Pyridine	−24.02	42.99 (4 H, q, *J* 7), 15.91 (6 H, t, *J* 7)	
5b $[U(cot)(OPr^i)_2]$	$[^2H_8]$thf[e]	−31.50	117.66 (1 H), 41.66 (6 H), −36.61 (6 H), −97.68 (1 H)	
	$[^2H_5]$Pyridine	−24.04	41.33 (2 H, sp, *J* 6), 15.79 (12 H, d, *J* 6)	
5c $[U(cot)(OBu^t)_2]$	$[^2H_8]$thf[f]	−28.86	11.99 (18 H)	

[a] At 30 °C. Data are given as chemical shift δ (relative integral, multiplicity, coupling constant *J* or half-height width $w_{\frac{1}{2}}$ in Hz); when not specified, the signal is a singlet with $w_{\frac{1}{2}}$ = 10–30 Hz. [b] The cot signal integrates for 8 H. [c] The signal corresponding to 18-crown-6 is at δ 4.33 (24 H). [d] The spectrum exhibits other peaks (see text). [e] The spectrum in $[^2H_8]$toluene is quite similar. [f] Immediately after dissolution of complex **5c** the spectrum exhibits signals at δ 42.80 (9 H), −27.44 (8 H) and −49.12 (9 H) corresponding to the dimeric form of **5c**.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s)

$[\{U(cot)(BH_4)(\mu\text{-}OEt)\}_2]$		$[\{U(cot)(OPr^i)(\mu\text{-}OPr^i)\}_2]$			
Uranium environment					
U···U′[a]	3.7892(5)	U(1)–U(2)	3.7805(6)		
U–B	2.594(8)	U(1)–O(1)	2.303(6)	U(2)–O(1)	2.297(6)
U–O	2.296(5)	U(1)–O(2)	2.317(6)	U(2)–O(2)	2.315(6)
		U(1)–O(3)	2.027(6)	U(2)–O(4)	2.070(8)
U–C(1)	2.655(8)	U(1)–C(51)	2.69(1)	U(2)–C(61)	2.68(1)
U–C(2)	2.667(7)	U(1)–C(52)	2.70(1)	U(2)–C(62)	2.72(1)
U–C(3)	2.669(7)	U(1)–C(53)	2.66(1)	U(2)–C(63)	2.77(2)
U–C(4)	2.645(7)	U(1)–C(54)	2.68(1)	U(2)–C(64)	2.68(2)
U–C(5)	2.637(8)	U(1)–C(55)	2.68(1)	U(2)–C(65)	2.66(3)
U–C(6)	2.678(8)	U(1)–C(56)	2.65(2)	U(2)–C(66)	2.69(3)
U–C(7)	2.695(8)	U(1)–C(57)	2.67(1)	U(2)–C(67)	2.64(4)
U–C(8)	2.680(9)	U(1)–C(58)	2.69(1)	U(2)–C(68)	2.71(4)
U–C[b]	1.94(1)	U(1)–C(5)[b]	1.99(2)	U(2)–C(6)[b]	1.98(3)
O–U–B	94.7(2)	O(1)–U(1)–C(5)	130.6(6)	O(2)–U(2)–C(6)	128.6(7)
O–U–O′	68.8(2)	O(1)–U(1)–O(3)	92.4(3)	O(2)–U(2)–O(4)	91.8(3)
O–U–C	127.3(2)	O(1)–U(1)–O(2)	69.6(2)	O(2)–U(2)–O(1)	69.8(2)
O′–U–C	124.5(2)	O(2)–U(1)–C(5)	127.4(6)	O(1)–U(2)–C(6)	125.7(6)
C–U–B	130.7(2)	O(2)–U(1)–O(3)	94.4(2)	O(1)–U(2)–O(4)	95.20(3)
U–O–U′	112.2(2)	O(3)–U(1)–C(5)	125.9(5)	O(4)–U(2)–C(6)	128.4(4)
U–O–C(9)	117.8(2)	U(1)–O(1)–U(2)	110.6(2)	U(1)–O(2)–U(2)	109.4(2)
U′–O–C(9)	130.3(3)	U(1)–O(1)–C(11)	112.2(6)	U(2)–O(1)–C(11)	134.2(6)
		U(1)–O(2)–C(21)	124.3(7)	U(2)–O(2)–C(21)	124.1(7)
		U(1)–O(3)–C(31)	161.7(6)	U(2)–O(4)–C(41)	168.3(7)
cot ligands					
⟨C–C⟩	1.39(1)	1.37(6)		1.40(2)	
⟨C–C–C⟩	135(1)	135(3)		135(3)	
Alkoxide ligands					
O–C(9)	1.466(8)	O(1)–C(11)	1.51(1)	O(2)–C(21)	1.47(2)
C(9)–C(10)	1.51(1)	O(3)–C(31)	1.55(2)	O(4)–C(41)	1.55(4)
O–C(9)–C(10)	108.9(6)				

[a] Symmetry code: (′) −*x*, −*y*, 1 − *z*. [b] C,C(5) and C(6) are the centroids of the cot rings.

analytical sample of **4b**. Moreover, the spectrum of **4b** in $[^2H_8]$toluene in the presence of 10 equivalents of thf shows the two signals corresponding to the thf protons (shifted from their diamagnetic positions at δ +1.24 and +0.35) and is otherwise identical to the spectrum of **4b** in $[^2H_8]$thf. These spectral features obviously indicate an important structural modification: it seems likely that **4b** exists as several associated species in toluene solution, with preferentially a dimeric structure similar to that established by X-ray analysis for **4a**, and should adopt a monomeric form in thf, presumably $[U(cot)(BH_4)(OPr^i)(thf)]$, resulting from a bridge-splitting reaction by the co-ordinating solvent. The spectra of the other mixed alkoxide–

tetrahydroborate compounds **4a** and **4c** in thf are analogous to that of **4b** in this solvent, the BH_4 and alkoxide signals being respectively in the high- and low-field regions, and reflect identical structures; the tetrahedral environment of the uranium atom, observed in the crystal structure of dimeric **4a**, is certainly retained in the monomeric species, a bridging alkoxide group being replaced by a solvent molecule. That thf is not firmly co-ordinated to complexes **4** was demonstrated by its total elimination when the solutions were evaporated to dryness and by the formation of thf-free samples after crystallization from thf–toluene. It is well established that autoassociation of alkoxides as dimers or oligomers is favoured over the formation of adducts,[13] and this phenomenon is frequently manifest by the complexity of the NMR spectra. The spectrum of the ethoxide derivative **4a** in toluene is in fact very complicated, revealing at least seven singlets. In contrast to **4a** and **4b**, the butoxide **4c** slowly decomposed in toluene but the spectrum, which exhibits a high-field tetrahydroborate signal, suggests that **4c** should exist as a monomer in this solvent; it is possible that the size of the Bu^{t}O ligand prevents the ready formation of associated species but the unsolvated complex [U(cot)(BH_4)(OBu^t)] is not very stable.

The bis(alkoxide) complexes [U(cot)$(OR)_2$] **5**. Compounds **5** also have structures and dynamic behaviours in solution which depend markedly on the nature of the OR group and the solvent. The NMR spectra of the bis(isopropoxide) **5b** in thf or toluene exhibit, in addition to the cyclooctatetraene resonance, two equal sets of two signals of relative intensities 6:1 which correspond to two inequivalent OPr^i groups; these two sets are visible in both the high- and low-field regions of the spectra. In [$^2H_5$]pyridine the spectrum of **5b** is quite different since it shows only one set of low-field signals corresponding to two equivalent isopropoxide ligands. These facts indicate that **5b** is dimeric in tetrahydrofuran or toluene solution, as it is in its crystalline form, and that the alkoxide bridges are cleaved in pyridine to give [U(cot)$(OPr^i)_2$(py)]; this latter easily eliminates pyridine under vacuum to give back the bridged dimer. The assignments of the high- and low-field signals respectively to the bridging and terminal alkoxides of [{U(cot)$(OPr^i)_2$}$_2$] in toluene or thf are based on the disappearance of the high-field resonances and the invariance of the low-field signals in pyridine. Similar spectral features have previously been observed for the complexes [U(η-C_3H_5)$_2$$(OR)_2$] which are dimeric in toluene and monomeric in tetrahydrofuran.[10] Intramolecular exchange of terminal and bridging OR groups in metal alkoxides is generally facile,[13] and by using the spin-saturation-transfer technique[14] such a permutation in **5b** was found to occur above 60 °C in toluene.

The spectrum of the bis(ethoxide) **5a** in [$^2H_5$]pyridine is analogous to that of **5b** in this solvent, showing low-field signals corresponding to equivalent alkoxide ligands. In tetrahydrofuran or toluene the spectra of **5a** are also similar to those of **5b**, revealing the presence of terminal and bridging ethoxide ligands, but the resonances are very broad. Below −10 °C the signals relative to two different terminal OEt groups (in the ratio 2:1) are visible in the low-field region, but the other high-field resonances, corresponding to the cot ligands and the bridging ethoxides, could not be assigned accurately. It seems possible that **5a** should exist in thf or toluene solution in the form of two equilibrating isomers, the *cis* and *trans* dimeric compounds [{U(cot)(OEt)(μ-OEt)}$_2$]; this mixture should give rise to the low-field signals which are observed at low temperature.

In contrast to **5a** and **5b**, the rupture of the butoxide bridges of [{U(cot)$(OBu^t)_2$}$_2$] was observed in tetrahydrofuran. Immediately after dissolution of **5c** in this solvent the spectrum revealed the presence of both the monomeric and dimeric forms of the complex; after 30 min the dimeric species, which gives rise, in both the high- and low-field regions of the spectrum, to two singlets corresponding to the bridging and terminal OBu^t groups, has been totally converted into the monomer, characterized by only one low-field signal attributed to the two equivalent butoxide ligands. The spectrum of **5c** in toluene is complicated and exhibits many signals among which could be detected those corresponding to the dimeric species observed in thf; moreover, **5c** slowly decomposed in aromatic solvent.

These NMR studies indicate that the alkoxide bridges are stronger in the complexes [{U(cot)$(OR)_2$}$_2$] than in [{U(cot)(BH_4)(OR)}$_2$] since the latter are readily transformed into monomeric species in thf whereas the bis(alkoxide) compounds, except **5c**, retain their dimeric structure in this solvent. This difference is similar to that observed between metal alkoxides and metal chloride–alkoxides; substitution of OR groups by more electronegative substituents enhances the Lewis-acid character of the metallic centre and the ability to form adducts with bases.[15]

Alkoxide exchange reactions between [{U(cot)$(OPr^i)_2$}$_2$] *and* Pr^{i}OH. Intermolecular exchange between OR groups of metal alkoxides and free alcohol molecules is generally observed.[13] The NMR spectrum of an equimolecular mixture of [{U(cot)$(OPr^i)_2$}$_2$] and Pr^{i}OH revealed the broadening of the resonances which correspond to the terminal OPr^i ligands, as well as those corresponding to the free alcohol, and spin saturation transfer was found to occur between these signals; the other peaks remained unaffected. These phenomena were more evident after further addition of alcohol (5 equivalents). These results clearly indicate that at 30 °C, while the terminal and bridging isopropoxide groups of [{U(cot)$(OPr^i)_2$}$_2$] are not permutating, there is a rapid exchange between the terminal alkoxide ligands and the free alcohol. Such a stereoselective exchange, which could be rarely detected in transition-metal alkoxides,[16] certainly proceeds by initial co-ordination of the alcohol molecule to the metallic centre, followed by a proton transfer; this mechanism should be favoured by formation of an hydrogen bond between the co-ordinated alcohol and the terminal alkoxide, similar to that recently observed in the zirconium complex [$Zr_2(OPr^i)_8(Pr^iOH)_2$].[17]

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 standard methods and distilled immediately before use. Deuteriated solvents were dried over Na/K alloy.

Elemental analyses were performed by the Analytische Laboratorien at Engelskirchen (Germany). The ^1H NMR spectra were recorded on a Bruker W 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The commercial anhydrous alcohols (Aldrich) were used without purification; [U(cot)$(BH_4)_2$] was prepared as described in ref. 5.

Reaction of [U(cot)$(BH_4)_2$] *with* NaOEt.—An NMR tube was charged with [U(cot)$(BH_4)_2$] (20 mg, 0.05 mmol) and NaOEt (3.5 mg, 0.05 mmol) in [$^2H_8$]thf (0.4 cm^3). After 30 min at 20 °C the spectrum showed the formation of NaU(cot)$(BH_4)_2$(OEt) **2** (55%), [U(cot)(BH_4)(OEt)] **4a** (35%) and NaU(cot)$(BH_4)_3$ (10%).

NaU(cot)$(BH_4)_2$(OEt) **2**.—A round-bottom flask (50 cm^3) was charged with [U(cot)(BH_4)(OEt)] **4a** (100 mg, 0.25 mmol) and $NaBH_4$ (11.3 mg, 0.3 mmol) and thf (20 cm^3) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 30 min at room temperature and the solvent evaporated. The residue was extracted with toluene (10 cm^3) and, after evaporation, red microcrystals of complex **2** were obtained (75 mg, 69%) (Found: C, 27.05; H, 4.65; B, 4.8. $C_{10}H_{21}BNaOU$ requires C, 27.25; H, 4.75; B, 5.0%).

[K(18-crown-6)][U(cot)$(BH_4)_3$] **3**.—A round-bottom flask

(50 cm^3) was charged with [U(cot)(BH$_4$)$_2$] (111.5 mg, 0.3 mmol), KBH$_4$ (16.2 mg, 0.3 mmol) and 18-crown-6 (88 mg, 0.33 mmol); thf (25 cm^3) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 30 min, then filtered and evaporated to dryness. The red powder was recrystallized from toluene–thf (3:1, 5 cm^3) and the dark red crystals of complex **3** were filtered off and dried under vacuum (109 mg, 53%) (Found: C, 34.70; H, 6.25; B, 4.55. $C_{20}H_{44}B_3KO_6U$ requires C, 34.8; H, 6.35; B, 4.8%).

[U(cot)(BH$_4$)(OEt)] **4a**.—A two-necked round-bottom flask (50 cm^3) was charged with [U(cot)(BH$_4$)$_2$] (120 mg, 0.32 mmol) and a bent tube containing EtOH (56.5 µl, 0.96 mmol) was attached to it; thf (25 cm^3) and the alcohol were subsequently transferred into the flask under vacuum at −78 °C. Gas was evolved and the reaction mixture stirred at 20 °C for 1.5 h; solvent (15 cm^3) was evaporated and after filtration a red powder precipitated following addition of toluene (10 cm^3) to the red solution. This powder was recrystallized from toluene–thf (5:1, 5 cm^3) and the red crystals were filtered off and dried under vacuum (67.5 mg, 52%) (Found: C, 29.7; H, 4.1; B, 2.8. $C_{10}H_{17}BOU$ requires C, 29.85; H, 4.25; B, 2.75%).

[U(cot)(BH$_4$)(OPr^i)] **4b**.—The preparation of complex **4b** was identical to that of **4a**. Reaction of [U(cot)(BH$_4$)$_2$] (156 mg, 0.42 mmol) with Pr^{i}OH (96 µl, 1.26 mmol) gave **4b** which was isolated as red crystals (120.5 mg, 69%) (Found: C, 31.6; H, 4.4; B, 2.45. $C_{11}H_{19}BOU$ requires C, 31.75; H, 4.55; B, 2.65%).

[U(cot)(BH$_4$)(OBu^t)] **4c**.—An NMR tube was charged with [U(cot)(BH$_4$)$_2$] (7.2 mg, 0.019 mmol) in [^{2}H$_8$]thf (0.4 cm^3) and Bu^{t}OH (1.5 mg) was added. Gas was evolved and the spectrum of the red solution showed the formation of **4c** in almost quantitative yield. This complex slowly decomposed in toluene and attempts to prepare analytically pure samples, by using the same procedure as for **4a** or **4b**, were unsuccessful.

[U(cot)(OEt)$_2$] **5a**.—A two-necked round-bottom flask (50 cm^3) was charged with [U(cot)(BH$_4$)(OEt)] (200 mg, 0.5 mmol) and a bent tube containing EtOH (102 µl, 1.75 mmol) was attached to it; thf (20 cm^3) and the alcohol were subsequently transferred into the flask under vacuum at −78 °C. Gas was evolved and the reaction mixture was stirred at 20 °C for 1.5 h; after evaporation of the solvent, the residue was washed with pentane (15 cm^3) and the orange microcrystalline powder was filtered off and dried under vacuum (167 mg, 72%) (Found: C, 33.05; H, 4.05. $C_{12}H_{18}O_2U$ requires C, 33.35; H, 4.15%).

[U(cot)(OPr^i)$_2$] **5b**.—The preparation of complex **5b** was similar to that of **5a**. Reaction of [U(cot)(BH$_4$)(OPr^i)] (208 mg, 0.5 mmol) with Pr^{i}OH (115 µl, 1.5 mmol) gave **5b** which was isolated in the form of an orange powder (203 mg, 79%) (Found: C, 36.35; H, 4.65. $C_{14}H_{22}O_2U$ requires C, 36.5; H, 4.8%).

[U(cot)(OBu^t)$_2$] **5c**.—An NMR tube was charged with [U(cot)(BH$_4$)$_2$] (7.5 mg, 0.02 mmol) in [^{2}H$_8$]thf (0.4 cm^3) and Bu^{t}OH (3.1 mg, 0.042 mmol) was introduced; gas was evolved and the spectrum of the orange solution indicated the almost quantitative formation of complex **5c**. The latter slowly decomposed in toluene and attempts to prepare analytically pure samples, by using the same procedure as for **5a** or **5b**, were unsuccessful.

Comproportionation Reactions of Complexes **1** *and* **5**.—An NMR tube was charged with [U(cot)(BH$_4$)$_2$] **1** (*ca.* 10 mg) and 1 mol equivalent of [U(cot)(OR)$_2$] **5** in [^{2}H$_8$]thf (0.4 cm^3). The spectrum indicated after 5 min the quantitative formation of the mixed alkoxide–tetrahydroborate [U(cot)(BH$_4$)(OR)] **4**.

Table 3 Crystallographic data and experimental details

	[{U(cot)(BH$_4$)-(µ-OEt)}$_2$]	[{U(cot)(OPr^i)-(µ-OPr^i)}$_2$]
Crystal data		
Formula	$C_{20}H_{34}B_2O_2U_2$	$C_{28}H_{44}O_4U_2$
M	804.18	920.72
Crystal size/mm	0.25 × 0.25 × 0.125	0.40 × 0.20 × 0.12
Colour	Red-brown	Red
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	9.318(4)	9.967(3)
b/Å	12.093(2)	16.906(5)
c/Å	10.187(5)	19.051(3)
β/°	94.37(3)	104.06(2)
U/Å^3	1144(1)	3114(2)
Z (dimer)	2	4
D_c/g cm^{-3}	2.333	1.964
µ(Mo-Kα)/cm^{-1}	134.11	98.7
F(000)	728	1344
Data collection		
θ limits/°	1, 25	1, 20
Scan type	ω–2θ	ω–2θ
Scan width/°	0.8 + 0.35 tanθ	0.8 + 0.35 tanθ
Scan speed/° min^{-1}	1.3–10	1.3–10
Transmission factors	0.940, 1.043	0.855, 1.397
h,k,l Range	−11 to 11, 0–14, 0–12	0–9, 0–16, −18 to 18
Crystal decay (%) linearly corrected	10	34
Reflections collected		
total	2329	3249
unique	1994	2664
with $I > 3\sigma(I)$	1204	1591
$R(F)$*	0.022	0.038
$R'(F)$†	0.026	0.044
Maximum shift/e.s.d.	0.01	0.01

* $R(F) = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. † $R'(F) = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ ($w = 1$).

Table 4 Fractional atomic coordinates with e.s.d.s for [{U(cot)-(BH$_4$)(µ-OEt)}$_2$]

Atom	x	y	z
U	0.497 90(4)	0.140 30(3)	0.917 11(4)
O	0.521 5(8)	0.047 3(6)	1.114 0(7)
C(1)	0.391(1)	0.326(1)	1.009(1)
C(2)	0.287(1)	0.248(1)	1.026(1)
C(3)	0.217(1)	0.168(1)	0.943(1)
C(4)	0.229(1)	0.132(1)	0.815(1)
C(5)	0.311(1)	0.164(1)	0.711(1)
C(6)	0.412(1)	0.247(1)	0.695(1)
C(7)	0.480(1)	0.328(1)	0.775(1)
C(8)	0.473(1)	0.361(1)	0.904(1)
C(9)	0.566(1)	0.111(1)	1.233(1)
C(10)	0.462(2)	0.087(1)	1.337(1)
B	0.770(1)	0.135(1)	0.881(1)

Intra- and Inter-molecular Alkoxide Exchange Reactions of [{U(cot)(OPr^i)$_2$}$_2$].—An NMR tube was charged with complex **5b** (15 mg, 0.03 mmol) in [^{2}H$_8$]toluene (0.4 cm^3); δ (80 °C) 97.95 (1 H), 35.43 (6 H), −26.04 (8 H), −31.89 (6 H) and −81.42 (1 H). Irradiation of the resonance at δ 35.43 caused a decrease in the intensity of the signal at δ −31.89 (50% of its original value). This spin saturation transfer was not observed at 30 °C. Isopropyl alcohol (2.5 µl, 0.03 mmol) was introduced into the tube. The NMR spectrum at 30 °C showed broadening of the low-field isopropoxide signals and of the free alcohol resonances ($w_{\frac{1}{2}}$ 30 Hz); the other peaks remained unchanged ($w_{\frac{1}{2}}$ 15 Hz). The intensity of the peak at δ 41.92 (6 H) decreased to 25% of its original value when the free alcohol signal at δ 0.99 was

Table 5 Fractional atomic coordinates with e.s.d.s for $[\{U(cot)(OPr^i)(\mu\text{-}OPr^i)\}_2]$

Atom	x	y	z	Atom	x	y	z
U(1)	−0.040 3(1)	0.348 45(6)	0.860 92(5)	C(42)	−0.316(6)	0.084(3)	1.020(2)
U(2)	−0.324 3(1)	0.194 72(7)	0.825 86(6)	C(43)	−0.228(7)	−0.011(3)	0.946(4)
O(1)	−0.108(2)	0.226 1(9)	0.811 9(9)	C(51)	0.094(3)	0.393(2)	0.761(2)
O(2)	−0.248(2)	0.311(1)	0.886 0(8)	C(52)	0.174(3)	0.420(2)	0.823(2)
O(3)	0.078(2)	0.300(1)	0.952 6(9)	C(53)	0.152(3)	0.461(2)	0.876(2)
O(4)	−0.254(2)	0.129(1)	0.919(1)	C(54)	0.048(3)	0.496(2)	0.897(2)
C(11)	0.012(3)	0.178(2)	0.799(2)	C(55)	−0.087(3)	0.503(2)	0.871(2)
C(12)	0.000(3)	0.173(2)	0.720(1)	C(56)	−0.174(3)	0.481(2)	0.813(2)
C(13)	0.031(4)	0.107(2)	0.840(2)	C(57)	−0.166(3)	0.436(2)	0.747(2)
C(21)	−0.300(4)	0.343(2)	0.946(2)	C(58)	−0.041(3)	0.395(2)	0.726(2)
C(22)	−0.240(5)	0.310(3)	1.014(2)	C(61)	−0.393(3)	0.130(2)	0.693(2)
C(23)	−0.404(3)	0.407(2)	0.924(2)	C(62)	−0.400(4)	0.209(2)	0.679(2)
C(31)	0.188(5)	0.291(3)	1.026(2)	C(63)	−0.464(3)	0.275(2)	0.703(2)
C(32)	0.304(3)	0.263(2)	0.499(2)	C(64)	−0.542(3)	0.279(2)	0.754(2)
C(32′)	0.318(8)	0.320(5)	0.022(4)	C(65)	−0.594(3)	0.223(2)	0.801(2)
C(33)	0.140(3)	0.265(2)	0.565(2)	C(66)	−0.582(4)	0.140(2)	0.816(2)
C(33′)	0.167(9)	0.217(6)	0.017(5)	C(67)	−0.511(4)	0.081(3)	0.790(2)
C(41)	−0.219(4)	0.066(3)	0.980(2)	C(68)	−0.441(4)	0.077(3)	0.735(2)

irradiated. The low-field isopropoxide signals and the free alcohol peak were much broader ($w_{\frac{1}{2}}$ 105 and 80 Hz respectively), after further addition of 4 equivalents of Pr^{i}OH; the other peaks remained unchanged.

Crystal Structure Determinations.—Complexes **4a** and **5b** were recrystallized from toluene. Single crystals were introduced into thin-walled Lindeman glass tubes in the glove-box. Reflection data were collected at 20 °C on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator [λ(Mo-Kα) = 0.710 73 Å]. Accurate unit-cell parameters were obtained from least-squares calculations based on the positions of 25 reflections at $8 < \theta < 12°$. Three standard reflections were measured every hour to monitor crystal decay. The data were corrected for Lorentz polarization effects and absorption (using the ABSCOR program[18]). For both compounds, the structures were solved by the heavy-atom method and refined by full-matrix least-squares procedures based on F. Anisotropic parameters were refined for all the atoms of **4a**; the U, O and methyl carbons [except C(32) and C(33), for which the difference electron-density map showed two positions introduced with an occupation factor of 0.5] were refined anisotropically for **5b**. Hydrogen atoms of the cot and alkoxide ligands of **4a**, and those of the cot ring of **5b**, were inserted at calculated positions with fixed isotropic thermal parameters (B = 6 Å^2); they were not refined but constrained to ride on their C atoms. Analytical scattering factors for neutral atoms[19] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Calculations were carried out with the SDP suite of programs[20] on a Micro Vax II computer. The crystal data and data collection conditions for each compound are reported in Table 3, final atomic coordinates in Tables 4 and 5 for **4a** and **5b** respectively.

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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