# Synthesis and crystal structure of pentavalent uranyl complexes. The remarkable stability of UO<sub>2</sub>X (X = I, SO<sub>3</sub>CF<sub>3</sub>) in non-aqueous solutions<sup>†</sup>

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The reaction of  $[UO_2I_2(THF)_3]$  with  $KC_3R_5$  (R = H, Me) or  $K_2C_8H_8$  in pyridine gave crystals of  $[{UO_2(py)_5} {KI_2(py)_5}]_{\infty}$  (1), which were desolvated under vacuum into pulverulent  $[UO_2(py)_2, KI_3]$  (2). Similar reactions with  $[UO_2(OTf)_2]$  afforded  $[UO_2(py)_2, K(OTf)_2]$  (3) as a powder and crystals of  $[{UO_2(py)_5}_2{K_3(OTf)_5}\cdot py]_{\infty}$  (4·py), which were also obtained together with crystals of  $[{UO_2(py)_5}_2{K(OTf)_2(py)_2}]$ [OTf] by (5 by) by treating  $[UO_2(OTf)_2]$  with KC<sub>4</sub>Me<sub>4</sub>P. Crystals of 6 by, the thallium analogue of  $5 \cdot py$ , were isolated from the reaction of  $[UO_2(OTf)_2]$  and  $TlC_5H_5$ . Treatment of  $[UO_{2}I_{2}(THF)_{3}]$  with LiCH<sub>2</sub>SiMe<sub>3</sub> in pyridine afforded crystals of  $[{UO_{2}(py)_{5}}]{LiI(py)_{2}}][I]$  (7) while [UO<sub>2</sub>(OTf)<sub>2</sub>] reacted with the alkyllithium reagent in acetonitrile to give crystals of  $[{UO_2(py)_5} {Li_2(OTf)_3}]_{\sim}$  (8) in pyridine. The crystal structures of 1, 4-py, 5-py, 6-py, 7 and 8 revealed the presence of U=O $\rightarrow$ M interactions (M = Li, K, Tl), and the rich diversity of these structures, from dinuclear (7) to 3D polymeric (4), is related to the distinct coordination numbers of the M<sup>+</sup> ion and ligation modes of the bridging iodide and triflate ligands as well as the presence of U=O $\rightarrow$ M interactions. The mononuclear complexes  $[UO_2(OTf)(THF)_n]$  (9) and  $[UO_2(OTf)(Et_2O)_{0.5}]$  (10) were respectively obtained by reaction of  $[UO_2(OTf)_2]$  with  $KC_5R_5$  in THF or LiCH<sub>2</sub>SiMe<sub>3</sub> in Et<sub>2</sub>O, and were transformed into  $[UO_2(OTf)(py)_2]$  (11) in pyridine. Treatment of  $[UO_2I_2(THF)_3]$  with  $TIC_5H_5$  in pyridine afforded crystals of  $[UO_2(py)_5][I] \cdot py$  (12 · py) which were desolvated under vacuum into the powder of [UO<sub>2</sub>I(py)<sub>2.5</sub>] (14). The same reaction in THF gave [UO<sub>2</sub>I(THF)<sub>2.7</sub>] (13) in powder form. Crystals of [UO<sub>2</sub>(CyMe<sub>4</sub>BTBP)(py)][OTf]·1.5py (15·1.5py) and the powder of [UO<sub>2</sub>I(CyMe<sub>4</sub>BTBP)] (16) were obtained by treating  $[UO_2(CyMeBTBP)X_2]$  (X = OTf, I) with KC<sub>5</sub>Me<sub>5</sub> or TlC<sub>5</sub>H<sub>5</sub>, respectively. The uranyl(v) chloride and nitrate compounds  $[UO_2Cl(py)_3]$  (17) and  $[UO_2(NO_3)(py)_3]$  (18) were prepared by reaction of the uranyl(VI) precursors with  $TlC_3H_5$  in pyridine; complex 18 was also obtained by treating 13 with TlNO<sub>3</sub>. Crystals of the neutral mononuclear complex  $[UO_2(OTf)(py)_4]$  (19) were isolated from reaction of  $[UO_2(OTf)_2]$  with Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> in acetonitrile. Similar reaction with  $[UO_2Cl_2(THF)_2]_2$  in pyridine gave crystals of  $[UO_2Cl_2(py)_3]$ . The crystal structures of 12 py, 15.1.5py and 19 were determined; the structure of 15 was compared with that of the uranyl(vi) counterpart. All the uranyl(v) compounds are remarkably stable in pyridine solution; the IR absorption at 816 cm<sup>-1</sup> is attributed to the  $v_{asym}$ (U=O) of the ubiquitous [UO<sub>2</sub>(py)<sub>5</sub>]<sup>+</sup> species.

# Introduction

Recent years have witnessed a fast growing interest in organouranium chemistry.<sup>1</sup> The low-valent U(III) and U(IV) complexes, in particular those of the tris and bis(pentamethylcyclopentadienyl)<sup>2</sup> and mono and bis(cyclooctatetraene) series,<sup>3</sup> were found to display unsuspected chemical behaviour. The discovery of novel reactions and structures are an incitement to further experimental and theoretical investigations in f element chemistry, especially for a better understanding of the nature of the metal–ligand bonding. In contrast, organouranium compounds in their highest oxidation state (+5 and +6) are still quite uncommon, although attracting a deeper attention. These were most generally prepared by oxidation of low-valent uranium compounds,<sup>4</sup> with a few exceptions which could be obtained from high-valent precursors.5 The uranium(VI) chemistry is dominated by the uranyl ion  $[UO_2]^{2+}$ , which is a remarkably stable moiety with an unusual linear structure. The strong oxophilicity of this ion was an obstacle to the isolation of anhydrous starting materials required for organometallic syntheses. It is only recently that practical routes to such uranyl species,  $[UO_2(OTf)_2]$  (OTf = OSO<sub>2</sub>CF<sub>3</sub>)<sup>6</sup> and  $[UO_2X_2(THF)_3]$  (X = Cl<sup>7</sup> I<sup>8</sup>), have been designed. From these precursors were obtained the first stable uranyl compounds containing U-C bonds, i.e. the bis-iminophosphorane complex  $[UO_2Cl(\eta^3-CH{Ph_2PNSiMe_3}_2)]_2$  and its derivatives,<sup>9</sup> the cyanido compound [UO<sub>2</sub>(CN)<sub>5</sub>][NEt<sub>4</sub>]<sub>3</sub>,<sup>10</sup> and a few N-heterocyclic carbene complexes.11 The synthesis of uranyl alkyl compounds remains a challenging goal, while first attempts at their preparation date back to the middle of the XIX century.12 The lack of success in the isolation of alkyl or cyclopentadienyl complexes of uranyl was related to the instability of the U-C bond toward hydrolysis and/or reduction processes leading to unidentified brown-orange U(IV) species.13

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Recently, we prepared the first cyclopentadienyl uranyl complex  $[UO_2(C_5Me_5)(CN)_3][NR_4]_2$  by oxidation of the U(IV) linear pentacyanido metallocene  $[U(C_5Me_5)_2(CN)_5][NR_4]_2$  with pyridine oxide.14 This result prompted us to take another look at the reactions of  $UO_2X_2$  (X = OTf, I, Cl, NO<sub>3</sub>) and their Lewis base adducts with the cyclopentadienyl and cyclooctatetraene anions,  $C_5 R_5^-$  (R = H, Me) and  $C_8 H_8^{2-}$ . These reactions did not afford the U(VI) organometallic compounds but involved a one electron transfer to give the corresponding pentavalent uranyl(v) compounds. Thus, we found a convenient access to stable complexes of the [UO<sub>2</sub>]<sup>+</sup> ion.<sup>15</sup> Because of its rapid disproportionation into [UO2]<sup>2+</sup> and U<sup>4+</sup> in aqueous solutions,<sup>16</sup> the [UO<sub>2</sub>]<sup>+</sup> ion was for a long time an elusive species, in contrast to the other actinvl(v) ions  $[AnO_2]^+$  (An = Np, Pu, Am). Suitable  $[UO_2]^+$  complexes were highly desirable for the study of the fundamental properties of the [AnO2]<sup>+</sup> compounds<sup>17</sup> which have important implications in nuclear fuel processing, waste treatment and environmental remediation.<sup>18</sup> The first uranyl(v) compound to have been crystallographically characterized, [UO<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>][OTf], was obtained serendipitously during the crystallization of its U(VI) parent.19 This result gave clear evidence that such complexes of the  $[UO_2]^+$  ion could be isolated in anhydrous conditions and stabilized by the choice of appropriate ligands and media. During the last two years, pentavalent uranyl(v) compounds were reproducibly synthesized and isolated by using such anhydrous and anaerobic experimental conditions. The 1D polymeric complex  $[{UO_2(py)_5} {KI_2(py)_2}]_{\infty}$ , that we described in our preliminary communication,<sup>15</sup> was prepared by Mazzanti et al. by following a distinct route via the oxidation of [UI<sub>3</sub>(THF)<sub>3</sub>],<sup>20</sup> and was transformed into the tetrameric and dimeric derivatives  $[{UO_2(dbm)_2}_4 {K_6(py)_{10}}^{2+}]$ and  $[UO_2(dbm)_2K(18\text{-crown-6})]_2$  (dbmH = dibenzoylmethane).<sup>21</sup> The mononuclear uranyl(v) β-diketiminate complexes  $[UO_2(Ar_2nacnac)(Ph_2MePO)_2] [Ar_2nacnac = (2,6^{-i}Pr_2C_6H_3)^{-1}]$  $NC(Me)CHC(Me)N(2,6-{}^{i}Pr_2C_6H_3)]^{22}$  and  $[UO_2(Ar_2nacnac) (\text{RCOCHCOR})^{-}$  (R = Me, Ph, CF<sub>3</sub>)<sup>23</sup> were synthesized by Hayton and Wu by reduction of the corresponding uranyl(VI)

precursors. However, all these compounds showed limited stability toward disproportionation in solution, while Ikeda et al. reported that some electrochemically generated, but not isolated, U(v) species like [UO<sub>2</sub>(dbm)(DMSO)]<sup>-</sup> and [UO<sub>2</sub>(salophen)(DMSO)]<sup>-</sup> (salophen = N, N'-disalicylidene-*ortho*-phenylenediaminate) were quite stable in DMSO.<sup>24</sup> Here, we report on the synthesis and characterization of uranyl(V) complexes obtained by reduction of  $UO_2X_2$  (X = I, OTf, Cl, NO<sub>3</sub>) with alkyl or cyclopentadienyl anions in organic solution. Depending on the nature of X, the solvent, the reducing agent and its metal salt, a variety of complexes, neutral or cationic, with distinct structures, from mononuclear to heteronuclear 3D polymeric, have been obtained. These complexes were found to be quite stable in organic solution. The X-ray crystal structures of  $[UO_2(py)_4(OTf)], [UO_2(py)_5][I], [UO_2(CyMe_4BTBP)(py)][OTf]$ (CyMe<sub>4</sub>BTBP = 6,6'-bis-(3,3,6,6-tetramethyl-cyclohexane-1,2,4-triazin-3-yl)-2,2'-bipyridine),  $[{UO_2(py)_5} {LiI(py)_2}][I],$  $[{UO_2(py)_5}_2{M(OTf)_2(py)_2}][OTf] (M = K, Tl), [{UO_2(py)_5}_2 \{K_3(OTf)_5\} \cdot py]_{\infty}$  and  $[\{UO_2(py)_5\}\{Li_2(OTf)_3\}]_{\infty}$  are described.

#### Results

# Polynuclear uranyl(v) complexes with $O=U=O \rightarrow M$ interactions (M = Li, K, Tl)

The syntheses of the complexes are summarized in Scheme 1.

 $KC_5R_5$ ,  $K_2C_8H_8$ ,  $KC_4Me_4P$  and  $TIC_5R_5$  as the reducing agents. Treatment of  $[UO_2I_2(THF)_3]$  with 1 mol equivalent of  $KC_5R_5$ (R = H, Me) or 0.5 mol equivalent of  $K_2C_8H_8$  in pyridine reproducibly led to an orange suspension, which was stable for many days at 20 °C. The clear solution obtained by heating under reflux deposited thin orange needles of  $[{UO_2(py)_5}{KI_2(py)_2}]_{\infty}$ (1) upon cooling down at room temperature. The 1D polymeric crystal structure of 1 has already been described and will not be further commented; it consists of infinite chains where  $[UO_2(py)_5]^+$ cations are linked by the oxo groups with the  $[KI_2(py)_2]^-$  anionic



powder of [UO<sub>2</sub>(py)<sub>2.3</sub>K(OTf)<sub>2</sub>] (3)



fragments.<sup>15</sup> Such  $O=U=O \rightarrow M$  interactions are well documented in uranyl(VI) and neptunyl(V) chemistry,<sup>25,26</sup> and reflect the Lewis basicity of the axial oxygen atoms. In view of the lower positive charge on the metal centre and consequently the greater electron density on the oxygen atoms, the [UO<sub>2</sub>]<sup>+</sup> moiety is expected to have a more pronounced basicity than its [UO<sub>2</sub>]<sup>2+</sup> analogue.

The bright orange compound 1 was found to desolvate under vacuum into an ochre powder, which analyses as  $[UO_2(py)_{2.2}KI_2]$  (2). Diffusion of diethyl ether into a pyridine solution of 2 gave back orange crystals of 1. An orange powder was also formed when uranyl iodide was reacted with K(Hg) in pyridine but separation of the product from the residual mercury was difficult.

The <sup>1</sup>H NMR spectra of the reaction mixtures of  $[UO_2I_2(THF)_3]$ and  $KC_5R_5$  (R = H, Me) showed the formation of  $C_5H_{6 \rightarrow n}D_n^{27}$  or  $(C_5Me_5)_2$ ,<sup>28</sup> resulting from hydrogen abstraction or coupling of the  $C_5R_5$  radical; reduction of the uranyl(vI) compound with  $K_2C_8H_8$ gave free cyclooctatetraene. These observations clearly indicate that the  $C_5R_5^-$  and  $C_8H_8^{2-}$  anions act as the reducing agents.

The high-valent uranium iodide complexes being generally less stable than the other halide (Cl, Br) or pseudo halide (OTf) congeners, the synthesis and isolation of more uranyl(v) derivatives involving different counter anions were anticipated. Replacing  $[UO_2I_2(THF)_3]$  with  $[UO_2(OTf)_2]$  in its reactions with KC<sub>5</sub>R<sub>5</sub> and K<sub>2</sub>C<sub>8</sub>H<sub>8</sub> in pyridine gave a clear brown-orange solution, which deposited a brown powder upon addition of diethyl ether. The latter turned beige when dried under vacuum and the elemental analyses are in agreement with the formula  $[UO_2(py)_{2,3}K(OTf)_2]$ (3), the triflate analogue of 2. Crystallization of the crude reaction mixture from pyridine-diethyl ether afforded orange crystals of the polymeric compound  $[\{UO_2(py)_5\}_2\{K_3(OTf)_5\}\cdot py]_{\!\scriptscriptstyle \infty}$  (4·py) (Table 1).

Crystals of 4·py were also obtained from the reaction of  $[UO_2(OTf)_2]$  and the potassium salt of the phospholyl anion  $KC_3Me_4P$ , together with orange crystals of the trinuclear complex  $[{UO_2(py)_5}_2{K(OTf)_2(py)_2}][OTf]$ ·py (5·py). As in the case of reactions with  $KC_5R_5$  (R = H, Me) and  $K_2C_8H_8$ , no organouranium complex was detected by <sup>1</sup>H NMR during the synthesis of 4 and 5. Similar treatment of  $[UO_2(OTf)_2]$  with  $TlC_5H_5$  in pyridine rapidly afforded a brown solution without precipitation of TlOTf, which displays good solubility in organic solvents. Attempts at crystallization by slow diffusion of pentane into the crude reaction mixture afforded dark-orange crystals of the trinuclear compound  $[{UO_2(py)_5}_2{Tl(OTf)_2(py)_2}][OTf]$ ·py (6·py), which are isomorphous with the potassium analogue 5-py (Table 2).

A view of the asymmetric unit of **4** is shown in Fig. 1a while selected bond distances and angles are listed in Table 1. The pentagonal bipyramidal UO<sub>2</sub>(py)<sub>5</sub> units are linked to K(OTf)<sub>3</sub> fragments *via* one (U1=O1) or two (O3=U2=O4) oxo groups, and K1 and K2 are bridged by a  $\mu$ - $\kappa^1$ : $\kappa^2$  triffate ligand. Each potassium atom is linked to two symmetry related atoms *via* bridging OTf ligands, so that the K atoms are the knots of a three dimensional network (Fig. 1b). While K1 and K2 are connected to three K atoms, K3 is linked to two K atoms, one of its OTf ligands being terminal and monodentate. A view of the cation of **5** is shown in Fig. 2; selected bond distances and angles are listed in Table 2. The complex is built up of two [UO<sub>2</sub>(py)<sub>5</sub>]<sup>+</sup> units which are attached to a [K(OTf)<sub>2</sub>(py)<sub>2</sub>]<sup>-</sup> fragment *via* a U=O→K interaction. Complexes **4**, **5** and **6** are unique examples of pentavalent

**Table 1** Selected bond lengths (Å) and angles (°) in  $[{UO_2(py)_5}_2{K_3(OTf)_5} \cdot py]_{\infty}$  (4·py)

Bond lengths/Å							
$\begin{array}{c} U(1)-O(1)\\ U(1)-O(2)\\ U(2)-O(3)\\ U(2)-O(4)\\ < U-O(yl) >\\ U(1)-N(1)\\ U(1)-N(2)\\ U(1)-N(3) \end{array}$	1.855(8) 1.816(8) 1.823(8) 1.844(8) 1.83(1) 2.614(10) 2.608(9) 2.622(8)	$\begin{array}{c} U(1)-N(4)\\ U(1)-N(5)\\ < U(1)-N>\\ U(2)-N(6)\\ U(2)-N(7)\\ U(2)-N(8)\\ U(2)-N(9)\\ U(2)-N(10)\\ \end{array}$	2.615(10) 2.617(7) 2.615(9) 2.606(11) 2.638(10) 2.591(10) 2.607(10) 2.588(11)	<u(2)-n> K(1)-O(1) K(2)-O(3) K(3)-O(4) K(1)-O(5) K(1)-O(6') K(1)-O(7') K(1)-O(8)</u(2)-n>	2.61(2) 2.611(9) 2.655(9) 2.672(9) 2.684(10) 2.773(10) 2.826(10) 2.802(12)	$\begin{array}{c} K(2)-O(9)\\ K(2)-O(10)\\ K(2)-O(12)\\ K(2)-O(13'')\\ K(3)-O(14)\\ K(3)-O(15)\\ K(3)-O(16'')\\ K(3)-O(17)\\ \end{array}$	3.07(3) 2.791(18) 2.897(13) 2.612(12) 2.797(18) 3.18(2) 2.642(16) 2.787(11)
Bond angles/°							
$\begin{array}{l} O(1)-U(1)-O(2)\\ N(1)-U(1)-N(2)\\ N(2)-U(1)-N(3)\\ N(3)-U(1)-N(4)\\ N(4)-U(1)-N(5)\\ N(5)-U(1)-N(1)\\ O(3)-U(2)-O(4)\\ N(6)-U(2)-N(7)\\ N(7)-U(2)-N(8)\\ N(8)-U(2)-N(9)\\ N(9)-U(2)-N(9)\\ N(9)-U(2)-N(10)\\ N(10)-U(2)-N(6)\\ U(1)-O(1)-K(1)\\ U(2)-O(3)-K(2)\\ U(2)-O(4)-K(3)\\ \end{array}$	)	179.6 69.3 72.0 76.9 72.5 70.7 178.7 75.6 69.4 69.1 69.5 76.4 173.1 177.0 168.0	(4) (3) (3) (3) (3) (3) (4) (4) (3) (3) (3) (3) (3) (4) (4) (5) (4)	$\begin{array}{c} O(1) \\ O(3) \\ O(3) \\ O(3) \\ O(3) \\ O(3) \\ O(3) \\ O(4) \\ O($	$\begin{array}{l} )-K(1)-O(5) \\ )-K(1)-O(6') \\ )-K(1)-O(7') \\ )-K(1)-O(8) \\ ')-K(2)-O(9) \\ )-K(2)-O(10) \\ )-K(2)-O(11) \\ )-K(2)-O(12) \\ )-K(2)-O(12) \\ )-K(2)-O(12) \\ )-K(3)-O(14) \\ )-K(3)-O(14) \\ )-K(3)-O(15) \\ )-K(3)-O(17) \\ 4)-K(3)-O(15) \\ \end{array}$		$\begin{array}{c} 94.3(3)\\ 133.0(3)\\ 88.9(3)\\ 80.4(3)\\ 51.1(3)\\ 85.9(4)\\ 123.5(4)\\ 137.2(3)\\ 87.4(3)\\ 98.6(4)\\ 44.8(3)\\ 50.3(3)\\ 127.8(4)\\ 84.2(3)\\ 110.4(5)\\ 90.3(3)\\ 47.3(4)\end{array}$

Symmetry codes: ' = 1 - x, y + 1/2, 1 - z; '' = -x, y + 1/2, 1 - z;  $^{\#} = -x$ , y - 1/2, -z.



**Fig. 1** (a) View of complex **4**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Symmetry codes: ' = 1 - x, y + 1/2, 1 - z; '' = -x, y + 1/2, 1 - z; '' = -x, y - 1/2, -z. (b) View of the three-dimensional assembly. The fluorine and carbon atoms of the triflate ligands are omitted. Atoms are represented as spheres of arbitrary radii.

uranyl derivatives involving both terminal and bridging oxo groups of the  $[UO_2]^+$  moiety. The terminal U=O bond lengths of 1.816(8) Å in 4 and 1.826(3) Å and 1.825(3) Å in 5 can be compared with those measured in the mononuclear complexes [UO<sub>2</sub>(Ar<sub>2</sub>nacnac)(Ph<sub>2</sub>MePO)<sub>2</sub>]<sup>22</sup> and [UO<sub>2</sub>(Ar<sub>2</sub>nacnac)(dbm)]<sup>-,23</sup> which vary from 1.79(1) to 1.828(4) Å. These U=O distances seem slightly shorter than those involved in U=O $\rightarrow$ K interactions which average 1.842(1), 1.84(2) Å and 1.835(5) Å in 1, 4 and 5, respectively. The mean U=O distance (total) of 1.83(1) Å in 4 and 5 is identical to that of 1.843(2) Å in 1. These values are larger by ca. 0.05–0.1 Å than those reported for uranyl(VI) compounds. The U–N distances of the  $[UO_2(py)_5]^+$  moieties in 1, 4 and 5 are very close to one another with mean values in the range 2.60(1)–2.62(1) Å. The K–O( $\infty$ o) distances in 4 average 2.64(3) Å and are significantly smaller than those of 2.757(2) and 2.80(1) Å in 5 and 1, respectively; this difference likely reflects the more electropositive charge of the K(OTf)<sub>3</sub> fragment, by comparison with the more electron rich  $KX_2(py)_2$  fragments (X = I, OTf), leading to stronger U=O $\rightarrow$ K interactions in 4. The average K-O(OTf) distances of 2.8(2) and 2.68(2) Å in 4 and 5, respectively, can be compared with those of 2.8(1) Å in  $[K_4(MeOH)_2(2,9-$ 



Fig. 2 View of the cation in complex 5. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

 $\begin{array}{l} Me_2phen)_4(\mu_2\text{-}\kappa^1\text{:}\kappa^1\text{-}OTf)_2(\mu_3\text{-}\kappa^1\text{:}\kappa^1\text{-}OTf)_2]^{29} \mbox{ and } 2.678(2) \mbox{ Å in } [K_2(phen)_4(\kappa^1\text{-}OTf)_2]^{30} \mbox{ In the structure of } 6, \mbox{ the Tl-O and Tl-N} \mbox{ distances are larger, by a mean value of } 0.1 \mbox{ Å, than the corresponding K-O and K-N distances in } 5, \mbox{ in agreement with the variation in the radii of the K^+ and Tl^+ ions (Table 2).^{31} \end{array}$ 

LiCH<sub>2</sub>SiMe<sub>3</sub> as the reducing agent. The stabilizing effect of the polarizable  $\alpha$ -silicon atom confers to the CH<sub>2</sub>SiMe<sub>3</sub> group a major utility for the synthesis of stable alkyl complexes. This group permitted to isolate unique examples of monocyclooctatetraene uranium alkyl compounds, [U(C<sub>8</sub>H<sub>8</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(hmpa)] and [Li(THF)<sub>3</sub>][U(C<sub>8</sub>H<sub>8</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>], while other alkyl derivatives were found to decompose into [U(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>].<sup>32</sup> For this reason, reactions of UO<sub>2</sub>X<sub>2</sub> (X = I, OTf) and LiCH<sub>2</sub>SiMe<sub>3</sub> were considered.

After 24 h at room temperature, slow diffusion of pentane into a red-brown solution of a 1 : 1 mixture of  $[UO_2I_2(THF)_3]$  and LiCH<sub>2</sub>SiMe<sub>3</sub> in pyridine led to the formation of dark orange crystals of the pentavalent uranyl compound  $[{UO_2(py)_3}{LiI(py)_2}][I]$  (7). Treatment of  $[UO_2(OTf)_2]$  with 1 mol equivalent of the alkyl lithium in acetonitrile readily gave a dark brown solution; after evaporation, crystallisation of the residue from pyridine-pentane afforded light green crystals of  $[{UO_2(py)_3}{Li_2(OTf)_3}]_{--}$  (8). Crystals of 7 and 8 were also obtained from the reaction of the corresponding uranyl(v1) species and LiC<sub>5</sub>Me<sub>5</sub>.

Views of the cation of 7 and the 1D polymer 8 are shown in Fig. 3 and 4, respectively, while selected bond lengths and angles of both complexes are listed in Table 3. The dinuclear compound 7 is the simplest example of a pentavalent uranyl complex with a single U=O $\rightarrow$ M interaction. The bridging U-O1 and terminal U-O2 bonds are surprisingly very long and short, with lengths of 1.881(9) and 1.750(10) Å, respectively, while the average U-N distance of 2.61(2) Å is similar to those in complexes in 1, 4 and 5. However, these U-O distances should be considered with some suspicion since the O1 and O2 atoms are affected by rather small thermal parameters by comparison with the U atom, possibly reflecting not well corrected absorption effects.

The infinite chains of **8** consist of  $[UO_2(py)_5]^+$  units attached *via* the two oxo groups to the lithium atoms of  $[Li_2(\mu_2-\kappa':\kappa'-OTf)_3]^-$  fragments. The geometrical parameters of the uranyl

Bond lengths/Å							
U(1)–O(1)	1.839(3)	U(1)–N(1)	2.606(5)	U(2)-N(6)	2.619(4)	M-O(1)	2.759(3)
U(1) O(2)	[1.836(4)] 1.826(3)	$\mathbf{U}(1)$ $\mathbf{N}(2)$	[2.601(5)]	$\mathbf{U}(2)$ $\mathbf{N}(7)$	[2.605(5)]	$M_{0}(2)$	[2.839(4)]
O(1) = O(2)	[1.828(4)]	O(1) - N(2)	[2.632(5)]	O(2) = I(7)	[2, 623(5)]	M=O(3)	[2.801(4)]
U(2)–O(3)	1.831(3)	U(1)–N(3)	2.618(4)	U(2)–N(8)	2.594(4)	M-O(5)	2.669(4)
	[1.833(4)]		[2.623(5)]		[2.581(5)]	~ /	[2.804(4)]
U(2)–O(4)	1.825(3)	U(1)–N(4)	2.620(5)	U(2)–N(9)	2.609(4)	M-O(8)	2.703(4)
	[1.829(4)]		[2.618(5)]		[2.606(5)]		[2.890(5)]
<u–o(yl)></u–o(yl)>	1.830(5)	U(1) - N(5)	2.600(5)	U(2)-N(10)	2.590(5)	M - N(11)	2.953(5)
	[1.831(3)]	TT(1) NT	[2.611(5)]		[2.588(5)]		[2.989(6)]
		<u(1)–n></u(1)–n>	[2.62(2)]	<u(2)–n></u(2)–n>	[2.60(1)]	M-N(12)	2.953(5) [3.076(5)]
Bond angles/°							
O(1)–U(1)–O(2)		177.67(17)		N(10)–U	(2)–N(6)		70.72(14)
		[177.92(18)]					[71.37(15)]
N(1)-U(1)-N(2)		70.92(15)		U(1)–O(	166.3(2)		
N(2) $U(1)$ $N(2)$		[70.94(16)]		$\mathbf{U}(2) \mathbf{O}(1)$	[164.2(2)] 175 44(10)		
N(2) = U(1) = N(3)		67.09(14)		U(2)=U(		[175.44(19)]	
N(3) = U(1) = N(4)		[07.08(13)] 71.95(13)		O(1)-M	-0(3)		175 42(12)
1(3) - 0(1) - 1(4)		[72, 54(14)]		0(1)-101-	-0(3)		$[174 \ 18(11)]$
N(4)-U(1)-N(5)		77.17(14)		O(5)-M-	-O(8)		157.46(15)
		[76.91(15)]					[148.76(15)]
N(5)-U(1)-N(1)		72.94(14)		N(11)–M	171.71(15)		
		[72.61(15)]			· /		[172.29(15)]
O(3)–U(2)–O(4)		179.37(17)		O(5)-M-	-N(11)		83.21(15)
		[179.74(19)]					[80.33(14)]
N(7)-U(2)-N(8)		73.23(14)		O(5)–M-	-N(12)		104.99(15)
		[73.21(16)]					[107.25(14)]
N(8)-U(2)-N(9)		75.20(13)		O(8)–M-	-N(11)		79.97(14)
		[74.87(15)]			NT(10)		[73.82(16)]
N(9) - U(2) - N(10)		72.53(14)		O(8)–M-	-N(12)		91.80(15)
		[/1.99(15)]					[98.52(16)]

Table 2 Selected bond lengths (Å) and angles (°) in  $[{UO_2(py)_5}_2{M(OTf)_2(py)_2}][OTf] \cdot py (M = K, 5 \cdot py \text{ or } Tl, 6 \cdot py);$  the values for the Tl derivative are in brackets



**Fig. 3** View of the cation in complex 7. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

moieties are identical to those previously described. The average Li–O(oxo) and Li–O(OTf) distances of 1.88(1) and 1.93(2) Å can be compared with those of 1.892(2) Å in [{UO<sub>2</sub>X<sub>4</sub>}{Li(12-crown-

4}\_2] (X = Cl, Br)^{33} and 1.95(1) Å in [(LiL)\_2(\mu\_2-\kappa^1:\kappa^1-OTf)\_2] [L = (MeOCH\_2CH\_2)\_2O].^{34}

# Mononuclear uranyl(v) compounds

The preparation of soluble  $[UO_2X(L)_n]$  compounds (L = THF, Et<sub>2</sub>O, py), which would be more convenient starting materials for the development of uranyl(v) chemistry than the polyheteronuclear  $[UO_2(py)_nMX_2]$  complexes (M = K, Li, Tl), was desirable. The elimination of MX salt from compounds 1–8 was endeavoured either by changing the solvent, THF or diethyl ether in place of pyridine, and/or by replacing the lithium or potassium cyclopentadienyl reagents  $MC_5R_5$  with thallium derivatives, which generally give insoluble TIX salts (X = halide) in metathesis reactions. The syntheses of the complexes are summarized in Scheme 2.

 $KC_5R_5$ , LiCH<sub>2</sub>SiMe<sub>3</sub> and TlC<sub>5</sub>H<sub>5</sub> as the reducing agents. Treatment of  $[UO_2(OTf)_2]$  or  $[UO_2I_2(THF)_3]$  with 1 mol equivalent of  $KC_5R_5$  (R = H, Me) in THF led to the immediate formation of a brown solution and a precipitate of KX;  $C_5H_{6n}D_n$  or  $(C_5Me_5)_2$ were detected by <sup>1</sup>H NMR. In the case of the uranyl triflate, the reaction was carried out on a preparative scale; the product was extracted with a THF-toluene mixture and, after precipitation

7							
U–O(1)	1.881(9)	U–N(2)	2.589(9)	U-N(5)	2.619(9)	Li–I(1)	2.87(2)
U–O(2)	1.750(10)	U–N(3)	2.652(8)	<u–n></u–n>	2.61(2)	Li–N(6)	2.16(2)
U–N(1)	2.589(8)	U–N(4)	2.595(10)	Li–O(1)	1.90(2)	Li–N(7)	2.04(2)
O(1)-U-O(2)		179.6(3)		O(1)–Li–N(6)		109.6(10)	
N(1)-U-N(2)		72.2(3)		O(1)-Li- $N(7)$		108.1(9)	
N(2)-U-N(3)		72.8(2)		O(1)-Li-I(1)		111.1(9)	
N(3)-U-N(4)		73.4(2)		N(6)-Li-N(7)		113.7(10)	
N(4) - U - N(5)		70.8(3)		N(6)-Li-I(1)		103.2(7)	
N(5)-U-N(1)		71.0(2)		N(7)–Li–I(1)		111.1(9)	
U–O(1)–Li		174.3(6)					
8	1.020(2)		2 (00/2)		1.004(7)	1.(2) 0(2)	1.075(7)
U(1) = O(1)	1.839(3)	U(1) - N(4)	2.600(3)	$L_1(1) = O(1)$	1.904(7)	$L_1(3) = O(3)$	1.8/5(/)
U(1) = O(2)	1.840(2)	U(1) - N(5)	2.5/6(3)	$L_1(1) = O(5)$	1.894(7)	$L_1(3) = O(21)$	1.913(7)
< U(1) - U >	1.8395(5)	$\langle U(1)-N\rangle$	2.588(8)	$L_1(1) = O(8)$	1.94/(/)	$L_1(3) = O(15)$	1.939(7)
U(2) = U(4) U(2) = O(2)	1.837(2) 1.828(2)	U(2) - IN(0) U(2) - IN(7)	2.003(3)	$L_{1}(1) = O(11)$	1.904(7)	Li(3) = O(18) Li(4) = O(4)	1.938(7)
U(2) = U(3)	1.838(2) 1.8275(5)	U(2) = IN(7) U(2) = N(8)	2.398(3)	L1(2) = O(2) L(2) = O(14)	1.881(0)	L1(4) = O(4) $L_1(4) = O(6'')$	1.8/1(7) 1.022(7)
< U(2) - U > U(1) N(1)	1.0373(3)	U(2) = IN(0) U(2) = N(0)	2.376(3) 2.501(2)	$L_{1(2)} = O(14)$	1.934(7) 1.045(7)	LI(4) = O(0'')	1.932(7)
U(1) = N(1) U(1) = N(2)	2.387(3) 2.595(3)	U(2) = IN(9) U(2) = IV(10)	2.591(3) 2.587(3)	$L_{1(2)} = O(17)$ $L_{1(2)} = O(20)$	1.945(7) 1.946(7)	Li(4) = O(9') Li(4) = O(12'')	1.900(7) 1.028(7)
U(1) = N(2) U(1) = N(3)	2.595(3) 2 584(3)	U(2) = N(10)	2.587(3) 2 591(8)	LI(2) = O(20)	1.940(7)	LI(4)=O(12)	1.928(7)
O(1) - U(1) - O(2)	2.304(3)	17816(11)	2.391(0)	U(2)=O(3)=U(3)		173 0(3)	
O(3)-U(2)-O(4)		178 82(12)		U(2) - O(4) - Li(4)		175 4(3)	
N(1)-U(1)-N(2)		73.97(9)		O(1)-Li(1)-O(5)		102.8(3)	
N(2)-U(1)-N(3)		71.74(10)		O(1)-Li(1)-O(8)		106.7(3)	
N(3)-U(1)-N(4)		72.42(10)		O(1)-Li(1)-O(11)		105.5(3)	
N(4) - U(1) - N(5)		71.53(9)		O(2)-Li(2)-O(14)		104.9(3)	
N(5) - U(1) - N(1)		70.48(9)		O(2) - Li(2) - O(17)		107.4(3)	
N(6) - U(2) - N(7)		73.60(9)		O(2)-Li(2)-O(20)		107.2(3)	
N(7)-U(2)-N(8)		72.07(9)		O(3)-Li(3)-O(15)		107.8(3)	
N(8)–U(2)–N(9)		74.29(9)		O(3)-Li(3)-O(18)		107.2(3)	
N(9)-U(2)-N(10)		70.74(10)		O(3)–Li(3)–O(21)		107.6(3)	
N(10)–U(2)–N(6)		69.65(9)		O(4)-Li(4)-O(6")		104.3(3)	
U(1)-O(1)-Li(1)		178.2(3)		O(4)–Li(4)–O(9'')		105.1(3)	
U(1)-O(2)-Li(2)		176.2(2)		O(4)–Li(4)–O(12")		110.4(3)	
U(1)-O(2)-Li(2)		176.2(2)		O(4)–Li(4)–O(12")		110.4(3)	

Symmetry code: '' = x - 1, y, z.



Fig. 4 View of the polymeric arrangement in complex 8. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Symmetry codes: ' = x + 1, y, z; '' = x - 1, y, z.

with pentane, isolated as a beige powder which analyzes as  $[UO_2(OTf)(THF)_n]$  (9) (n = 1.5 or 2) in 84% yield.

Another route to a  $[UO_2(OTf)(L)_n]$  compound was considered by reacting  $[UO_2(OTf)_2]$  and 1 mol equivalent of LiCH<sub>2</sub>SiMe<sub>3</sub> in diethyl ether, and a pale brown powder analyzing as  $[UO_2(OTf)(Et_2O)_{0.5}]$  (10) was thus obtained in 80% yield. Complexes 9 and 10 are soluble in pyridine, and evaporation of the solution led to an ochre powder of the adduct  $[UO_2(OTf)(py)_2]$ (11). While reaction of  $[UO_2(OTf)_2]$  and  $TIC_5H_5$  in pyridine gave the trinuclear compound **6**·py, slow diffusion of pentane into a 1 : 1 mixture of  $[UO_2I_2(THF)_3]$  and  $TIC_5H_5$  in pyridine led to the precipitation of a yellow powder of thallium iodide and the formation of dark-orange crystals of  $[UO_2(py)_5][I]$ ·py (**12**·py). The same reaction in THF afforded, after elimination of TII by filtration and addition of pentane, a brown product which was dried under vacuum to give a powder analyzing as  $[UO_2I(THF)_{2.7}]$ (**13**) in 95% yield. Evaporation of a pyridine solution of **12** or



Scheme 2 Synthesis of the mononuclear uranyl(v) complexes.

13 gave a brown powder which analyzes as  $[UO_2I(py)_{2.5}]$  (14). Addition of excess KI into pyridine solutions of the mononuclear compounds 9–14 led to brown-orange solutions which deposited orange needles of the 1D polymer 1 after some days.

A view of the cation of **12** is shown in Fig. 5, selected bond distances and angles being listed in Table 4. This complex represents, after  $[UO_2(OPPh_3)_4]^+$ ,<sup>19</sup> a new example of a structurally characterized  $[UO_2(L)_n]^+$  ion. The structural parameters of the pentagonal bipyramidal complex, in particular the mean U–O distance of 1.83(1) Å, are similar to those of the  $[UO_2(py)_5]^+$  units in the polynuclear compounds **1** and **4–8**. It is noteworthy that, in contrast to the crystals of  $[UI_3(py)_4]$ ,<sup>35</sup>  $[UI_4(py)_3]^{36}$  and  $[UO_2I_2(py)_3]$ ,<sup>8</sup> those of the uranyl(v) iodide **12** are composed of



**Fig. 5** View of the cation in complex **12**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

discrete ion pairs, following pyridine substitution of the iodide ligand.

Attempts at growing crystals of other  $[UO_2(L)_n][X]$  or  $[UO_2X(L)_n]$  complexes (L = THF, MeCN, pyridine) by crystallization of the powders of  $[UO_2(OTf)(THF)_n]$  (9),  $[UO_2(OTf)(Et_2O)_{0.5}]$  (10),  $[UO_2(OTf)(py)_2]$  (11) or  $[UO_2I(THF)_{2.7}]$  (13) in the corresponding solvent have been unsuccessful. However, addition of KC<sub>5</sub>Me<sub>5</sub> into a 1 : 1 mixture of  $[UO_2(OTf)_2]$  and CyMe<sub>4</sub>BTBP<sup>37</sup> in pyridine led to the formation of dark brown-green crystals of the mononuclear compound  $[UO_2(CyMe_4BTBP)(py)][OTf] \cdot 1.5py$  (15·1.5py). The brown iodide derivative  $[UO_2I(CyMe_4BTBP)]$  (16) was isolated similarly, in 92% yield, from the treatment in THF of  $[UO_2I_2(THF)_3]$  and CyMe<sub>4</sub>BTBP with TIC<sub>5</sub>H<sub>5</sub>.

The crystal structure of **15** can be compared with that of the corresponding uranyl(v1) compound  $[UO_2(CyMe_4BTBP)-(py)][OTf]_2$ ,<sup>38</sup> thus providing a new pair of crystallographically characterized penta- and hexavalent uranyl complexes differing

 $Table 4 Selected bond lengths (Å) and angles (°) in [UO_2(py)_5][I] py (12 py), [UO_2(CyMe_4BTBP)(py)][OTf] 1.5 py (15 1.5 py) and [UO_2(OTf)(py)_4] (19) py (15 1.5 py) and [UO_2(OTf)(py)_4] py (15 1.5 py) and [UO_2(OTf$ 

12.pv							
U - O(1)	1.839(4)	U–N(1)	2.609(6)	U-N(3)	2.609(6)	U-N(5)	2.623(6)
U-O(2)	1.823(5)	U-N(2)	2.589(6)	U-N(4)	2.620(6)		
<u-0></u-0>	1.831(8)	<u-n></u-n>	2.61(1)				
O(1) - U - O(2)		179.5(2)		N(1)-U-N(2)		72.03(18)	
N(2) - U - N(3)		72.11(18)		N(3) - U - N(4)		70.92(19)	
N(4) - U - N(5)		72.78(18)		N(1) - U - N(5)		73.82(17)	
15.1.5py							
U - O(1)	1.816(4)	U–N(1)	2.562(4)	U-N(3)	2.611(4)	U-N(9)	2.533(4)
U-O(2)	1.822(4)	U-N(2)	2.606(4)	U-N(4)	2.570(4)		
<u-0></u-0>	1.819(3)	<u-n(btbp)></u-n(btbp)>	2.58(2)				
O(1) - U - O(2)		178.25(13)		N(1)-U-N(2)		62.48(12)	
N(2) - U - N(3)		63.14(12)		N(3) - U - N(4)		62.76(12)	
N(1) - U - N(9)		83.62(14)		N(4) - U - N(9)		88.05(14)	
19							
U–O(1)	1.831(6)	U–O(2)	2.525(8)	U–N(1)	2.605(6)	U–N(2)	2.590(5)
				<u-n></u-n>	2.59(1)		
O(1)-U-O(1')		177.3(3)		N(1)-U-N(2)		69.76(19)	
N(2)–U–N(2')		71.0(2)		N(1)–U–O(2)		74.85(14)	
Summatery and a '							

Symmetry code: ' = -x, y, 1.5 - z.

only by their electronic charge, after the  $[UO_2(OPPh_3)_4]^{n+}$  (n = 1, 1)2)<sup>19</sup> and  $[UO_2(Ar_2nacnac)(dbm)]^{n-}$  (*n* = 0, 1) couples.<sup>23</sup> However, the metrical parameters of the uranyl moieties in the mixed  $\beta$ -diketiminate/ $\beta$ -diketonate complexes are indistinguishable because of the low precision of the structure of the U(v) compound. Crystals of 15.1.5py are composed of discrete cation-anion pairs; a view of the cation is shown in Fig. 6 and selected bond distances and angles are presented in Table 4. The U(v) and U(vi) complexes adopt the same pentagonal bipyramidal configuration. In 15, the equatorial plane defined by the N1, N2, N3, N4 and N9 atoms (rms deviation of 0.035 Å) is perpendicular to the almost linear UO<sub>2</sub> fragment and forms a dihedral angle of 2.60(14)° with the planar CyMe<sub>4</sub>BTBP ligand (rms deviation of 0.117 Å for the aromatic rings). The average U–O and U–N(BTBP) distances of 1.819(3) and 2.58(2) Å are ca. 0.07 Å larger than the corresponding distances in the U(VI) analogue. This lengthening of the U=O bond, which is identical to that observed between the  $[UO_2(OPPh_3)_4]^{n+}$  (n = 1, 2) complexes, can be compared with the variation of 0.03 Å in the radii of the  $[UO_2]^{2+}$  and  $[UO_2]^+$  ions,<sup>31</sup> and with the difference of 0.1 Å between the U=O bond lengths in  $[UO_2(CO_3)_3]^{5-}$  and  $[UO_2(CO_3)_3]^{4-}$ , as measured by EXAFS.<sup>39</sup> It is noteworthy that the U=O bond lengths in 15 and its uranyl(VI) analogue correspond nicely to those calculated in  $[UO_2(H_2O)_5]^+$  (1.810 Å) and  $[UO_2(H_2O)_5]^{2+}$  (1.756 Å) using density functional theory and relativistic effective core potentials.<sup>17a</sup> These calculations also indicated that the elongation of the equatorial U- $O(H_2O)$  bonds would be larger than that of the axial U–O(oxo) bonds when passing from the  $U(v_1)$  to the U(v) compound. If such a difference was observed with the  $[UO_2(OPPh_3)_4]^{n+}$  (n =1, 2) complexes, where the  $U^{V}$ –O(OPPh<sub>3</sub>) distances are 0.14 Å larger than the U<sup>VI</sup>–O(OPPh<sub>3</sub>) distances, the similar lengthening of both the U-N(BTBP) bonds and U-O(oxo) bonds in 15 is likely related to the limited size of the cavity of the polydentate nitrogen ligand. The U-N1 and U-N4 distances of the lateral triazine groups (U-N<sub>1</sub>) average 2.566(4) Å and are 0.04 Å smaller than the mean  $U-N_c$  distance of 2.608(2) Å between the metal and the N2 and N3 atoms of the central pyridyl units. This trend, already observed in the U(VI) counterpart,<sup>38</sup> does not reflect the distinct Lewis basicities of the N<sub>c</sub> and N<sub>1</sub> atoms since a stronger interaction of the Lewis acidic group [UO<sub>2</sub>]<sup>2+</sup> would be expected with the stronger  $\sigma$ -donating nitrogen atoms of the central pyridyl groups. It can rather be ascribed to the cavity size of the rigid and



Fig. 6 View of the cation in complex 15. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

planar ligand as well as the size of the metal ions. Distinct Ln–N<sub>1</sub> and Ln–N<sub>c</sub> distances were also noticed in the series of lanthanide complexes [Ln(Et<sub>4</sub>BTBP)(NO<sub>3</sub>)<sub>3</sub>] (Ln = La–Lu), where the ratio Ln–N<sub>c</sub>/Ln–N<sub>1</sub> varies with Ln, being > 1 for the largest lanthanides (La–Eu), and < 1 for the heaviest elements (Dy–Yb).<sup>40</sup> The U–N(py) distance of 2.533(4) Å in **15** is 0.03 Å larger than that in the U(v<sub>I</sub>) analogue. This short U–N(py) bond, by comparison with those of the [UO<sub>2</sub>(py)<sub>5</sub>]<sup>+</sup> cation [2.59(1)–2.61(1) Å], could be related to the stronger Lewis acidity of the uranyl moiety induced by the weak σ-donating capacity of the BTBP ligand.

The synthesis of uranyl(v) complexes with chloride or nitrate counter ions was attempted with the aim to structurally characterize a mononuclear  $[UO_2X(L)_n]$  or  $[UO_2(L)_n][X]$  species (X = Cl, NO<sub>3</sub>). Two distinct routes to such compounds, either from uranyl(v1) or uranyl(v) precursors, were considered. Treatment of  $[UO_2Cl_2(THF)_2]_2$  or  $[UO_2(NO_3)_2(MeCN)]$  with 1 mol equivalent of TlC<sub>5</sub>H<sub>5</sub> in pyridine led to the precipitation of TlCl or TlNO<sub>3</sub> and formation of C<sub>5</sub>H<sub>6</sub> resulting from abstraction of a H atom of a THF molecule by the C<sub>5</sub>H<sub>5</sub> <sup>•</sup> radical. After usual work-up, the brown powder of  $[UO_2(NO_3)(py)_3]$  (17) was obtained in 89% yield. The nitrate analogue  $[UO_2(NO_3)(py)_3]$  (18) was isolated as a brown powder in 96% yield from the reaction of the uranyl(v) iodide  $[UO_2I(THF)_{2,7}]$  (13) with TlNO<sub>3</sub>. Crystallization of 17 and 18 did not afford crystals suitable for X-ray diffraction analysis.

 $Me_3SiC_5R_5$  as the reducing agent. Since reactions of  $UO_2X_2$  $(X = Cl, I, OTf, NO_3)$  with  $MC_5R_5$  (M = Li, K, Tl; R =H, Me) gave invariably uranyl(v) complexes, other routes to cyclopentadienyl uranyl(VI) compounds, precluding the use of the reducing anion  $C_5R_5^-$ , have been devised. Burns *et al.* attempted to introduce a C<sub>5</sub>Me<sub>5</sub> group in a uranyl species by protonolysis of the [U]-NR<sub>2</sub> bond of the amide compound  $[Na(THF)_2]_2[UO_2{N(SiMe_3)_2}_4]$  with  $C_5Me_5H$ .<sup>41</sup> This reaction led to the successful protonation of one of the silvlamido ligand, as shown by the formation of HN(SiMe<sub>3</sub>)<sub>2</sub>, but afforded the trisamido derivative [Na(THF)<sub>2</sub>][UO<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>], following elimination of NaC<sub>5</sub>Me<sub>5</sub>. Another approach is the treatment of a metal halide MX with a silvlated cyclopentadiene  $Me_3SiC_5R_5$  for giving  $MC_5R_5$  and  $Me_3SiX$ . This metathetical exchange reaction was successfully applied in d and f element chemistry,42 in particular for the synthesis of the U(IV) polynuclear compound  $[U_3(C_5H_5)_6Cl_5][U_2(C_5H_5)_2Cl_7]$  from UCl<sub>4</sub> and Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub>.<sup>42a</sup>

Reactions of  $UO_2X_2$  (X = Cl, I, OTf) and  $Me_3SiC_5R_5$  (R = H, Me) led to complicated mixtures of unidentified reduced products and did not afford cyclopentadienyl uranyl complexes nor represent interesting synthetic routes to uranyl(v) compounds. Treatment of [UO<sub>2</sub>(OTf)<sub>2</sub>] with 1 or 2 mol equivalents of Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> in acetonitrile-d<sub>3</sub> gave a green-yellow solution containing free cyclopentadiene; after heating, a brown powder was deposited from the green solution. Dissolution in pyridine-d<sub>5</sub> gave a clear solution the <sup>1</sup>H NMR spectrum of which showed signals of unidentified paramagnetic species at  $\delta$  72, 61 and 48 ppm. Similar reactions of [UO<sub>2</sub>I<sub>2</sub>(THF)<sub>3</sub>] or [UO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub>]<sub>2</sub> with  $Me_3SiC_5R_5$  (R = H, Me) also afforded, at room temperature, mixtures of unidentified complexes; the NMR spectra exhibit signals in the  $\delta$  50–60 ppm region. These spectra, which are similar to those of mixtures of  $UX_4$  (X = Cl, OTf) and NaOSiMe<sub>3</sub> (see Experimental), strongly suggest that uranium(IV) complexes with OSiMe<sub>3</sub> ligands were formed. These U<sup>IV</sup>-OSiMe<sub>3</sub> species would

Bond lengths/Å							
U–O(1) U–O(2)	1.767(3) 1.764(3)	U–N(1) U–N(2)	2.561(4) 2.588(4)	U–N(3) <u–n></u–n>	2.563(4) 2.57(1)	U–Cl(1) U–Cl(2)	2.7338(12) 2.6926(12)
Bond angles/°							
O(1)-U-O(2) N(1)-U-Cl(1) N(1)-U-Cl(2)		177.36(14) 74.77(9) 73.74(9)		N(2)–U–N(3) N(2)–U–Cl(1) N(3)–U–Cl(2)		66.36(12) 74.45(9) 74.41(9)	

Table 5	Selected	bond	lengths (	(Å)	and angles	$(^{\circ})$	in	IUO-	$Cl_{r}$	w),1	
rabic 5	Sciected	oonu	lenguis	(n)	and angles	U	m	[002	$2C_{12}$	<i>y j</i> 3]	

result from the reductive silylation of the uranyl oxo groups, a process which was recently illustrated with the formation of the uranium(v) compound [UO(OSiMe<sub>3</sub>)(THF)(M<sub>2</sub>I<sub>2</sub>)(L)] (M = Fe, Zn; H<sub>4</sub>L = polypyrrolic macrocycle) from [UO<sub>2</sub>(THF)(H<sub>2</sub>L)].<sup>43</sup> However, during one attempt at crystallization of the crude reaction mixture containing [UO<sub>2</sub>Cl<sub>2</sub>(THF)<sub>2</sub>]<sub>2</sub> and Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> in pyridine-Et<sub>2</sub>O, crystals of [UO<sub>2</sub>Cl<sub>2</sub>(py)<sub>3</sub>] were obtained (Table 5).

Attempts to isolate any product from these reactions of  $UO_2X_2$ and  $Me_3SiC_5R_5$  were unsuccessful, except in the case of X = OTfand R = H, where crystallization of the reaction mixture from pyridine-pentane gave a few red crystals of  $[UO_2(OTf)(py)_4]$  (19) together with yellow crystals of  $[UO_2(OTf)_2(py)_3]$ . These results indicate that  $Me_3SiC_5R_5$  is able to reduce uranyl(v1) complexes, as it is the case with the  $Me_3SiX$  reagents which are efficient in the reduction of  $[UO_2I_2(THF)_3]$  or  $[UO_2(OTf)_2]$  into the uranium(Iv) derivatives  $[UX_4(MeCN)_4]$  (X = Cl, Br, I).<sup>44</sup>

Complex 19 is, after  $[UO_2(Ar_2nacnac)(Ph_2MePO)_2]$ , a novel example of a neutral mononuclear complex of uranyl(v) to have been crystallographically characterized. A view of 19 is shown in Fig. 7, while selected bond distances and angles are listed in Table 4. The uranium atom is found in the classical pentagonal bipyramidal configuration, with the linear UO<sub>2</sub> fragment perpendicular to the equatorial plane defined by four nitrogen atoms of the pyridine ligands and one oxygen atom of the monodentate



**Fig. 7** View of complex **19**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted. Only one position of the disordered atoms is represented. Symmetry code: ' = -x, y, 1.5 - z.

triflate ligand. The U–O(oxo) bond length of 1.831(6) Å is quite identical to those measured in the [UO<sub>2</sub>(py)<sub>5</sub>]<sup>+</sup> cations and can be compared with that of 1.82(1) Å in the octahedral compound [UO<sub>2</sub>(Ar<sub>2</sub>nacnac)(Ph<sub>2</sub>MePO)<sub>2</sub>];<sup>22</sup> this distance is expectedly larger than that of 1.745(2) Å in  $[UO_2(OTf)_2(py)_3]$ .<sup>6</sup> The U–O(OTf) and mean U-N distances of 2.525(8) and 2.59(1) Å are 0.14 and 0.06 Å larger than in the uranyl(VI) complex (2.38(1) and 2.53(1) Å), respectively. The mean U–N(py) distance in 19 is similar to those found in the [UO<sub>2</sub>(py)<sub>5</sub>]<sup>+</sup> cation in the variety of complexes described here [2.58-2.61 Å] and close to that determined in the U(VI) complex  $[UO_2Cl_2(py)_3]$  [2.57(1) Å]. It must be underlined that the difference between the equatorial U-O distances in the U(v)/U(vi) counterparts is much more important than that between the U-N distances. Thus, the variation of 0.14 Å in the mean U–O(OTf) distances of 19 and  $[UO_2(OTf)_2(py)_3]$  is identical to that measured in the mean U-O(OPPh<sub>3</sub>) distances in the  $[UO_2(OPPh_3)_4]^{n+}$  compounds.

#### Infrared spectra of the complexes

The IR spectra of the uranyl(v) complexes in Nujol mulls exhibit medium to strong peaks in the 800-850 cm<sup>-1</sup> region, corresponding to the asymmetric stretch  $v_{asym}$  (U=O); these frequencies are expectedly lower than those of 905–980 cm<sup>-1</sup> observed for the uranyl(VI) compounds, in agreement with the more electron-rich 5f<sup>1</sup> species and the longer U=O bonds. In particular, the  $v_{asym}$ (U=O) of  $801 \text{ cm}^{-1}$  for  $[UO_2I(CyMe_4BTBP)]$  (16) is 144 cm<sup>-1</sup> lower than that observed for the parent cationic uranyl(VI) complex.<sup>38</sup> This value is at the upper limit of the range of the differences between the  $v_{asym}$ (U=O) for penta- and hexavalent uranyl complexes differing only by their electronic charge, which vary from 58 cm<sup>-1</sup> for  $[UO_2(Ar_2nacnac)(CF_3COCHCOCF_3)]^{n-}$   $(n = 0, 1)^{23}$  to 131 cm<sup>-1</sup> for  $[UO_2(dbm)_2(dmso)]^{n-}$  (n = 0, 1).<sup>24c</sup> A decrease of 145 cm<sup>-1</sup> was also observed in the wave number of the  $v_{asym}(Np=O)$  with the reduction of [NpO<sub>2</sub>]<sup>2+</sup> into [NpO<sub>2</sub>]<sup>+</sup> in aqueous solution.<sup>45</sup> The  $v_{asym}$ (U=O) values are in the range of the  $v_{asym}$ (Np=O) in neptunyl(v) compounds;<sup>26c,45</sup> for example, this value is 826 cm<sup>-1</sup> for [NpO<sub>2</sub>(OPPh<sub>3</sub>)<sub>4</sub>][ReO<sub>4</sub>].<sup>46</sup> The uranyl(v) absorption bands are broader than those of uranyl(VI). This feature was explained by the lower bending frequency for the  $[UO_2]^+$  ion, which is of the order of  $kT_{298}$ , leading to thermal excitation of a large proportion of the ions to excited states of the bending vibration, thus broadening the absorption maximum.45

Variations in the  $v_{asym}(U=O)$  of the  $[UO_2XL_n]$  and  $[UO_2(py)_nMX_2]$  species (X = I, OTf, Cl; L = py, THF, Et<sub>2</sub>O; M = K, Li, Tl) in Nujol mulls are difficult to interpret because of the



Fig. 8 IR spectra of the uranyl(VI) compounds in pyridine solution.



Fig. 9 IR spectra of the uranyl(v) compounds in pyridine solution.

undetermined coordination of the uranyl moiety in the desolvated compounds, with likely the presence of bridging iodide and triflate ligands in various ligation modes and U=O $\rightarrow$ M or U=O $\rightarrow$ U interactions. The IR spectra of the uranyl(v) and (vI) compounds in pyridine are shown in Fig. 8 and 9, respectively. The  $v_{asym}$  (U=O) for the  $[UO_2X_2(py)_3]$  (X = I, Cl, OTf) and  $[UO_2(NO_3)_2(py)_2]$ complexes, which range from 924-934 cm<sup>-1</sup>, decrease in the order  $OTf > NO_3 \sim I > Cl$ , reflecting the increasing electron donating capacity of X. The uranyl(v) iodide and triflate complexes exhibit a  $v_{asym}$ (U=O) of 816 cm<sup>-1</sup>, except those of general formula  $[UO_2(OTf)L_n]$  (L = py, THF, Et<sub>2</sub>O) which display a  $v_{asym}(U=O)$ of 812 cm<sup>-1</sup>. These two absorption bands can be respectively attributed to  $[UO_2(py)_5]^+$ , in view of the ubiquity of this cation in the crystals of compounds with X = I and/or U=O $\rightarrow$ MX interactions (X = I, OTf), and to  $[UO_2(OTf)(py)_4]$  (19), which crystallized from pyridine.

The IR spectra in pyridine of the uranyl(v) chloride and nitrate  $[UO_2X(py)_3]$  [X = Cl (17) or NO<sub>3</sub> (18)] display broad bands at *ca.* 810 cm<sup>-1</sup> (Fig. 10 and 11). However, the peak at 924 cm<sup>-1</sup> indicates that the uranyl(v) chloride is contaminated with its U(v1) precursor. This easier U<sup>v</sup>  $\rightarrow$  U<sup>v1</sup> oxidation for X = Cl by comparison with X = I, OTf and NO<sub>3</sub>, could be related to the

greater electron donating ability of the chloride ligand, giving a more electron-rich complex, as seen by the  $v_{asym}$ (U=O) of 924 cm<sup>-1</sup>, which is lower than those of the other uranyl(v1) compounds.

#### Discussion

Reactions of uranyl(VI) complexes with the alkali metal and thallium salts of the  $C_5R_5^-$ ,  $C_8H_8^-$ ,  $C_4Me_4P^-$  and  $Me_3SiCH_2^-$  anions do not afford organometallic compounds but represent convenient routes to pentavalent uranyl complexes, which proved stable with respect to disproportionation, in contrast to what is observed in aqueous solutions. These results further point up the necessary use of strictly anhydrous and anaerobic experimental conditions for the development of this uranyl chemistry. The only other examples of controlled  $[UO_2]^{2+} \rightarrow [UO_2]^+$  chemical reduction leading to stable and isolated compounds are given by the synthesis of the  $\beta$ -diketiminate complexes  $[UO_2(Ar_2nacnac)(Ph_2MePO)_2]^{22}$ and  $[UO_2(Ar_2nacnac)(RCOCHCOR)]^-$  (R = Me, Ph, CF<sub>3</sub>)<sup>23</sup> by treatment of the uranyl(VI) precursors with  $[Co(C_5R_5)_2]$ . It was previously observed that reactions of  $[UO_2Cl_2]$  with a variety of alkyllithium and Grignard reagents in organic solvents gave brown-orange solutions of unidentified compounds, presumably



Fig. 10 IR spectra of the uranyl(v) nitrate in pyridine solution. Pink curve: from the in situ reaction of  $UO_2(NO_3)_2 + TIC_3H_5$ . Blue curve: from the in situ reaction of  $UO_2I_2 + TIC_3H_5 + TINO_3$ .



Fig. 11 IR spectra of the uranyl(v) chloride in pyridine solution.

unstable  $UO_2R_2$  species which decompose into  $UO_2$  with elimination of the R–R coupling product or a mixture of the alkane RH and alkene R(–H) molecules; the possible involvement of uranyl(v) complexes in these reactions was not considered.<sup>13</sup>

With the exception of  $[UO_2(OTf)(py)_4]$  (19) and the BTBP adduct 15, all the pentavalent uranyl complexes crystallographically characterized in this work contain the cationic  $[UO_2(py)_5]^+$ moiety. The average U-O distance of 1.82-1.83 Å in this species is similar to that measured in the few other uranyl(v) complexes and the variety of neptunyl(v) compounds,  $^{\rm 26c,45}$  being 0.07 Å larger than the typical U-O distance in uranyl(VI) compounds. This lengthening goes together with the decrease of the  $v_{asym}(U=O)$ by ca. 110 cm<sup>-1</sup>, reflecting the weakening of the U=O bond due to the reduced charge on the metal ion and the destabilizing effect of the single 5f electron. Uranyl(v) complexes will therefore exhibit, by comparison with the U(VI) counterparts, a weaker Lewis acidic character of the metal centre and a stronger Lewis basicity of the oxo goups. This difference explains why uranyl(v) complexes are so easily desolvated under vacuum, leading to the formation of apparently coordinatively unsaturated compounds like  $[UO_2(py)_{2.2}KI_2]$  (1) or  $[UO_2(OTf)(Et_2O)_{0.5}]$  (10). These compounds are likely polymeric in the solid state, their structure being ensured by bridging iodide or triflate ligands and U=O→M interactions. The involvement of the  $[UO_2]^+$  ion in such so-called cation–cation interactions, *via* one or two oxo groups, is clearly favored by the Lewis basicity of the U=O oxygen atoms.

The diversity of structures of the complexes with  $O=U=O \rightarrow M$ interactions (M = Li, K), from the simplest dinuclear compound 7 to the 3D coordination polymer 4, is obviously related to the basicity of the U=O oxygen atoms, but also the distinct coordination numbers of the Li<sup>+</sup> and K<sup>+</sup> ions, and the distinct ligation modes of the triflate and iodide ligands. Depending on the nature of the solvent, M<sup>+</sup> and the counterion X<sup>-</sup>, it is likely that the complexes of the  $[UO_2]^+$  ion may exist under various forms as revealed by the crystallization of both the polymeric compound 4 and the trinuclear complex 5 from the same solution. However, crystallization of 5 and 6, whereas the iodide analogue 1 is a 1D polymer in the solid state, is difficult to explain.

There is no significant difference between the two U–O distances of the O=U=O $\rightarrow$ M fragments (M = K, Tl) in complexes 4–6, while

in uranyl(VI) complexes like [Na(THF)<sub>2</sub>][UO<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>]<sup>41</sup> and  $[Na(THF)_{2}(PhCN)_{0.5}][UO_{2}(NCN)_{3}]$   $[NCN = PhC(NSiMe_{3})_{2}]^{47}$ the bridging U-O(Na) bond is 0.03 Å longer than the U-O(terminal) bond. The lengthening of the An-O(bridging) versus An-O(terminal) bond in cation-cation complexes of neptunyl(v) and uranyl(vi) with An= $O \rightarrow An$  interactions is typically equal to 0.04 Å and as large as 0.1 Å in the trimeric complex [UO<sub>2</sub>(CF<sub>3</sub>COCHCOCF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>.<sup>48</sup> In the tetrameric complex of pentavalent uranyl  $[{UO_2(dbm)_2}_4 {K_6(py)_{10}}]^{2+}$ , which exhibit  $K \leftarrow O=U=O \rightarrow U$  fragments, the mean U-O(K) distances of 1.82(1) Å is similar to that measured in 4-6, but is 0.11 Å smaller than the U-O distance for the oxo group coordinated to a vicinal uranyl moiety.<sup>21</sup> These observations would indicate that in pentavalent as well as in hexavalent uranyl complexes with  $O=U=O \rightarrow M$  interactions, the U-O bond lengths are less unsymmetrical with M = alkali metal than with M = U in di- or oligomeric complexes.

While various heteronuclear uranyl(v) complexes with an  $O=U=O \rightarrow M$  interaction (M = Li, K, Tl) were characterized, no such homonuclear compound with  $M = UO_2$  was identified. This is perhaps not surprising in view of the remarkable stability, in the solid state or in solution, of all the uranyl(v) compounds isolated in this work, since it was demonstrated that the formation of such inner-sphere cation–cation ( $[UO_2]^+/[UO_2]^+$ ) complexes is likely responsible for the disproportionation of pentavalent uranyl into U<sup>IV</sup> and U<sup>VI</sup> species.<sup>16,49</sup> The sole uranyl(V) complex exhibiting an  $O=U=O\rightarrow UO_2$  interaction in the solid state is the electron-rich species  $[{UO_2(dbm)_2}_4{K_6(py)_{10}}]^{2+}$ , which retains its tetrameric structure in pyridine solution where it rapidly decomposes, and which is transformed in DMSO into a more stable monomeric species.<sup>21</sup> The bulky Ar<sub>2</sub>nacnac ligand, which provides steric protection along the uranyl equatorial plane and also along the O=U=O axis, was used to stabilize the  $[UO_2]^+$  ion against disproportionation by blocking its dimerization via cation-cation interaction. However, the isolated compounds [UO2(Ar2nacnac)(Ph2MePO)2] and  $[UO_2(Ar_2nacnac)(RCOCHCOR)]^-$  (R = Me, Ph, CF<sub>3</sub>) were found to decompose in CH<sub>2</sub>Cl<sub>2</sub> or THF, likely following ligand exchange reactions with the solvent.<sup>22,23</sup> The stability in pyridine solution of the uranyl(v) complexes presented here could be related to the strong U-py interaction in the electron-poor  $[UO_2(py)_5]^+$ and  $[UO_2(py)_5(OTf)]$  species, preventing ligand dissociation and formation of a dimeric cation-cation complex. In these compounds, the uranyl oxo groups are apparently insufficiently basic to compete with the pyridine solvent of the  $[UO_2(py)_5]^+$  moiety while they can bind to the Li<sup>+</sup> or K<sup>+</sup> ions which certainly display weaker M-py<sup>+</sup> interaction. Furthermore, the synthesis and relative stability of the iodide and triflate uranyl(v) complexes  $[UO_2X(THF)_n]$  9 and 13 in THF demonstrate that bulky or strongly coordinating ligands are not prerequisite to the stability of the  $[UO_2]^+$  ion. It seems patent that the electron richness of the uranyl(v) complexes has a major influence on their reactivity. By comparison with the aforementioned complexes which are anionic and/or contain the strongly electron-donating  $\beta$ -diketiminate and  $\beta$ -diketonate ligands, the uranyl(v) compounds under study have a lesser electron density and their stability could be related to their lesser propensity to both ligand dissociation and disproportionation via a  $O=U=O \rightarrow UO_2$  intermediate. Such an electronic effect is reminiscent of that found in the electron-rich uranyl(VI)

alkoxides where the presence of cation-cation interactions led to the formation of aggregates or induced unusual reactivity of the U=O bond.<sup>25g</sup>

#### Conclusion

Whereas  $[U(NR)_2]^{2+}$ , an imido analogue of the uranyl ion, readily gives the stable organouranium(VI)  $U(NR)_2(C_3R_5)_2$  and  $UI(NR)_2(C_3R_5)$  derivatives in its reaction with the  $C_3R_5^-$  anion (R = H, Me),<sup>5b</sup> treatment of the uranyl(VI) compounds  $[UO_2X_2]$  $(X = I, Cl, OTf, NO_3)$  with the alkali metal salts of a variety of organometallic anions such as  $KC_3R_5$  (R = H, Me),  $TIC_5H_5$ ,  $KC_4Me_4P, K_2C_8H_8$  and  $LiCH_2SiMe_3$  or the neutral silane molecule  $Me_3SiC_5R_5$  (R = H, Me) permit the convenient and efficient chemical reduction of the  $[UO_2]^{2+}$  ion into stable pentavalent uranyl(v) complexes, which are potential precursors for further developments in uranium(v) chemistry. Reactions of  $[UO_2X_2]$  with the neutral silane molecules  $Me_3SiC_5R_5$  (R = H, Me) do not represent a synthetic route to cyclopentadienyl uranyl complexes or  $[UO_2]^+$  compounds.

The distinct coordination numbers of the metal ion in the reducing agents (M = Li, K, Tl), the various ligation modes of the bridging iodide and triflate ligands and the involvement of the uranyl fragment in O=U=O→M interactions led to a rich diversity in the crystal structures of the uranyl(v) complexes, from mononuclear compounds to heteronuclear 3D polymers. The dinuclear compound [ $\{UO_2(py)_5\}$  {LiI(py)<sub>2</sub>}][I] (7) is a unique example of a pentavalent uranyl complex with a single O=U=O→M interaction, while [ $UO_2(py)_5$ ][I] (12) and [ $UO_2(OTf)(py)_4$ ] (19) are the simplest mononuclear uranyl(v) compounds to have been isolated and characterized.

The remarkable stability towards disproportionation of all these uranyl(v) complexes in pyridine solution, where the  $[UO_2(py)_s]^+$  ion appears to be an ubiquitous entity, and the stability of  $[UO_2X(THF)_n](X = I, OTf)$  in THF, likely related to the absence of a cation–cation  $O=U=O \rightarrow UO_2$  interaction, clearly show that pentavalent uranyl compounds can be isolated from various organic media and not only, as generally believed, with a restricted choice of suitably bulky equatorial ligands. Such convenient access to  $[UO_2]^+$  species would induce further developments in the chemistry of uranium(v) and favour better understanding of the chemical behaviour of the stable but highly radioactive  $[AnO_2]^+$  ions (An = Np, Pu, Am).

#### Experimental

All experiments were carried out under ultra high purity argon atmosphere with rigorous exclusion of air and water (less than 2 ppm oxygen and 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. Deuterated acetonitrile, THF and pyridine (Eurisotop) were distilled over NaH and acetonitrile was then stored over 3 Å molecular sieves. The <sup>1</sup>H NMR spectra, given for a temperature of 23 °C, were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane ( $\delta 0$  ppm). The IR spectra of the complexes in pyridine solution or in Nujol mulls between KBr round cell windows were recorded on a Perkin-Elmer FT-IR 1725X spectrometer. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

UCl<sub>4</sub>,<sup>50</sup> U(OTf)<sub>4</sub>,<sup>51</sup> [UO<sub>2</sub>(OTf)<sub>2</sub>],<sup>6</sup> [UO<sub>2</sub>I<sub>2</sub>(THF)<sub>3</sub>],<sup>8</sup> [UO<sub>2</sub>Cl<sub>2</sub>-(THF)<sub>2</sub>]<sub>2</sub><sup>7</sup> and [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(MeCN)]<sup>52</sup> were prepared as previously described. MC<sub>5</sub>Me<sub>5</sub> (M = Li, K) and KC<sub>5</sub>H<sub>5</sub> were prepared by treating C<sub>5</sub>Me<sub>5</sub>H or freshly distilled C<sub>5</sub>H<sub>6</sub> (Aldrich) with Li in Et<sub>2</sub>O or KH in THF at room temperature. K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>,<sup>53</sup> KC<sub>4</sub>Me<sub>4</sub>P,<sup>54</sup> TlC<sub>5</sub>H<sub>5</sub><sup>55</sup> and Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub><sup>56</sup> were obtained as previously described; Me<sub>3</sub>SiC<sub>5</sub>Me<sub>5</sub> (Aldrich) was degassed and dried over molecular sieves under argon, NaOSiMe<sub>3</sub> (Aldrich) was used after drying under vacuum. The solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (1.0 M in pentane, Aldrich) was evaporated to dryness to give a white powder which was stored under argon.

#### Synthesis

[{UO<sub>2</sub>(py)<sub>5</sub>}{KI<sub>2</sub>(py)<sub>2</sub>}]<sub>∞</sub> (1). An NMR tube was charged with [UO<sub>2</sub>I<sub>2</sub>(THF)<sub>3</sub>] (10.0 mg, 13.5 μmol) and KC<sub>5</sub>R<sub>5</sub> (R = H: 2.26 mg, 13.5 μmol; R = Me: 3.1 mg, 13.5 μmol) in pyridine-d<sub>5</sub> (0.4 mL). The reaction mixture was heated at 100 °C for 2 h and thin orange needles of 1 suitable for X-ray diffraction were deposited in a few hours upon cooling to room temperature. The <sup>1</sup>H NMR spectrum of the solution showed the formation of C<sub>5</sub>H<sub>6-n</sub>D<sub>n</sub> or (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>. δ (C<sub>5</sub>D<sub>5</sub>N, 23 °C) for C<sub>5</sub>H<sub>6</sub>:6.63 (br, CH, 2H), 6.49 (br, CH, 2H), 2.92 (br, CH<sub>2</sub>, 2H), for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>:1.74 (s, 6H), 1.68 (s, 6H), 1.14 (s, 3H). The same reaction with K<sub>2</sub>C<sub>8</sub>H<sub>8</sub> (0.5 mol equivalent) in place of KC<sub>5</sub>R<sub>5</sub> also gave crystals of 1 and the NMR spectrum showed the formation of C<sub>8</sub>H<sub>8</sub> characterized by a singlet at δ 5.8 ppm.

**[UO<sub>2</sub>(py)<sub>2.2</sub>KI<sub>2</sub>] (2).** (a) Pyridine (15 mL) was condensed at -70 °C under vacuum into a 50 mL round bottom flask containing  $[UO_2I_2(THF)_3]$  (250 mg, 0.33 mmol) and KC<sub>5</sub>Me<sub>5</sub> (59 mg, 0.33 mmol). The orange suspension was stirred for 2 h at room temperature and after condensation of THF (5 mL), the orange powder was filtered off. During drying under vacuum (20 h at 23 °C), the colour of the powder turned from bright orange to ochre (200 mg, 80%). (Found: C 18.03, H 1.48; N 4.24; I 34.66.  $C_{11}H_{11}I_2KN_{2.2}O_2U$  requires C 17.93, H 1.50; N 4.34; I 34.44%). IR (Nujol) v/cm<sup>-1</sup>: 1378 s, 1216 w, 1152 w, 1066 m, 1038 m, 1007 m, 922 w, 797 vs [ $v_{asym}$  (U=O)], 754 s, 701 vs, 626 m. IR (pyridine) v/cm<sup>-1</sup>: 816 s [ $v_{asym}$  (U=O)]. The same reaction with 1 mol equivalent of KC<sub>5</sub>H<sub>5</sub> or 0.5 mol equivalent of K<sub>2</sub>C<sub>8</sub>H<sub>8</sub> gave identical results. Slow diffusion of diethyl ether into a pyridine solution of **2** gave crystals of **1**.

(b) An NMR tube was charged with  $[UO_2I_2(THF)_3]$  (10.0 mg, 0.013 mmol) and KC<sub>5</sub>Me<sub>5</sub> (2.3 mg, 0.013 mmol) in THF-d<sub>8</sub> (0.5 mL) The tube was immersed in an ultrasound bath for 30 min affording a brown solution and a white precipitate. The NMR spectrum showed the presence of  $(C_5Me_5)_2$ .

 $[UO_2(py)_{2.3}K(OTf)_2]$  (3). (a) Pyridine (20 mL) was condensed in a 50 mL round bottom flask containing  $[UO_2(OTf)_2]$  (2000 mg, 3.52 mmol) and  $KC_5Me_5$  (613.6 mg, 3.5 mmol). After stirring for 15 h at room temperature, the volume of the brown orange solution was reduced to 10 mL. Addition of diethyl ether (50 mL) led to the precipitation of a brown powder, which was filtered off; its colour turned beige upon drying under vacuum for 20 h at 25 °C (2480 mg, 91%). (Found C 20.33, H 1.53; N 4.30; F 14.35.  $C_{12.5}H_{11.5}F_6KN_{2.3}O_8S_2U$  requires C 20.54, H 1.47; N 4.08; F 14.44%) IR (Nujol) v/cm<sup>-1</sup>: 1637 w, 1603 s, 1260 (broad, vs), 1208 s, 1177 s, 1069 m, 1033 vs, 927 w, 890 m, 793 s shoulder [ $v_{asym}$  (U=O)], 757 vs, 701 s, 636 vs, 581 m, 518 m. IR (pyridine) v/cm<sup>-1</sup>: 816 s [ $v_{asym}$  (U=O)].

(b) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 0.017 mmol) and  $KC_5Me_5$  (3.1 mg, 0.017 mmol) in pyridine- $d_5$  (0.3 mL). After 10 h at 20 °C, the spectrum showed the formation of  $(C_5Me_5)_2$ .

 $[{UO_2(py)_5}_2 {K_3(OTf)_5} \cdot py]_{\infty}$  (4·py). (a) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) and KC<sub>5</sub>R<sub>5</sub> (R = H: 1.8 mg, 17.6 µmol; R = Me: 2.5 mg, 17.6 µmol) in pyridine (0.4 mL). After 24 h at 20 °C, pentane (1 mL) was added to the brown solution, leading to the formation of orange crystals of 4-py.

(b) An NMR tube was charged with  $[UO_2(OTf)_2]$  (7.9 mg, 14.0 µmol) and KC<sub>4</sub>Me<sub>4</sub>P (2.5 mg, 14.0 µmol) in pyridine (0.4 mL). After 24 h at 100 °C, the brown solution was cooled to room temperature and addition of pentane (1.5 mL) led to the formation of orange crystals of 4 py.

 $[{UO_2(py)_5}_2{M(OTf)_2(py)_2}][OTf] py (M = K, 5 py; M = Tl, 6 py). (a) An NMR tube was charged with <math>[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) and KC<sub>4</sub>Me<sub>4</sub>P (3.1 mg, 17.6 µmol) in THF (0.4 mL). After 30 min at room temperature, the brown solution was evaporated to dryness. The residue was dissolved in pyridine (0.4 mL) affording a clear orange solution in which pentane (1.5 mL) was slowly diffused. Large orange crystals of 5 py were obtained after 5 d at 20 °C, together with orange crystals of 4 py.

(b) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) and TlC<sub>3</sub>H<sub>5</sub> (4.7 mg, 17.6 µmol) in pyridine (0.5 mL). The tube was immersed in an ultrasound bath (80 W, 40 kHz) for 24 h. Slow diffusion of pentane (1.5 mL) into the dark brown solution gave dark orange crystals of **6**·py (7.8 mg, 40%).

 $[{UO_2(py)_5}{Lil(py)_2}][I]$  (7). (a) An NMR tube was charged with  $[UO_2I_2(THF)_3]$  (10.0 mg, 13.5 µmol) in pyridine (0.4 mL) and LiCH<sub>2</sub>SiMe<sub>3</sub> (15.3 mg, 16.3 µmol) was added *via* a microsyringe. After 24 h at 20 °C, the red solution was evaporated to dryness and the red powder was washed with pentane (2 mL). The powder was dissolved in pyridine (0.5 mL) and slow diffusion of pentane (2 mL) into the solution led to the formation of dark orange crystals of 7 (4.7 mg, 32%).

(b) An NMR tube was charged with  $[UO_2I_2(THF)_3]$  (10.0 mg, 13.5 µmol) and LiC<sub>5</sub>Me<sub>5</sub> (1.9 mg, 13.5 µmol) in pyridine-d<sub>5</sub> (0.4 mL). After 24 h at 20 °C, the NMR spectrum of the red solution showed the presence of  $(C_5Me_5)_2$ . Slow diffusion of pentane (2 mL) into the solution led to the formation of dark orange crystals of 7 (5.0 mg, 34%). IR (pyridine) v/cm<sup>-1</sup>: 816 s [ $v_{asym}$  (U=O)].

 $\{UO_2(py)_5\}$   $\{Li_2(OTf)_3\}\$  (8). (a) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) and LiCH<sub>2</sub>SiMe<sub>3</sub> (16.5 mg; 17.6 µmol) in acetonitrile (0.4 mL). After stirring for 24 h at 20 °C, the dark brown solution was evaporated to dryness, leaving a brown powder which was washed with pentane (2 mL). The powder was dissolved in pyridine (0.4 mL) and slow diffusion of pentane (2 mL) into the solution led to the formation of light green crystals of 8 (5.9 mg, 30%).

(b) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) and LiC<sub>5</sub>Me<sub>5</sub> (2.2 mg, 17.6 µmol) in pyridine-d<sub>5</sub>

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(0.4 mL). After 48 h at 20 °C, the NMR spectrum of the red solution showed the presence of  $(C_5Me_5)_2$ . Slow diffusion of pentane (2 mL) into the solution led to the formation of light green crystals of **8** (6.9 mg, 35%). IR (pyridine) v/cm<sup>-1</sup>: 816 s [ $v_{asym}$  (U=O)].

**[UO<sub>2</sub>(OTf)(THF)<sub>n</sub>] (9).** (a) n = 1.5. A flask was charged with [UO<sub>2</sub>(OTf)<sub>2</sub>] (300 mg, 0.53 mmol) and KC<sub>5</sub>Me<sub>5</sub> (92.0 mg, 0.53 mmol) and THF (20 mL) was condensed in it. The suspension was stirred at 20 °C for 15 h, affording a brown solution with a white precipitate of KOTf. After filtration, two extractions from the salts with a 1.5 : 1 mixture of toluene–THF (25 mL) and evaporation of the solvents afforded a brown powder, which was recrystallized from a 1 : 4 mixture of THF–pentane (25 mL). The beige powder was then dried under vacuum for 15 h at room temperature. (233 mg, 84%). (Found C 16.32, H 2.14, F 10.44. C<sub>7</sub>H<sub>12</sub>F<sub>3</sub>O<sub>6.5</sub>SU requires C 15.95, H 2.29, F 10.81%). IR (Nujol) v/cm<sup>-1</sup>: 1332 vs, 1236 vs, 1202 vs, 1024 vs, 947 s, 920 m, 853, 847 vs [ $v_{asym}$  (U=O)], 681 s, 634 vs, 586 m, 513 s. IR (pyridine) v/cm<sup>-1</sup>: 812 m [ $v_{asym}$  (U=O)].

(b) n = 2. By following a procedure similar to that in (a), the reaction of  $[UO_2(OTf)_2](306 \text{ mg}, 0.54 \text{ mmol})$  and  $KC_5H_5$  (58.0 mg, 0.55 mmol) gave a beige powder which was dried for 10 h at 20 °C (220 mg, 72%). (Found C 19.03, H 2.43, F 9.88. C<sub>9</sub>H<sub>16</sub>F<sub>3</sub>O<sub>7</sub>SU (563.31) requires C 19.19, H 2.86, F 10.12%). IR (Nujol) v/cm<sup>-1</sup>: 1337 vs, 1237 s, 1202 vs, 1013 vs, 949 s, 885 w, 851 vs [ $v_{asym}$  (U=O)], 829 m, 679 m, 635 vs, 586 w, 513 m. IR (pyridine) v/cm<sup>-1</sup>: 812 m [ $v_{asym}$  (U=O)].

(c) An NMR tube was charged with  $[UO_2(OTf)_2]$  (15.0 mg, 0.026 mmol) and  $KC_5Me_5$  (4.6 mg, 0.026 mmol) in THF-d<sub>8</sub> (0.4 mL). After 10 h at 20 °C, the <sup>1</sup>H NMR spectrum showed the signals of the dimer ( $C_5Me_5$ )<sub>2</sub> ( $\delta$  1.77 (s, 6H), 1.65 (s, 6H), 1.07 (s, 3H)). Evaporation of the volatiles and dissolution of the residue in pyridine-d<sub>5</sub> showed only the presence of the dimer ( $C_5Me_5$ )<sub>2</sub>.

(d) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.2 mg, 0.018 mmol) and  $KC_5H_5$  (1.9 mg, 0.018 mmol) in THF-d<sub>8</sub> (0.4 mL). After 10 h at 20 °C, the spectrum showed the formation of  $C_5H_{6-n}D_n$ .  $\delta$  (C<sub>4</sub>D<sub>8</sub>O, 23 °C) 6.51 (br, CH, 2H), 6.38 (br, CH, 2H), 2.92 (br, CH<sub>1-n</sub>).

**[UO<sub>2</sub>(OTf)(Et<sub>2</sub>O)<sub>0.5</sub>] (10).** A solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (85.0 mg, 0.90 mmol) in Et<sub>2</sub>O (10 mL) was added into a flask containing a yellow suspension of  $[UO_2(OTf)_2]$  (510 mg, 0.89 mmol) in Et<sub>2</sub>O (15 mL). The immediately formed brown suspension was stirred for 90 min at 20 °C. After evaporation to dryness, the product was extracted by the Soxhlet method with diethyl ether (40 mL). The volume of the solution was reduced to 15 mL and addition of pentane (30 mL) led to the precipitation of a pale brown powder which turned beige after 15 h drying under vacuum at 25 °C (330 mg, 80%). (Found C 7.48, H 0.97. C<sub>3</sub>H<sub>5</sub>F<sub>3</sub>O<sub>5.5</sub>SU requires C 7.90, H 1.10%). IR (Nujol) v/cm<sup>-1</sup>:1309 s, 1225 vs, 1039 vs, 972 w, 799 s [ $v_{asym}$  (U=O)], 640 s, 516 w. IR (pyridine) v/cm<sup>-1</sup>: 812 m [ $v_{asym}$  (U=O)].

**[UO<sub>2</sub>(OTf)(py)<sub>2</sub>] (11).** Addition of pentane (15 mL) into a red brown solution of **10** (100 mg) in pyridine (5 mL) led to the precipitation of a brown powder. After filtration and drying under vacuum (20 °C, 15 h) the ochre pyridine adduct **11** was obtained in quantitative yield (106 mg). (Found C 23.09, H 1.77, N 4.82.  $C_{11}H_{10}F_3N_2O_5SU$  requires C 22.89, H 1.75, N 4.85%). IR (Nujol)

 $v/cm^{-1}$ : 1637 w, 1602 mw, 1262 m, 1169 s, 1067 w, 1040 vs, 944 w, 821 s [ $v_{asym}$  (U=O)], 755 m, 641 s, 518 m. IR (pyridine)  $v/cm^{-1}$ : 812 m [ $v_{asym}$  (U=O)]. Complex **11** was similarly obtained from **9**.

 $[UO_2(py)_5][I]$ -py (12-py). An NMR tube was charged with  $[UO_2I_2(THF)_3]$  (10.0 mg, 0.013 mmol) and  $TIC_5H_5$  (3.6 mg, 0.013 mmol) in pyridine-d<sub>5</sub> (0.5 mL). The mixture was stirred in an ultrasound bath for 24 h at room temperature, affording a dark brown solution and a yellow precipitate of TII. The NMR spectrum showed the presence of free  $C_5H_{6-n}D_n$ . After filtration, slow diffusion of pentane (3 mL) into the solution led to the formation of dark-red crystals of 12-py. IR (pyridine) v/cm<sup>-1</sup>: 816 m [ $v_{asym}$  (U=O)].

**[UO<sub>2</sub>I(THF)**<sub>2.75</sub>] **(13).** THF (15 mL) was condensed in a 50 mL round bottomed flask containing [UO<sub>2</sub>I<sub>2</sub>(THF)<sub>3</sub>] (2000 mg, 2.7 mmol) and freshly sublimed TlC<sub>5</sub>H<sub>5</sub> (728.2 mg, 2.7 mmol). The suspension was stirred at room temperature for 15 h, affording a brown solution and a yellow precipitate of TlI. After decantation and slow filtration of the solution, which was repeated three times, the volume of the solution was reduced to 5 mL and a brown powder precipitated upon addition of pentane (15 mL). (1580 mg, 95%). (Found: C 22.41; H 3.71; I 21.35. C<sub>11</sub>H<sub>22</sub>IO<sub>4.75</sub>U requires C 22.20, H 3.72, I 21.32%). IR (Nujol) v/cm<sup>-1</sup>: 1308 s, 1261 m, 1198 m, 1170 m, 1075 m, 1013 vs, 921 vs, 847 s [ $v_{asym}$  (U=O)], 800 m, 634 m, 427 m. IR (pyridine) v/cm<sup>-1</sup>: 816 m [ $v_{asym}$  (U=O)].

 $[UO_2I(py)_{2.5}]$  (14). Pyridine (10 mL) was condensed in a 50 mL flask containing 13 (100 mg, 0.17 mmol). The brown solution was stirred at room temperature for 10 min. Addition of pentane (30 mL) induced the precipitation of a dark brown powder of 14 (99.2 mg, 97%). (Found: C 25.83; H 2.26; I 21.18.  $C_{12.5}H_{12.5}IN_{2.5}O_2U$  requires C 25.23; H 2.10; I 21.36%). IR (pyridine)  $\nu/cm^{-1}$ : 816 m [ $\nu_{asym}$  (U=O)]. The powder of 14 was similarly obtained from 12.

**[UO<sub>2</sub>(CyMe<sub>4</sub>BTBP)(py)][OTf]-1.5py** (15-1.5py). An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol), CyMe<sub>4</sub>BTBP (9.38 mg, 17.6 µmol) and KC<sub>5</sub>Me<sub>5</sub> (3.07 mg, 17.6 µmol) in pyridine-d<sub>5</sub> (0.4 mL). After 24 h at 20 °C, the spectrum of the brown solution showed the formation of  $(C_5Me_5)_2$  and the disappearance of the signals corresponding to CyMe<sub>4</sub>BTBP. Slow diffusion of pentane (3 mL) into the solution led to the formation of brown-green crystals of 15·1.5py. Reactions of  $[UO_2(CyMe_4BTBP)X_2]$  (X = I, OTf) with 1 mol equivalent of TlC<sub>5</sub>H<sub>5</sub> in THF-d<sub>8</sub> or MeCN-d<sub>3</sub> afforded orange or dark red solutions whose NMR spectra showed the signals of  $C_5H_{6-n}D_n$ and of traces of the starting uranyl(VI) compound. The NMR spectra of 1 : 1 mixtures of  $[UO_2X]$  compounds (X = I, OTf) and CyMe<sub>4</sub>BTBP only exhibited the signals corresponding to traces of the uranyl(VI) complexes  $[UO_2(CYMe_4BTBP)X_2]$ .

**[UO<sub>2</sub>I(CyMe<sub>4</sub>BTBP)] (16).** THF (30 mL) was condensed in a 50 mL flask containing  $[UO_2I_2(THF)_3]$  (69.3 mg, 0.094 mmol) and CyMe<sub>4</sub>BTBP (50.1 mg, 0.094 mmol). The brown suspension was stirred at 20 °C for 20 h and addition of TIC<sub>5</sub>H<sub>5</sub> (25.2 mg, 0.094 mmol) gave rapidly a brown solution and a yellow precipitate of TII. After decantation and slow filtration, the volume of the solution was reduced to 5 mL and a brown powder precipitated upon addition of diethyl ether (20 mL). The brown solid was filtered off, washed with a 1:4 mixture of THF and Et<sub>2</sub>O (30 mL), and dried under vacuum for 20 h (80.5 mg, 92%). (Found C, 41.52; H, 4.21; N, 12.00.  $C_{32}H_{38}IN_8O_2U$  requires C, 41.25; H, 4.11; N, 12.03%). No NMR signal was detected. IR (Nujol) v/cm<sup>-1</sup>: 1600 w, 1531 w, 1261 vs, 1100 s, 1031 vs, 949 w, 903 w, 801 vs [ $v_{asym}$  (U=O)], 638 w, 634 w.

**[UO<sub>2</sub>Cl(py)<sub>3</sub>] (17).** Pyridine (25 mL) was condensed in a 50 mL round bottom flask containing  $[UO_2Cl_2(THF)_2]_2$  (200 mg, 0.41 mmol) and TlC<sub>5</sub>H<sub>5</sub> (111 mg, 0.41 mmol). The suspension was stirred at 20 °C for 4 h, leading to a brown solution and a pale yellow precipitate of TlCl. After decantation and slow filtration, the volume of the solution was reduced to 5 mL and a brown powder precipitated upon addition of pentane (20 mL). The powder was filtered off, washed with a 1 : 4 mixture of pyridine–pentane (20 mL) and dried under vacuum during 10 h (199 mg, 89%). (Found C 32.90, H 2.95, N 7.61. C<sub>15</sub>ClH<sub>15</sub>N<sub>3</sub>O<sub>2</sub>U requires C 33.19, H 2.78, N 7.74%). IR (Nujol) v/cm<sup>-1</sup>: 1264 w, 1218 s, 1153 m, 1067 s, 1038 s, 1008 s, 905 vs, 801 s [ $v_{asym}$  (U=O)], 753 s, 697 s, 627 m, 465 s. A similar experiment was carried out in pyridine-d<sub>5</sub> and the NMR spectrum revealed the formation of C<sub>5</sub>H<sub>6</sub>. IR (pyridine) v/cm<sup>-1</sup>: 924 m [ $v_{asym}$  (U<sup>V1</sup>=O)], 812 m [ $v_{asym}$  (U<sup>V1</sup>=O)].

**[UO<sub>2</sub>(NO<sub>3</sub>)(py)<sub>3</sub>] (18).** (a) Pyridine (25 mL) was condensed in a 50 mL round bottom flask containing [UO<sub>2</sub>I(THF)<sub>2,7</sub>] (200 mg, 0.34 mmol) and TlNO<sub>3</sub> (91.1 mg, 0.34 mmol). The suspension was stirred at 20 °C for 2 h, affording a brown-red solution and a yellow precipitate of TlI. After decantation and slow filtration, the volume of the solution was reduced to 5 mL and a brown powder precipitated upon addition of pentane (20 mL). The powder was filtered off, washed with a 1 : 4 mixture of pyridine–pentane (20 mL) and dried under vacuum for 10 h (184 mg, 96%). (Found: C 31.32, H 2.79, N 9.63.  $C_{15}H_{15}N_4O_5U$  requires C 31.64, H 2.65, N 9.84%). IR (Nujol)  $\nu/cm^{-1}$ : 1269 vs, 1068 m, 1023 vs, 927 s, 884 s, 804 w, 761 s, 692 s, 630 vs, 513 m. IR (pyridine)  $\nu/cm^{-1}$ : 812 m [ $v_{asym}$  (U=O)].

(b) An NMR tube was charged with  $[UO_2(NO_3)_2(MeCN)]$ (10.0 mg, 0.023 mmol) and  $KC_5Me_5$  (4.0 mg, 0.023 mmol) or  $TIC_5H_5$  (6.2 mg, 0.023 mmol) in pyridine-d<sub>5</sub> (0.4 mL). The yellow solution turned brown rapidly, and a white precipitate of  $TINO_3$  was deposited. The NMR spectra showed the formation of either  $(C_5Me_5)_2$  or  $C_5H_{6\rightarrow}D_n$ . The solution was filtered and evaporated to dryness, leaving the brown powder of **18**.

**Reactions of [UO<sub>2</sub>(OTf)<sub>2</sub>] and Me<sub>3</sub>SiC<sub>5</sub>R<sub>5</sub> (R = H, Me). Crystals of [UO<sub>2</sub>(OTf)(py)<sub>4</sub>] (19). (a) An NMR tube was charged with [UO<sub>2</sub>(OTf)<sub>2</sub>] (10.0 mg, 17.6 µmol) in acetonitrile (0.3 mL) and Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> (2.97 µL, 17.6 µmol) was added** *via* **a microsyringe. After 48 h at 25 °C, the colour of the solution turned from light yellow to green yellow. The solution was evaporated to dryness, leaving a green yellow powder which was washed with pentane (2 mL) and then dissolved in pyridine (0.4 mL). Slow diffusion of pentane (2 mL) into the orange solution led to the formation of yellow crystals of [UO<sub>2</sub>(OTf)<sub>2</sub>(py)<sub>3</sub>] together with a few red crystals of <b>19**. The same compound was obtained by using 2 mol equivalents of Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub>.

(b) An NMR tube was charged with  $[UO_2(OTf)_2]$  (10.0 mg, 17.6 µmol) in acetonitrile-d<sub>3</sub> (0.3 mL) and Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> (5.94 µL, 35.2 µmol) was added *via* a microsyringe. After 20 h refluxing, the colour of the solution turned from light yellow to green with a brown precipitate. The NMR spectrum of the green solution in pyridine- $d_5$  showed broad singlets at  $\delta$  72, 61 and 57 ppm corresponding to undefined paramagnetic compounds. Attempts at crystallization in pyridine-Et<sub>2</sub>O led to the formation of yellow crystals of  $[UO_2(OTf)_2(py)_3]$  only. The same reaction with a large excess of Me<sub>3</sub>SiC<sub>3</sub>H<sub>5</sub> gave an orange solution in acetonitrile. Undefined green crystals were obtained from a pyridine-pentane mixture.

(c) An NMR tube was charged with  $[UO_2(OTf)_2]$  (11.5 mg, 20.4 µmol) in acetonitrile-d<sub>3</sub> (0.3 mL) and Me<sub>3</sub>SiC<sub>5</sub>Me<sub>5</sub> (4.9 µL, 20.4 µmol) was added *via* a microsyringe. After 48 h at 25 °C, the green solution was evaporated to dryness and the residue dissolved in pyridine-d<sub>5</sub> (0.3 mL). The spectrum of the orange solution showed signals at  $\delta$  61 and 58 ppm. By using 2 mol equivalents of Me<sub>3</sub>SiC<sub>5</sub>Me<sub>5</sub>, the spectrum exhibited a major signal at  $\delta$  60 ppm and minor peaks at  $\delta$  46, 27 and 22 ppm.

Reactions of  $[UO_2I_2(THF)_3]$  or  $[UO_2CI_2(THF)_2]_2$  with  $Me_3SiC_5R_5$  (R = H, Me). Crystals of  $[UO_2CI_2(py)_3]$ . (a) An NMR tube was charged with  $[UO_2I_2(THF)_3]$  (10.0 mg, 13.5 µmol) and  $Me_3SiC_5H_5$  (2.27 µL, 13.5 µmol) in acetonitrile-d<sub>3</sub> (0.3 mL). After 2 h at 20 °C, the spectrum of the red brown solution showed the presence of  $C_5H_{6-n}D_n$  and a signal at  $\delta$  60.5 ppm.

(b) An NMR tube was charged with  $[UO_2Cl_2(THF)_2]_2$  (10.0 mg, 0.02 mmol) and  $Me_3SiC_5H_5$  (3.37 µL, 0.020 mmol) in acetonitriled<sub>3</sub> (0.3 mL). After 20 h at 20 °C, the spectrum of the yellow solution showed signals at  $\delta$  65 and 58 ppm. The solution was evaporated to dryness and the residue dissolved in pyridine (0.4 mL) to give a green solution. Slow diffusion of  $Et_2O$  (2 mL) into this solution gave yellow crystals of  $[UO_2Cl_2(py)_3]$  suitable for X-ray diffraction. By using  $Me_3SiC_5Me_5$  in place of  $Me_3SiC_5H_5$ , the NMR spectrum showed a signal at  $\delta$  54 ppm. Crystals of  $[UO_2Cl_2(py)_3]$  were again obtained by slow diffusion of  $Et_2O$  into the pyridine solution.

**Reactions of UX<sub>4</sub> (X = Cl, OTf) and NaOSiMe<sub>3</sub>.** (a) An NMR tube was charged with UCl<sub>4</sub> (12.0 mg, 0.031 mmol) and NaOSiMe<sub>3</sub> (6.9 mg, 0.062 mmol) in pyridine-d<sub>5</sub> (0.4 mL). After 48 h at 110 °C, the spectrum of the pale green solution showed large signals at  $\delta$  56 and 0 ppm.

(b) An NMR tube was charged with U(OTf)<sub>4</sub> (11.5 mg, 0.014 mmol) and NaOSiMe<sub>3</sub> (3.1 mg, 0.028 mmol) in pyridined<sub>5</sub> (0.4 mL). After 48 h at 110 °C, the spectrum of the brown solution showed broad signals at  $\delta$  60, 27, 24, 15.5 and 0.3 ppm.

#### Crystallography

The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer<sup>57</sup> using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  0.71073 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of  $\varphi$ - and  $\omega$ -scans giving complete data sets up to  $\theta = 25.7^{\circ}$  and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.<sup>58</sup> The structures were solved by Patterson map interpretation (**8**, **15**·1.5py, **19**) or by direct methods (all other compounds) with SHELXS-97, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>59</sup> Absorption effects

	<b>4</b> ⋅py	<b>5</b> ⋅py	<b>6</b> ⋅py	7	8	<b>12</b> ·py	<b>15</b> ·1.5py	19	$UO_2Cl_2(py)_3$
Chemical formula	$C_{60}H_{55}F_{15}K_{3}$ -	C <sub>68</sub> H <sub>65</sub> F <sub>9</sub> -	$C_{68}H_{65}F_9N_{13}$ -	C <sub>35</sub> H <sub>35</sub> I <sub>2</sub> -	C <sub>28</sub> H <sub>25</sub> F <sub>9</sub> Li <sub>2</sub> -	C <sub>30</sub> H <sub>30</sub> IN <sub>6</sub> -	C45.5H50.5F3-	$C_{21}H_{20}F_{3}$ -	$C_{15}H_{15}Cl_2$ -
	$N_{11}O_{19}S_5U_2$	$KN_{13}O_{13}S_{3}U_{2}$	$O_{13}S_3TlU_2$	$LiN_7O_2U$	$N_5O_{11}S_3U$	$O_2U$	$N_{10.5}O_5SU$	N₄O₅SU	$N_3O_2U$
$M/g \text{ mol}^{-1}$	2272.81	2054.67	2219.94	1084.47	1126.62	871.53	1151.55	735.50	578.23
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$Pna2_1$	$P2_{1}/c$	Pbca	<i>P</i> 1	C2/c	$P2_{1}/c$
a/Å	17.5189(6)	19.0805(4)	19.1433(5)	17.1377(8)	21.6519(4)	16.5129(7)	12.5854(12)	13.2614(8)	11.1335(8)
b/Å	11.7341(2)	20.0091(8)	19.9724(5)	12.3158(11)	21.3781(6)	17.2053(8)	14.1686(19)	12.2270(10)	13.0944(9)
c/Å	20.1579(7)	20.5906(8)	20.6551(7)	18.5640(19)	19.0730(5)	22.4464(7)	14.4513(19)	15.2571(10)	13.2043(6)
$\alpha/^{\circ}$	90	90	90	90	90	90	110.201(6)	90	90
$\beta/^{\circ}$	99.510(2)	90	90	90	111.162(2)	90	98.845(8)	98.720(5)	112.600(4)
$\gamma/^{\circ}$	90	90	90	90	90	90	94.538(9)	90	90
$V/Å^3$	4086.9(2)	7861.2(5)	7897.2(4)	3918.2(6)	8233.1(4)	6377.2(4)	2365.2(5)	2445.3(3)	1777.2(2)
Ζ	2	4	4	4	8	8	2	4	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.847	1.736	1.867	1.838	1.818	1.815	1.617	1.998	2.161
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	4.343	4.336	6.294	5.757	4.194	6.094	3.544	6.785	9.445
F(000)	2200	4000	4248	2044	4344	3304	1144	1396	1072
Reflections collected	106 663	128 320	175 501	158 854	264 858	207 093	91 21 1	40910	51 854
Independent	15426	14875	14973	7075	15603	6034	8946	2317	3363
Observed reflections	14246	12835	13 364	5982	12270	4291	7820	1801	2968
$[I > 2\sigma(I)]$									
$R_{\rm int}$	0.074	0.072	0.043	0.066	0.027	0.033	0.093	0.034	0.048
Parameters refined	1034	983	983	434	1063	361	603	176	208
$R_1$ (observed	0.055	0.034	0.030	0.045	0.029	0.043	0.043	0.036	0.031
reflections)									
$wR_2$ (all data)	0.139	0.072	0.064	0.113	0.072	0.095	0.106	0.096	0.079
S	1.092	0.993	1.014	1.043	1.019	1.091	1.078	1.116	1.001
Flack parameter	0.007(8)	-0.009(3)	-0.007(4)	0.500(8)					
$\Delta \rho_{\rm min}/{\rm e~A^{-3}}$	-1.18	-0.99	-1.09	-1.03	-1.28	-1.23	-1.29	-1.42	-2.09
$\Delta  ho_{ m max}$ /e Å <sup>-3</sup>	2.04	0.82	1.23	1.77	1.13	1.00	1.34	1.48	1.38

were corrected empirically with the program SCALEPACK.<sup>58</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Specific details are as follows:

Compound 4-py. One of the pyridine molecules (containing N5) was refined as an idealized hexagon. Some restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in the triflate groups.

Compound 12 py. Restraints on displacement parameters were applied for five carbon atoms from two coordinated pyridine molecules, seemingly affected with unresolved disorder.

Compound 15.1.5py. Restraints on bond lengths were applied for atoms C16, C17 and C26, C27 as well as restraints on displacement parameters for some badly behaving atoms. One solvent pyridine molecule is disordered around a symmetry centre.

Compound 19. The triflate ion is disordered over two equally populated positions related by the binary axis and sharing atoms O2 and F1; a restraint was applied on the S1–C11 bond length. Restraints on displacement parameters were applied for some carbon atoms of the pyridine rings and one pyridine molecule was refined as an idealized hexagon. The large displacement parameters of several carbon atoms of the pyridine rings, as well as a short O4… C6 contact, likely indicate some unresolved disorder of the pyridine molecules.

Crystal data and structure refinement parameters are given in Table 6. The molecular plots were drawn with SHELXTL<sup>59</sup> and Balls & Sticks.<sup>60</sup>

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