Exploring the Auxiliary Co-ordination Sphere of Tripodal Amino(triamido) Actinide Complexes†

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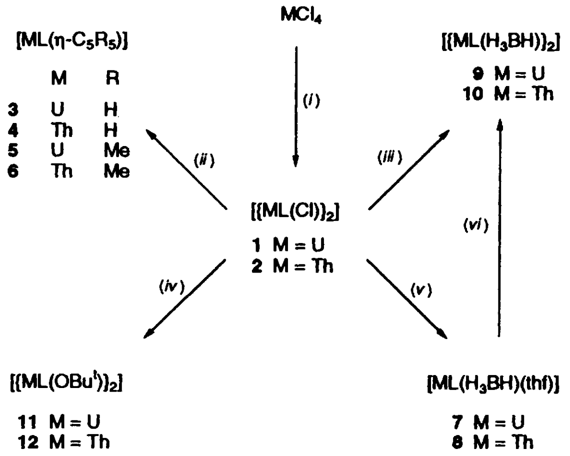
High-yield syntheses of the soluble, volatile complexes [{ML(Cl)}$_2$] [M = U or Th, L = N(CH$_2$CH$_2$NSiMe$_3$)$_3$] have been achieved. The molecular structure of the uranium complex shows it to be a dimer bridged by long U–(μ-Cl) bonds. These compounds are shown to be versatile starting materials for exploration of the chemistry of the amino(triamido) actinide fragment. Their reactions with Na[C$_5$R$_5$] (R = H or Me) gave high yields of the monomeric complexes [ML(C$_5$R$_5$)] for which analogous non-chelate compounds are unknown. These species are fluxional and display apparent three-fold symmetry on the NMR time-scale in solution at room temperature, although an exchange process *via* a trigonal-bipyramidal transition state is postulated on the basis of variable-temperature NMR studies for the compound M = Th, R = Me. The molecular structure of the compound M = U, R = Me has been determined by X-ray diffraction. Reaction of the chloro complexes with lithium tetrahydroborate in tetrahydrofuran (thf) gave high yields of [ML(H$_3$BH)(thf)]. The uranium derivative has been structurally characterised and has distorted-octahedral geometry. Sublimation of these compounds *in vacuo* led cleanly to the base-free complexes [{ML(H$_3$BH)}$_2$]. The volatile dimeric alkoxide derivatives [{ML(OBu^t)}$_2$] have been prepared similarly.

The sterically demanding amide N(CH$_2$CH$_2$NSiMe$_3$)$_3$ has previously been used in the synthesis of complexes of main-group elements[1,2] and transition metals.[3] We were interested as to whether this diverse and interesting chemistry could be extended to the much larger actinide metals, and have recently reported the first examples thereof.[4] These latter compounds are related to the non-chelate complexes [M{N(SiMe$_3$)$_2$}$_3$Cl] (M = U or Th) which have an extensive chemistry.[5] It is well established that the use of tripodal ligands can lead to new types of reactivity at the metal centre, not only because of the extra stability conferred by the chelate effect, but also since the ligating atoms are constrained to facial co-ordination. Indeed it might be expected that the M{N[CH$_2$CH$_2$N(SiMe$_3$)]$_3$} (ML) fragment would be somewhat more robust than M[N(SiMe$_3$)$_2$]$_3$. In an attempt to learn what kinds of ligand environments can be supported, and what kinds of steric constraints are manifest in the ML system, we report here the synthesis of a variety of derivatives of this fragment (Scheme 1).



Scheme 1 (*i*) Li$_3$L, thf, −80 °C, sublimation; (*ii*) Na[C$_5$R$_5$], thf, −80 °C, sublimation; (*iii*) Li[BH$_4$], thf, −80 °C, sublimation; (*iv*) K[OBu^t], thf, −80 °C, sublimation; (*v*) Li[BH$_4$], thf, −80 °C; (*vi*) sublimation

Results and Discussion

Synthesis of [{ML(Cl)}$_2$].—The preparation of [{ML(Cl)}$_2$] (M = U **1** or Th **2**) *via* the tetrahydrofuran adducts [ML(Cl)(thf)$_n$] has been described previously.[4] Characterising data for these and all new compounds are given in Table 1.

The molecular structure of complex **1** as determined by X-ray diffraction[4] is shown in Fig. 1. Positional parameters are given in Table 2 and selected bond lengths and angles in Table 3. The structure consists of a dimer of distorted edge-sharing octahedral [UL(Cl)] units bridged through the Cl atoms, with a crystallographic inversion centre midway between the uranium atoms.

The ^{1}H NMR spectra of paramagnetic complex **1** and diamagnetic **2** in [^{2}H$_8$]toluene at room temperature each consist of one signal for the trimethylsilyl groups and two for the ethylene backbone. This is consistent with these species having trigonal-bipyramidal structures similar to that found in analogous main-group and transition-metal complexes,[2,3] but is perhaps more likely to be due to the presence of a fast fluxional process (see below). This behaviour, which persists at low temperatures, was found in all the new complexes described herein unless otherwise stated.

Cyclopentadienyl Derivatives.—Addition of cold tetrahydrofuran to a mixture of complex **1** or **2** and an excess of Na[C$_5$H$_5$] followed by warming to room temperature gives green (M = U) and colourless (M = Th) solutions. Evaporation of volatiles and sublimation of the residue at 150 °C and 10^{-6} mbar leads to isolation of the pure compounds [ML(η-C$_5$H$_5$)] (M = U **3** or Th **4**) as oils which crystallise slowly at room temperature. Analogous reactions with Na[C$_5$Me$_5$] give, after sublimation, crystalline [ML(C$_5$Me$_5$)] (M = U **5** or Th **6**). All

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: bar = 10^5 Pa.

Table 1 Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%)			
		C	H	N	Spectroscopic data[b]
1	Bright green	28.25 (28.45)	6.20 (6.20)	8.75 (8.85)	^{1}H NMR ([^{2}H$_8$]toluene, $w_{\frac{1}{2}}$ = *ca.* 50 Hz): 12.8 (27 H, s, Me$_3$Si), 11.5 (6 H, s, CH$_2$), −46.5 (6 H, s, CH$_2$) Mass spectrum (EI): *m/z* 652 [7, (M^+ + Cl) − Me], 632 (42, M^+), 616 (38%, M − Me) Solution molecular weight (CH$_2$Cl$_2$): 1252 IR: 1378s, 1350w, 1283m, 1143w, 1130w, 1089m, 1059m, 1026w, 950m, 930m, 906m, 838s (br), 775m, 722m, 669m
2	White	28.50 (28.70)	6.30 (6.25)	8.85 (8.95)	^{1}H NMR: 3.38 (6 H, t, J 5, CH$_2$), 2.46 (6 H, t, J 5, CH$_2$), 0.38 (27 H, s, Me$_3$Si) ^{13}C-{^{1}H} NMR ([^{2}H$_8$]toluene): 58.7 (s, CH$_2$), 46.3 (s, CH$_2$), 0.7 (s, Me$_3$Si) Mass spectrum (EI): *m/z* 646 [5, (M^+ + Cl) − Me], 626 (48, M^+), 611 (52, M^+ − Me), 591 (58%, M^+ − Cl) Solution molecular weight (CH$_2$Cl$_2$): 1260 IR: 1377s, 1350w, 1285m, 1143w, 1130w, 1089m, 1059m, 1026w, 951w, 930m, 904m, 840s (br), 775m, 720m, 665m
3	Pale green	35.75 (36.25)	6.65 (6.70)	8.25 (8.45)	^{1}H NMR ($w_{\frac{1}{2}}$ = *ca.* 20 Hz): 3.30 (27 H, s, Me$_3$Si), −0.53 (5 H, s, η-C$_5$H$_5$), −7.36 (6 H, s, CH$_2$), −16.02 (6 H, s, CH$_2$) Mass spectrum (EI): *m/z* 662 (7, M^+), 649 (4, M − Me), 597 (100%, M − C$_5$H$_5$)
4	White	36.35 (36.55)	6.75 (6.75)	8.25 (8.55)	^{1}H NMR ([^{2}H$_8$]toluene): 6.60 (5 H, s, η-C$_5$H$_5$), 3.05 (6 H, t, J 5, CH$_2$), 2.29 (6 H, t, J 5, CH$_2$), 0.16 (27 H, s, Me$_3$Si) ^{13}C ([^{2}H$_8$]toluene): 116.9 (s, η-C$_5$H$_5$), 66.7 (s, CH$_2$), 42.8 (s, CH$_2$), 1.9 (s, Me$_3$Si) Mass spectrum (EI): *m/z* 656 (25, M^+), 641 (12, M − Me), 591 (100%, M − C$_5$H$_5$)
5	Red-orange	40.80 (40.95)	7.35 (7.45)	7.60 (7.65)	^{1}H NMR[c] ($w_{\frac{1}{2}}$ = *ca.* 200 Hz): 79.5 (2 H, s), 41.5 (2 H, s), −5.4 (18 H, s), −8.3 (2 H, s), − 19.1 (2 H, s), −26.2 (9 H, s), −45.8 (2 H, s), −88.6 (2 H, s) Mass spectrum (EI): *m/z* 733 (1, M^+), 718 (6, M − Me), 688 (1, M − 3Me), 632 (2), 618 (4), 599 (100%, M − C$_5$Me$_5$)
6	White	40.90 (41.30)	7.60 (7.50)	7.50 (7.70)	^{1}H NMR ([^{2}H$_8$]toluene): 2.99 (6 H, t, J 6, CH$_2$), 2.44 (6 H, t, J 6, CH$_2$), 2.09 (15 H, s, η-C$_5$Me$_5$), 0.21 (27 H, s, Me$_3$Si) ^{13}C-{^{1}H} NMR (DEPT, [^{2}H$_8$]toluene): 63.8 (s, CH$_2$), 46.5 (s, CH$_2$), 12.6 (s, η-C$_5$*Me*$_5$), 1.7 (s, Me$_3$Si) Mass spectrum (EI): *m/z* 711 (5, M − Me), 681 (6), 623 (2), 611 (8), 591 (100%, M − C$_5$Me$_5$)
7	Pale green	32.95 (33.35)	7.55 (7.50)	8.05 (8.20)	^{1}H NMR ($w_{\frac{1}{2}}$ = *ca.* 20 Hz): 27.32 (4 H, s, thf), 16.47 (6 H, s, CH$_2$), 13.75 (27 H, s, Me$_3$Si), −34.84 (6 H, s, CH$_2$), −109.2 (4 H, vbr, q, BH$_4$) Mass spectrum (EI): *m/z* 685 (23, M^+), 616 (22), 612 (M − thf), 598 (55%, M − thf − BH$_3$) IR: 2452s (B–H$_t$ str.), 2349w, 2300m, 2256s, 2201s, 2163s and 2135m (B–H$_b$ str.), 1246vs (bridge def.)
8	White	33.45 (33.60)	7.55 (7.55)	8.00 (8.25)	^{1}H NMR: 4.12[d,e] (4 H, br q, J 85, BH$_4$), 3.75 (4 H, m, thf), 3.31 (6 H, t, J 7, CH$_2$), 2.44 (6 H, t, J 7, CH$_2$), 1.29 (4 H, m, thf), 0.33 (27 H, s, Me$_3$Si) ^{13}C-{^{1}H} NMR: 71.5 (s, thf), 60.3 (s, CH$_2$), 46.1 (s, CH$_2$), 25.3 (s, thf), 0.9 (s, Me$_3$Si) ^{11}B NMR: −11.9 (qnth, J_{BH} 85). ^{11}B-{^{1}H} NMR: −11.9 (s) Mass spectrum (EI): *m/z* 606 (20, M − thf), 591 (29, M − thf − BH$_4$), 577 (29%) IR: 2452s (B–H$_t$ str.), 2348w, 2302m, 2257s, 2200s, 2165s and 2135m (B–H$_b$ str.), 1246vs (bridge def.)
9	Pale green	29.65 (29.40)	6.95 (7.05)	9.40 (9.15)	^{1}H NMR ($w_{\frac{1}{2}}$ = *ca.* 15 Hz): 9.96 (27 H, s, Me$_3$Si), 7.51 (6 H, s, CH$_2$), −32.20 (6 H, s, CH$_2$), −64.52 (4 H, q, J, 85, BH$_4$) Mass spectrum (EI): *m/z* 612 (12, M^+), 598 (55%, M − BH$_3$) Solution molecular weight (C$_6$H$_6$): 1220 IR: 2460s (B–H$_t$ str.), 2362w, 2210m, 2144s (B–H$_b$ str.), 1247 of 1263vs (bridge def.)
10	White	30.00 (29.70)	7.15 (7.15)	8.80 (9.25)	^{1}H NMR: 4.60[e] (4 H, br q, J 85, BH$_4$), 3.32 (6 H, t, J 5, CH$_2$), 2.35 (6 H, t, J 7, CH$_2$), 0.24 (27 H, s, Me$_3$Si) ^{13}C-{^{1}H} NMR ([^{2}H$_8$]toluene): 63.9 (s, CH$_2$), 45.5 (s, CH$_2$), 0.3 (s, Me$_3$Si) ^{11}B NMR: −9.1 (qnt, J_{BH} 85). ^{11}B-{^{1}H} NMR: 9.1 (s) Mass spectrum (EI): *m/z* 606 (25, M^+), 591 (65, M − Me), 578 (50%) Solution molecular weight (C$_6$H$_6$): 1205 IR: 2461s (B–H$_t$ str.), 2362w, 2209m, 2146s (B–H$_b$ str.), 1247 or 1262vs (bridge def.)
11	Light purple	33.70 (34.00)	7.15 (7.20)	7.95 (8.35)	^{1}H NMR ($w_{\frac{1}{2}}$ = *ca.* 15 Hz): 64.81 (6 H, s, CH$_2$), 59.12 (9 H, s, Bu^t), 9.87 (6 H, s, CH$_2$), − 28.79 (27 H, Me$_3$Si) Mass spectrum (EI): *m/z* 670 (36, M^+), 614 (13, M − Bu^t), 597 (12%, M − OBu^t) Solution molecular weight (C$_6$H$_6$): 1310
12	White	33.90 (34.30)	7.45 (7.30)	8.50 (8.45)	^{1}H NMR: 3.36 (6 H, t, J 5, CH$_2$), 2.40 (6 H, t, J 5, CH$_2$), 1.41 (9 H, s, OBu^t), 0.31 (27 H, s, Me$_3$Si) ^{13}C NMR ([^{2}H$_8$]toluene): 78.7 (s, O*C*Me$_3$), 63.7 (s, CH$_2$), 45.2 (s, CH$_2$), 33.7 (s, OC*Me*$_3$), 0.7 (s, Me$_3$Si) ^{29}Si-{^{1}H} NMR ([^{2}H$_8$]toluene): −5.5 (s, Me$_3$Si) Mass spectrum (EI): *m/z* 665 (15, M^+), 592 (M − OBu^t) Solution molecular weight (C$_6$H$_6$): 1205

[a] Calculated values in parentheses. [b] All NMR spectra obtained on solutions in [^{2}H$_6$]benzene at 298 K unless otherwise stated. Data given as chemical shift (δ), relative intensity, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, m = multiplet, br = broad), coupling constant J in Hz, assignment. Assignment of ^{13}C-{^{1}H} NMR spectra made with reference to DEPT (distortionless enhancement of polarisation transfer) spectra where appropriate. Infrared bonds in cm^{-1}. [c] Not assigned. See text. [d] One peak of BH$_4$ quartet overlaps with adjacent multiplet due to thf ligand. [e] ^{1}H-{^{11}B} NMR spectrum gave broad singlet.

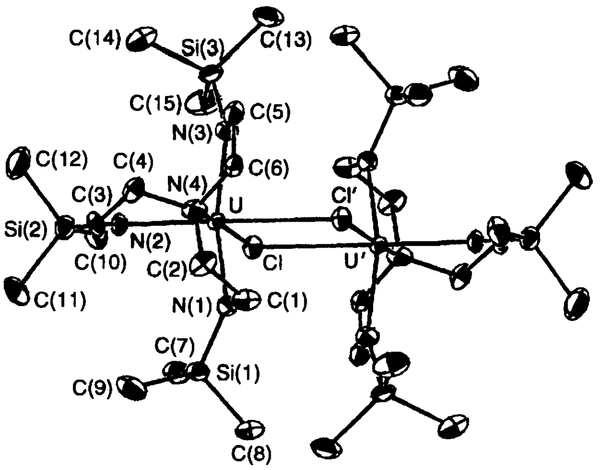

Fig. 1 An ORTEP[6] drawing of complex **1**

Table 2 Fractional atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
U	0.183 92(5)	0.099 65(4)	0.160 90(3)
Cl	−0.135 2(3)	0.078 0(3)	0.053 9(2)
Si(1)	0.103 3(4)	−0.128 2(3)	0.285 1(2)
Si(2)	0.155 4(4)	0.329 8(3)	0.403 9(3)
Si(3)	0.306 8(4)	0.349 0(3)	0.084 5(3)
N(1)	0.198 2(10)	−0.076 1(8)	0.208 2(7)
N(2)	0.254 6(10)	0.225 6(9)	0.335 1(7)
N(3)	0.346 6(10)	0.208 5(9)	0.109 8(7)
N(4)	0.467 7(10)	0.080 2(9)	0.246 6(7)
C(1)	0.339 9(13)	−0.132 1(11)	0.202 5(9)
C(2)	0.481 0(13)	−0.035 9(10)	0.276 0(9)
C(3)	0.408 6(13)	0.221 8(12)	0.404 2(8)
C(4)	0.525 8(13)	0.195 9(11)	0.341 9(9)
C(5)	0.503 8(14)	0.188 4(11)	0.118 6(9)
C(6)	0.542 1(14)	0.081 2(11)	0.165 3(9)
C(7)	−0.074 1(15)	−0.051 1(12)	0.282 2(10)
C(8)	0.050 7(15)	−0.304 1(11)	0.234 4(10)
C(9)	0.222 3(16)	−0.087 4(14)	0.429 7(10)
C(10)	−0.046 5(15)	0.321 2(14)	0.316 5(10)
C(11)	0.146 6(16)	0.290 9(14)	0.527 9(10)
C(12)	0.254 9(18)	0.496 0(14)	0.452 4(12)
C(13)	0.344 0(17)	0.354 9(14)	−0.042 5(10)
C(14)	0.428 7(17)	0.488 2(12)	0.197 2(11)
C(15)	0.100 8(16)	0.362 3(13)	0.074 9(11)

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

U–Cl	2.820(3)	U–N(2)	2.259(8)
U–Cl′	2.911(2)	U–N(3)	2.247(11)
U–N(1)	2.236(10)	U–N(4)	2.567(9)
U–N(4)–C(2)	111.4(6)	N(4)–U–N(3)	67.8(3)
U–N(4)–C(4)	104.3(7)	N(4)–U–N(2)	73.5(3)
U–N(4)–C(6)	105.4(7)	N(4)–U–N(1)	69.9(3)
U–N(3)–C(5)	124.8(9)	N(4)–U–Cl′	98.2(2)
U–N(3)–Si(3)	121.1(5)	N(3)–U–Cl	117.2(2)
U–N(2)–C(3)	116.9(7)	N(3)–U–Cl′	81.9(2)
U–N(2)–Si(2)	130.7(5)	N(3)–U–N(2)	96.3(3)
U–N(1)–C(1)	113.6(8)	N(3)–U–N(1)	132.0(4)
U–N(1)–Si(1)	129.1(5)	N(2)–U–Cl	112.5(2)
Cl–U–Cl′	75.49(8)	N(2)–U–Cl′	171.5(2)
U–Cl–U′	104.51(9)	N(2)–U–N(1)	92.5(3)
N(4)–U–Cl	170.7(2)	N(1)–U–Cl	102.2(2)
		N(1)–U–Cl′	82.7(2)

the compounds may be recrystallised from pentane at low temperature.

A small evacuated glass tube containing complex **5** was heated in an oven at 60 °C overnight to produce large clear red crystals which were subjected to a single-crystal X-ray structural analysis. Two views of one of the three independent molecules in the unit cell are shown in Figs. 2 and 3. Positional parameters (for all three molecules) are given in Table 4 and selected bond lengths and angles (molecule 1) in Table 5. The other molecules have essentially the same structure, differing only in conformation of the C_2 linkages in the tripodal fragment or by small rotations of the C_5Me_5 ring about its centre relative to the rest of the molecule. The atom U(1) lies *ca.* 0.850 Å (molecule 2, 0.873; molecule 3, 0.856 Å) out of the plane defined by N(1), N(2) and N(3), away from the apical N(4). The position of the C_5Me_5 group is best described by the angle N(3)–U(1)–Cp(1) of *ca.* 152.8° (143.3, 152.3°). Some distortion of the ligands arises as a consequence of steric compression between the C_5Me_5 ligand and the Me_3Si groups. For example, while C(21) (which does not point toward a Me_3Si group) lies only 0.04(2) Å out of the plane of the C_5Me_5 carbocycle, the other methyl group carbon atoms C(22)–C(25) lie out of this plane by between 0.17(2) and 0.28(2) Å away from U(1). Also, atoms Si(1) and Si(2) lie out of the planes U(1)–N(1)–C(2) and U(1)–N(2)–C(4) by 0.406(6) and 0.344(7) Å respectively. In contrast, the relatively unencumbered group containing Si(3) is almost planar.

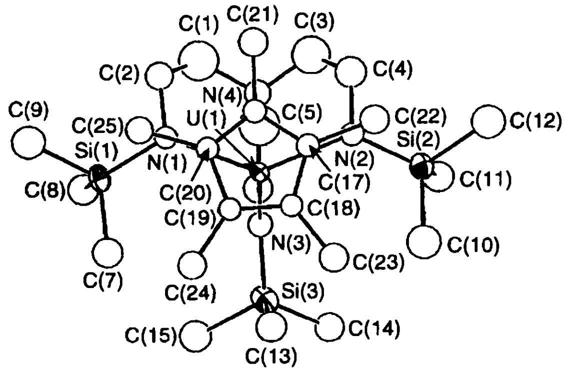

Fig. 2 An ORTEP drawing of complex **5** viewed perpendicular to the η-C_5Me_5 ligand

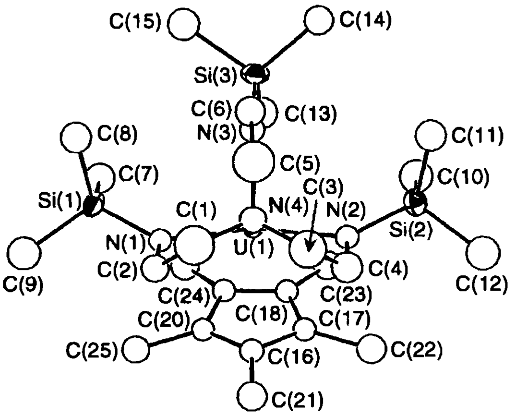

Fig. 3 An ORTEP drawing of complex **5** viewed nearly along the apical N–U bond

While complexes **3** and **4** display apparent three-fold symmetry according to NMR spectroscopy, the ^1H NMR spectrum of **5** was extremely complicated; the number of peaks precludes the possibility of the presence a highly fluxional species analogous to **3**. However, it must also be considered that the effective time-scale of the ^1H NMR experiment is somewhat greater for paramagnetic uranium(IV) compared to the analogous thorium(IV) compounds because of the extremely wide chemical shift range of the former. We have recently reported similar observations for highly sterically encumbered tris(tetramethylcyclopentadienyl) derivatives of the actinide

Table 4 Fractional atomic coordinates for compound **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1							
U(1)	0.368 76(7)	0.184 71(4)	0.218 97(3)	C(10)	0.396 8(27)	0.277 0(15)	0.339 1(10)
Si(1)	0.448 7(6)	0.036 6(3)	0.138 3(2)	C(11)	0.630 5(24)	0.360 2(14)	0.281 2(9)
Si(2)	0.444 1(7)	0.343 4(3)	0.285 6(2)	C(12)	0.359 4(28)	0.439 8(16)	0.297 3(10)
Si(3)	0.624 7(6)	0.091 7(4)	0.277 0(3)	C(13)	0.459 1(25)	0.065 0(14)	0.314 0(9)
N(1)	0.400 8(14)	0.130 5(8)	0.148 5(5)	C(14)	0.736 5(23)	0.134 0(13)	0.314 5(8)
N(2)	0.398 6(15)	0.306 0(8)	0.236 6(5)	C(15)	0.721 4(26)	0.000 3(14)	0.257 2(9)
N(3)	0.583 2(15)	0.151 3(9)	0.231 0(6)	C(16)	0.096 6(19)	0.219 6(10)	0.205 2(7)
N(4)	0.531 1(17)	0.261 6(9)	0.151 6(6)	C(17)	0.099 2(18)	0.238 9(10)	0.252 7(7)
C(1)	0.512 4(35)	0.234 6(20)	0.104 5(12)	C(18)	0.115 6(18)	0.171 6(10)	0.281 4(6)
C(2)	0.418 6(22)	0.179 5(12)	0.104 7(8)	C(19)	0.116 6(18)	0.110 8(10)	0.253 8(6)
C(3)	0.499 4(32)	0.343 3(18)	0.156 5(11)	C(20)	0.102 0(18)	0.142 7(10)	0.205 9(6)
C(4)	0.411 1(25)	0.359 9(14)	0.195 2(9)	C(21)	0.075 6(23)	0.277 5(13)	0.163 0(8)
C(5)	0.654 4(36)	0.241 9(20)	0.160 6(13)	C(22)	0.077 7(23)	0.322 1(13)	0.270 1(8)
C(6)	0.699 6(23)	0.187 2(13)	0.195 6(8)	C(23)	0.103 4(23)	0.164 7(13)	0.335 7(8)
C(7)	0.402 4(24)	−0.024 0(13)	0.194 0(8)	C(24)	0.101 0(22)	0.026 1(13)	0.272 5(8)
C(8)	0.635 1(24)	0.021 5(14)	0.119 1(9)	C(25)	0.078 4(22)	0.095 1(12)	0.163 8(8)
C(9)	0.364 9(27)	−0.001 2(15)	0.089 8(10)				
Molecule 2							
U(2)	0.187 62(7)	0.732 78(4)	0.448 64(2)	C(35)	0.291 7(22)	0.869 0(12)	0.353 9(8)
Si(4)	0.173 3(6)	0.627 5(3)	0.569 7(2)	C(36)	0.260 6(24)	0.782 3(14)	0.270 9(9)
Si(5)	0.329 0(6)	0.784 5(4)	0.328 5(2)	C(37)	0.515 6(24)	0.775 4(14)	0.311 0(9)
Si(6)	0.442 3(6)	0.853 7(3)	0.480 6(2)	C(38)	0.280 8(26)	0.912 7(15)	0.492 8(9)
N(5)	0.168 3(13)	0.640 4(7)	0.510 0(5)	C(39)	0.515 8(24)	0.841 3(14)	0.536 0(9)
N(6)	0.258 9(14)	0.715 2(8)	0.369 9(5)	C(40)	0.571 7(26)	0.904 8(15)	0.434 8(9)
N(7)	0.394 8(13)	0.771 7(8)	0.461 9(5)	C(41)	−0.080 6(17)	0.719 1(10)	0.428 4(6)
N(8)	0.366 4(13)	0.616 9(8)	0.434 9(5)	C(42)	−0.098 6(18)	0.725 6(10)	0.479 3(6)
C(26)	0.302 9(19)	0.548 8(10)	0.460 2(7)	C(43)	−0.065 2(18)	0.799 7(10)	0.487 3(7)
C(27)	0.164 1(20)	0.569 5(11)	0.485 0(7)	C(44)	−0.035 8(18)	0.841 5(10)	0.443 9(6)
C(28)	0.408 2(20)	0.607 4(11)	0.383 7(7)	C(45)	−0.048 5(18)	0.793 2(10)	0.406 9(7)
C(29)	0.290 6(20)	0.635 8(11)	0.358 3(7)	C(46)	−0.119 2(23)	0.650 5(13)	0.403 0(8)
C(30)	0.478 0(20)	0.637 6(11)	0.457 9(7)	C(47)	−0.163 3(22)	0.662 5(12)	0.518 4(8)
C(31)	0.513 6(21)	0.719 6(12)	0.447 9(7)	C(48)	−0.085 8(24)	0.831 1(13)	0.537 6(8)
C(32)	0.195 1(24)	0.720 6(14)	0.591 4(9)	C(49)	−0.023 2(23)	0.930 7(13)	0.435 2(8)
C(33)	0.029 6(23)	0.580 7(13)	0.606 2(8)	C(50)	−0.050 5(21)	0.816 5(12)	0.354 0(8)
C(34)	0.323 4(24)	0.563 9(14)	0.584 5(9)				
Molecule 3							
U(3)	−0.109 65(6)	0.695 37(4)	0.110 49(3)	C(60)	0.059 6(23)	0.546 6(13)	0.053 2(8)
Si(7)	0.031 0(6)	0.819 6(4)	0.005 4(2)	C(61)	0.335 9(24)	0.617 6(14)	0.027 1(9)
Si(8)	−0.106 2(6)	0.588 9(4)	0.224 9(2)	C(62)	0.268 4(26)	0.514 9(15)	0.116 3(9)
Si(9)	0.193 9(5)	0.589 6(3)	0.077 2(2)	C(63)	−0.108 2(23)	0.508 8(13)	0.186 7(8)
N(9)	−0.058 1(13)	0.801 7(7)	0.061 4(5)	C(64)	−0.232 4(25)	0.573 2(14)	0.280 3(9)
N(10)	−0.136 0(14)	0.673 3(8)	0.192 0(5)	C(65)	0.060 9(27)	0.586 9(15)	0.245 4(10)
N(11)	0.110 4(14)	0.665 8(8)	0.105 4(5)	C(66)	−0.382 8(18)	0.644 2(10)	0.134 2(6)
N(12)	0.002 6(14)	0.796 6(8)	0.152 2(5)	C(67)	−0.333 0(17)	0.605 2(10)	0.093 7(6)
C(51)	−0.007 0(24)	0.871 1(14)	0.124 8(9)	C(68)	−0.310 7(19)	0.659 0(10)	0.053 3(7)
C(52)	−0.081 2(22)	0.871 2(12)	0.086 0(8)	C(69)	−0.352 0(18)	0.731 8(10)	0.067 3(7)
C(53)	0.137 7(30)	0.774 9(17)	0.151 6(11)	C(70)	−0.395 1(18)	0.723 3(10)	0.118 4(6)
C(54)	0.202 0(21)	0.712 4(12)	0.125 7(8)	C(71)	−0.441 8(21)	0.608 4(12)	0.183 5(7)
C(55)	−0.062 8(29)	0.796 9(17)	0.201 5(10)	C(72)	−0.325 2(20)	0.516 2(12)	0.091 6(7)
C(56)	−0.145 0(23)	0.738 1(13)	0.220 7(8)	C(73)	−0.276 2(21)	0.637 1(12)	0.001 0(7)
C(57)	0.038 0(26)	0.734 9(15)	−0.027 1(9)	C(74)	−0.365 8(21)	0.805 4(12)	0.036 0(8)
C(58)	0.208 3(25)	0.846 4(14)	0.004 5(9)	C(75)	−0.456 3(20)	0.788 7(12)	0.148 8(7)
C(59)	−0.048 6(27)	0.896 8(15)	−0.031 4(10)				

metals.[7] At 223 K only two resonances were observed. That at δ 12.80 was sufficiently sharp to resolve ^{29}Si satellites of appropriate intensity, indicating that this is due to one or more of the trimethylsilyl groups. The peak at δ −9.42 was of similar intensity but with $w_{\frac{1}{2}}$ = *ca.* 375 Hz. For diamagnetic **6** the results of variable-temperature ^{1}H NMR studies were rather more conclusive. At 223 K, broad peaks in the expected region for backbone CH_2 resonances, a single sharp η-C_5Me_5 resonance, and two resolved Me_3Si resonances at δ 0.36 and 0.23 were observed. The latter peaks coalesced at 243 K. At room temperature, sharp resonances for the trimethylsilyl groups, the ethylene backbone and the pentamethylcyclopentadienyl ligand were observed. Notably, the appearance of the latter peak did not change significantly over this range in temperature. Hence, although the room-temperature NMR spectra of all these compounds indicate *average* C_{3v} symmetry, we expect that the ground-state geometry is close to that displayed in the solid state (Fig. 2). A fluxional process like that in Fig. 4 proceeding *via* a distorted trigonal-bipyramidal transition state is in accord with the variable-temperature NMR spectra described above.

A complex related to **3**–**6**, *viz.* [U(NEt_2)$_3$(η-C_5H_5)] has been reported in a mixture,[8] but interestingly while the four-membered metallacycle [U{$CH_2SiMe_2N(SiMe_3)$}{N($SiMe_3$)$_2$}$_2$] reacts under mild conditions with compounds containing acidic C–H bonds, its reaction with cyclopentadiene did not give the expected [U{N($SiMe_3$)$_2$}$_3$(η-C_5H_5)] which is still unknown.[9]

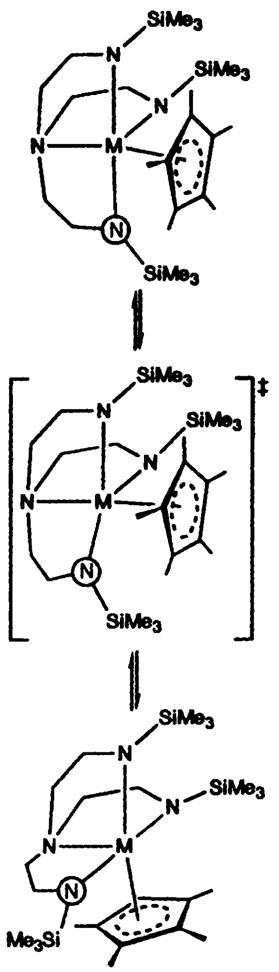

Fig. 4 Proposed fluxional process leading to apparent three-fold symmetry at room temperature for complex **6**

Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

U(1)–C(C_5H_5)$_{av}$	2.85(1)	U(1)–N(3)	2.25(2)
U(1)–Cp(1)*	2.58	U(1)–N(4)	2.61(2)
U(1)–N(1)	2.264(15)	C–C(C_5H_5)$_{av}$	1.40(1)
U(1)–N(2)	2.28(2)		
U(1)–N(4)–C(1)	108(2)	N(2)–U(1)–Cp(1)	100.2
U(1)–N(4)–C(3)	107(1)	N(3)–U(1)–Cp(1)	152.8
U(1)–N(4)–C(5)	104(2)	N(4)–U(1)–Cp(1)	133.3
U(1)–N(3)–C(6)	117(1)	N(1)–U(1)–N(2)	131.5(5)
U(1)–N(3)–Si(3)	125.2(8)	N(1)–U(1)–N(3)	91.0(5)
U(1)–N(2)–C(4)	113(1)	N(1)–U(1)–N(4)	66.7(5)
U(1)–N(2)–Si(2)	133.0(8)	N(2)–U(1)–N(3)	90.9(5)
U(1)–N(1)–C(2)	119(1)	N(2)–U(1)–N(4)	67.4(5)
U(1)–N(1)–Si(1)	128.1(8)	N(3)–U(1)–N(4)	73.9(5)
N(1)–U(1)–Cp(1)	99.6		

* Cp = Centroid of C_5H_5 ring.

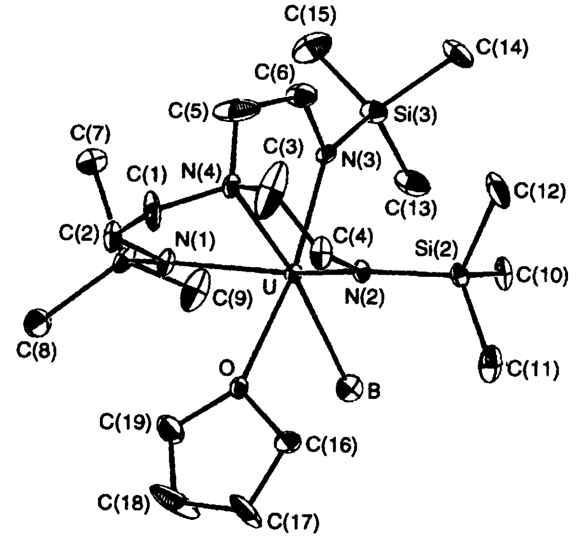

Fig. 5 An ORTEP drawing of complex **7**

Table 6 Fractional atomic coordinates for compound **7**

Atom	*x*	*y*	*z*
U	0.122 39(4)	0.213 11(3)	0.122 81(3)
Si(1)	−0.119 3(4)	0.337 4(2)	0.163 8(2)
Si(2)	0.378 6(3)	0.095 4(2)	0.090 2(2)
Si(3)	0.270 3(4)	0.367 7(2)	0.011 6(2)
O	0.019 6(7)	0.104 4(4)	0.197 9(5)
N(1)	−0.005 0(9)	0.274 8(6)	0.203 1(5)
N(2)	0.282 9(8)	0.135 1(6)	0.157 6(5)
N(3)	0.246 4(9)	0.311 7(5)	0.097 7(6)
N(4)	0.238 9(10)	0.248 6(6)	0.267 9(6)
C(1)	0.145 8(14)	0.251 3(10)	0.327 0(9)
C(2)	0.023 9(12)	0.280 2(9)	0.296 9(8)
C(3)	0.334 7(16)	0.194 3(10)	0.293 7(9)
C(4)	0.325 2(12)	0.125 0(8)	0.249 1(8)
C(5)	0.291 8(19)	0.323 6(11)	0.253 6(10)
C(6)	0.328 5(14)	0.337 9(9)	0.171 1(8)
C(7)	−0.069 5(14)	0.436 3(9)	0.190 4(9)
C(8)	−0.269 0(14)	0.320 1(9)	0.210 7(10)
C(9)	−0.145 4(15)	0.328 7(9)	0.047 3(9)
C(10)	0.338 8(13)	0.132 9(9)	−0.017 3(8)
C(11)	0.360 0(14)	−0.007 8(8)	0.087 4(9)
C(12)	0.547 7(14)	0.119 7(11)	0.124 0(10)
C(13)	0.174 4(14)	0.335 9(9)	−0.087 1(9)
C(14)	0.441 0(13)	0.365 1(10)	−0.008 3(9)
C(15)	0.228 4(18)	0.466 9(9)	0.028 3(11)
C(16)	0.045 5(14)	0.025 9(7)	0.180 9(10)
C(17)	−0.059 5(15)	−0.017 3(10)	0.202 6(13)
C(18)	−0.145 4(17)	0.030 7(10)	0.231 6(18)
C(19)	−0.107 0(14)	0.107 2(9)	0.221 7(10)
B	−0.012 1(15)	0.150 3(9)	−0.011 4(10)

Tetrahydroborato Derivatives.—The chloro complexes **1** and **2** react smoothly with an excess of lithium tetrahydroborate in thf to give pale green and colourless solutions respectively of [ML(H_3BH)(thf)] (M = U **7** or Th **8**) which were obtained by crystallisation at low temperature from pentane. The molecular structure of **7** is shown in Fig. 5. Positional parameters are given in Table 6 and a list of selected bond lengths and angles in Table 7. The structure is related to that of **1** and **5** in that the tripodal amino(triamido) ligand occupies four sites of a distorted octahedron. Although hydrogen atoms associated with the tetrahydroborate ligand were not located, the U–B distance of 2.68(2) Å and IR data (Table 1) support the assignment of H_3BH co-ordination of the BH_4 group.[10] Unlike the more sterically congested compounds **1** and **5**, the amido fragments in **7** are virtually planar.

Complexes **7** and **8** sublime cleanly at 150 °C and 10^{-6} mbar to give essentially quantitative yields of the thf-free compounds [{ML(BH_4)}$_2$] (M = U **9** or Th **10**). Large clear crystals of these compounds have been grown by crystallisation from various solvents and by vapour diffusion, but none has yielded sufficiently strong reflections for a structure determination by X-ray diffraction. Their formulation as dimers is based on solution molecular-weight determinations in benzene (see Experimental section). Mass spectra gave no higher mass peaks than those expected for the monomeric unit.

Table 7 Selected bond lengths (Å) and angles (°) for complex **7**

U–B	2.68(2)	U–N(2)	2.234(9)
U–O	2.585(8)	U–N(3)	2.266(10)
U–N(1)	2.253(10)	U–N(4)	2.572(9)
U–N(4)–C(1)	106.7(8)	N(4)–U–N(3)	74.3(3)
U–N(4)–C(3)	110.4(8)	N(4)–U–N(2)	69.5(3)
U–N(4)–C(5)	104.0(8)	N(4)–U–N(1)	68.8(3)
U–N(3)–C(6)	115.0(8)	N(3)–U–B	117.4(4)
U–N(3)–Si(3)	136.6(5)	N(3)–U–O	162.1(3)
U–N(2)–C(4)	117.5(7)	N(3)–U–N(2)	94.5(3)
U–N(2)–Si(2)	126.9(5)	N(3)–U–N(1)	97.0(4)
U–N(1)–C(2)	121.6(7)	N(2)–U–B	105.4(4)
U–N(1)–Si(1)	124.3(5)	N(2)–U–O	76.9(3)
B–U–O	80.3(4)	N(2)–U–N(1)	131.5(3)
N(4)–U–B	168.0(4)	N(1)–U–B	110.3(4)
N(4)–U–O	87.9(3)	N(1)–U–O	162.1(3)

Alkoxide Derivatives.—The reaction of complex **1** or **2** with an excess of potassium *tert*-butoxide leads to the formation of an intractable mixture. In contrast, addition of thf at −80 °C to a stoichiometric (1 : 1) mixture of the chloride compounds with potassium *tert*-butoxide, stirring for 3 d at ambient temperature and sublimation (80 °C and 10^{-6} mbar) leads to moderate yields of the alkoxo derivatives [{ML(OBu^t)}$_2$] (M = U **11** or Th **12**). Presumably the dimers (solution molecular weight) are bridged by alkoxide groups to give structures analogous to that of **1**. The appearance of only one peak in the ^{29}Si NMR spectrum and the absence of ^{29}Si satellites on the Bu^t resonance preclude the possibility that **11** and by analogy **12** are the trimethylsilyl derivatives [ML(SiMe$_3$)] which would have similar mass spectra.

Conclusion

We have described the synthesis of the chloride-bridged dimers [{ML(Cl)}$_2$] (M = U **1** or Th **2**) *via* the thf adducts [ML(Cl)(thf)]. These compounds, like all the other species reported here, are thermally stable, crystalline, highly soluble in hydrocarbons, and sublime readily *in vacuo*. The ML fragment is quite robust, and under suitable conditions the chlorine atoms in **1** and **2** can be replaced in high yield by other ligands without significant disruption of the tripodal chelate.

With transition metals, N(CH$_2$CH$_2$NSiMe$_3$)$_3$ forms complexes of three-fold symmetry (*e.g.* trigonal bi- and mono-pyramidal structures).[3] In the case here of the much larger actinide metals we have found that in the solid state the amino(triamido) fragment occupies four cofacial co-ordination sites of a distorted octahedron. Despite this, all NMR spectra indicate that if this structure is retained in solution then a facile fluxional process is taking place which leads to apparent three-fold symmetry. In the case of [{ML(μ-Cl)}$_2$] **1** and **2** and the alkoxide derivatives [{ML(μ-OBu^t)}$_2$] **11** and **12** this process must be preceded by scission of the bridging bonds in the dimer, while for [ML(H$_3$BH)(thf)] **7** and **8** reversible loss of the thf ligand is likely. In the case of the highly sterically encumbered compounds [ML(η-C$_5$Me$_5$)] **5** and **6** only, these processes could be slowed on the NMR time-scale at accessible temperatures.

We are currently engaged in attempts to make higher-oxidation-state derivatives of the uranium compounds and other reactivity studies.

Experimental

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques, or in a N$_2$-filled dry-box. The NMR samples were made up in the dry-box and the sample tubes sealed *in vacuo*. Solvents were pre-dried over sodium wire and then distilled over potassium (tetrahydrofuran) or sodium–potassium alloy (light petroleum, b.p. 40–60 °C) under a slow passage of nitrogen. Deuteriated solvents were dried over molten potassium and distilled. The NMR spectra were recorded on Bruker AC-250, WM-360 or AMX-500 spectrometers, and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0), or to external tetramethylsilane in the case of ^{29}Si spectra. Infrared spectra were obtained as Nujol mulls in an air-tight holder using a Perkin-Elmer FTIR spectrometer, electron impact (EI) mass spectra obtained on a VG Autospec mass spectrometer by Dr. Ali Abdul-Sada. Elemental Analyses were performed by Medac, Brunel University, UK, or by Canadian Microanalytical Services, Delta, B.C., Canada. Solution molecular-weight determinations were by the isopiestic (Signer) method in dry benzene on *ca.* 200 mg samples.[11] Literature methods were used for the preparation of Li$_3$L,[1] UCl$_4$[12] and Na[C$_5$Me$_5$],[13] Na[C$_5$H$_5$] was prepared by titration of Na in liquid ammonia with freshly distilled C$_5$H$_6$ and dried *in vacuo* overnight, LiBH$_4$ and KOBu^t (Aldrich Chemical Company) were dried at 100 °C *in vacuo* for a few hours before use and ThCl$_4$ (CERAC) was used without further purification.

[UL(η-C$_5$H$_5$)] **3**.—Tetrahydrofuran (10 cm^3) was added at −80 °C to a mixture of complex **1** (0.250 g, 0.20 mmol) and Na[C$_5$H$_5$] (0.15 g, excess) and the mixture was stirred for 8 h at ambient temperature to give a clear green solution. After evaporation of volatiles the green residue was sublimed at 150 °C and 10^{-6} mbar to give an analytically pure emerald-green oil which solidified over a period of 1 h (0.243 g, 92%). The analogous thorium compound **4** was prepared similarly (0.248 g, 94%).

[UL(η-C$_5$Me$_5$)] **5**.—Tetrahydrofuran (10 cm^3) was added at −80 °C to a mixture of complex **1** (0.250 g, 0.20 mmol) and Na[C$_5$Me$_5$] (0.20 g, excess) and the mixture was stirred for 8 h at ambient temperature to give a clear bright orange solution. After evaporation of volatiles the residue was sublimed at 120 °C and 10^{-6} mbar to give analytically pure red crystals (0.265 g, 90%) which may be further crystallised from light petroleum at low temperature to give thick red needles. The analogous thorium compound **6** was prepared similarly (0.278 g, 96%).

[UL(H$_3$BH)(thf)] **7**.—Tetrahydrofuran (10 cm^3) was added at −80 °C to a mixture of complex **1** (0.250 g, 0.20 mmol) and LiBH$_4$ (0.10 g, excess) and the mixture was stirred for 8 h at ambient temperature to give a pale green solution. After evaporation of volatiles the residue was recrystallised from light petroleum at low temperature to give large green needles suitable for X-ray diffraction (0.252 g, 92%). The analogous thorium compound **8** was prepared similarly (0.250 g, 93%).

[{UL(H$_3$BH)}$_2$] **9**.—Tetrahydrofuran (40 cm^3) was added at −80 °C to a mixture of complex **1** (1.00 g, 0.79 mmol) and LiBH$_4$ (0.40 g, excess) and the mixture was stirred for 8 h at ambient temperature to give a pale green solution. After evaporation of volatiles the residue was sublimed at 150 °C and 10^{-6} mbar to give an analytically pure light green solid (0.904 g, 93%). The analogous thorium compound **10** was prepared similarly (0.900 g, 94%).

[{UL(OBu^t)}$_2$] **11**.—Tetrahydrofuran (10 cm^3) was added at −80 °C to a mixture of complex **1** (0.250 g, 0.20 mmol) and KOBu^t (0.045 g, 0.040 mmol) and the mixture was stirred for 3 d at ambient temperature to give a light brown solution. After evaporation of volatiles the residue was sublimed at 80 °C and 10^{-6} mbar to give analytically pure light purple crystals (0.245 g, 87%). Recrystallisation from light petroleum at low temperature gave brown needles. The analogous thorium compound **12** was prepared similarly but in somewhat lower yield (0.150 g, 54%).

Table 8 Experimental data for the X-ray diffraction study of complexes **1**, **5** and **7** *

	1	**5**	**7**
Molecular formula	$C_{30}H_{78}Cl_2N_8Si_6U_2$	$C_{25}H_{54}N_4Si_3U$	$C_{19}H_{51}BN_4OSi_3U$
M	1266.4	733.0	684.7
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	9.123(4)	9.903(2)	10.705(4)
b/Å	11.170(3)	17.610(4)	17.863(6)
c/Å	13.598(7)	28.384(4)	15.848(4)
α/°	106.84(4)	84.98(2)	90
β/°	105.59(4)	81.16(2)	96.31(2)
γ/°	93.05(3)	87.92(2)	90
U/Å^3	1257.0	4871(2)	3012
Z	1	6	4
D_c/g cm^{-3}	1.67	1.50	1.51
F(000)	616	2196	1360
λ(Mo-Kα)/Å	0.710 69	0.710 73	0.710 69
μ/cm^{-1}	63.8	48.7	52.4
T/K	173	293	173
Crystal size/mm	0.25 × 0.20 × 0.08	0.2 × 0.15 × 0.2	0.25 × 0.25 × 0.25
$2\theta_{max}$/°	46	44	46
Unique reflections	3482	11 916	4315
Significant reflections, $\|F^2\| > 2\sigma(F^2)$	3097	7776	2872
No. of variables	217	457	262
Empirical absorption correction, T_{max}, T_{min}	0.99, 0.48 (from ψ scans)	1.00, 0.88 (from ψ scans)	0.999, 0.908
Goodness of fit	2.0	1.5	1.2
$(\Delta\rho)_{max,min}$/e Å^{-3})	+1.49, −0.43 (near U)	+1.20, −0.34 (near U atoms)	+0.81, −0.36 (near U)
$(\Delta/\sigma)_{max}$	0.01	0.05	0.02
R, R'	0.042, 0.056	0.061, 0.061	0.046, 0.047

* Details in common: scan mode θ–2θ; weighting scheme, $w = \sigma^2(F)$.

Crystallography.—A crystal of complex **5** was mounted in a glass capillary, while that of **7** was coated with inert oil and transferred to the cold (173 K) nitrogen gas stream on the diffractometer (Enraf-Nonius CAD4). Non-H atoms were located by heavy-atom methods (SHELXS 86)[14] and refined by full-matrix least squares with anisotropic thermal parameters (except for C and N atoms in **5** which were refined isotropically) using the MOLEN program package[15] and scattering factors from ref. 16. Hydrogen atoms on the η-C_5Me_5 ligand in **5** and the BH_4 ligand in **7** were omitted and the rest fixed in calculated positions. Table 8 lists full experimental data.

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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