Synthesis of Organouranium(IV) Triflates from $U(OTf)_4$ or from Alkyl or Amide Precursors

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The uranium(IV) triflate $[U(OTf)_4]$ (**1**) (OTf = OSO_2CF_3) gives stable adducts with Lewis bases, such as $[U(OTf)_4(py)]$ (**2**) (py = pyridine). The crystal structure of a solvate of $[U(OTf)_4(OPPh_3)_3]$ (**3**), which exhibits a bidentate OTf group, has been determined. Substitution of the triflate ligands of **1** with $LiNEt_2$, Kacac (acac = MeCOCHCOMe), KCp (Cp = η-C_5H_5), and K_2COT (COT = η-C_8H_8) has led to the formation of $[U(NEt_2)_4]$, $[U(acac)_4]$, $[U(Cp)_3(OTf)]$ (**4**), and $[U(COT)(OTf)_2(py)]$ (**5**), respectively. However, the bis(cyclopentadienyl) compounds $[U(Cp^*)_2(OTf)_2]$ (**6**) (Cp^* = η-C_5Me_5) and $[U(Cp)_2(OTf)_2(py)]$ (**7**) could not be prepared from **1**. Complexes **4**–**7** have been isolated in good yields from the protonolysis reactions of the corresponding alkyl or amide precursors by means of pyridinium triflate. Compound **5** has also been prepared by treating $[U(COT)_2]$ with either [pyH][OTf] or **1** in pyridine. The crystal structures of $[U(Cp)_2(OTf)_2(py)_2]$ (**8**) and $[U(COT)(OTf)_2(OPPh_3)_2]\cdot0.5py$ (**9**) have been determined.

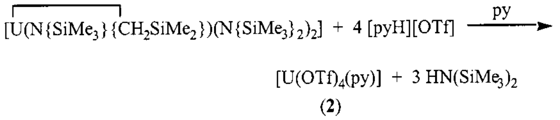
Introduction

The growing interest in metal triflates (trifluoromethanesulfonates), which proved to be effective Lewis acid catalysts in a number of organic reactions[1] and valuable precursors in inorganic and organometallic syntheses,[2] prompted us to study the preparation and properties of such complexes of uranium. In a preliminary communication,[3] we described the synthesis of $[U(OTf)_4(py)]$ (OTf = OSO_2CF_3; py = pyridine) and some organouranium(IV) triflates using the pyridinium salt [pyH][OTf] as a novel reagent for the protonolysis of U−C and U−N bonds. Following these initial results, we found that the base-free uranium(IV) triflate $[U(OTf)_4]$ (**1**) could be prepared in a more expeditious and simple way by treatment of U, UH_3, UCl_3, or UCl_4 with pure triflic acid.[4] The uranium(III) triflate $[U(OTf)_3]$ has also been obtained in a good yield by performing the reactions with U, UH_3, or UCl_3 at a lower temperature. These large-scale preparations of **1** allowed us to consider it as a possible good precursor for the syntheses of the derivatives. Here we present some reactions of $[U(OTf)_4]$, with special attention to those leading to organouranium(IV) triflate complexes. These preparations are compared with the alternative synthetic routes starting from the parent chloride, alkyl or amide compounds. The X-ray crystal structures of $[U(OTf)_4(OPPh_3)_3]\cdot0.5py\cdot0.5Et_2O$, $[U(Cp)_2(OTf)_2(py)_2]$ (Cp = η-C_5H_5), and $[U(COT)(OTf)_2(OPPh_3)_2]\cdot0.5py$ (COT = η-C_8H_8) are also described.

Results and Discussion

Reactions of $[U(OTf)_4]$ − X-ray Crystal Structure of $[U(OTf)_4(OPPh_3)_3]\cdot0.5py\cdot0.5Et_2O$

The uranium(IV) triflate $[U(OTf)_4]$ (**1**) is a strong Lewis acid and is quite soluble in coordinating solvents giving stable adducts. Thus, $[U(OTf)_4(py)]$ (**2**) was isolated from the reaction of the metallacycle $[U(N\{SiMe_3\}\{CH_2SiMe_2\})(N\{SiMe_3\}_2)_2]$ with [pyH][OTf] in pyridine [Equation (1)]. It is worth noting that similar treatment of $[U(NEt_2)_4]$ gave a mixture of unidentified amide products; this difference is not understood as the NEt_2 group, which is sterically less demanding and has a more basic character than $N(SiMe_3)_2$, is expected to be more easily protonated.[5]



$$[U(N\{SiMe_3\}\{CH_2SiMe_2\})(N\{SiMe_3\}_2)_2] + 4\,[pyH][OTf] \xrightarrow{py} \underset{(\mathbf{2})}{[U(OTf)_4(py)]} + 3\,HN(SiMe_3)_2 \quad (1)$$

In the presence of 2 equiv. of $OPPh_3$, **1** was transformed into $[U(OTf)_4(OPPh_3)_2]$ in pyridine or dimethoxyethane,[4] while green crystals of a solvate of $[U(OTf)_4(OPPh_3)_3]$ (**3**) were obtained by slow diffusion of diethyl ether into a pyridine solution of **1** and excess $OPPh_3$. Complex **3** is the first actinide tetratriflate to have been crystallographically characterized. Such metal complexes with four coordinated OTf ligands are not common and to the best of our knowledge, only the crystal structures of the neutral chromium compound $[Cr(OTf)_4(C_6H_4\{NH_2\}_2)]$,[6] and of the anionic species $[Fe(OTf)_4]^{2-}$ [7] and $[Na(OTf)_4]^{3-}$ [8] have been determined. The crystal structure of **3** is shown in Figure 1; selected bond lengths and angles are listed in Table 1. The

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uranium atom is surrounded by eight oxygen atoms in a dodecahedral arrangement defined by the two trapezia O(1)O(2)O(13)O(14) and O(3)O(4)O(7)O(10) intersecting at an angle of 90.4(4)°. The most salient feature of the structure is the presence of the η^2-O,O′ triflate ligand. This mode of ligation of the OTf group remains rare in d-transition metal complexes,[9] as well as in the f-block element compounds where only the two trivalent lanthanum and uranium complexes $[La(OTf)_2(HMPA)_4][OTf]$ (HMPA = hexamethylphosphoramide)[10] and $[U(OTf)_2(OPPh_3)_4][OTf]$[4] exhibit such a bidentate triflate ligand in their crystal structure. The $U-O(\eta^2\text{-OTf})$ bond lengths of 2.563(3) and 2.593(3) Å are ca 0.2 Å longer than the three $U-O(\eta^1\text{-OTf})$ distances which average 2.39(2) Å. Such a difference between the metal−oxygen bond lengths of the mono- and bidentate OTf ligands has been previously observed, in particular in the aforementioned uranium(III) compound.[4] The lengths of the $U-O(OPPh_3)$ bonds have an average value of 2.26(7) Å.

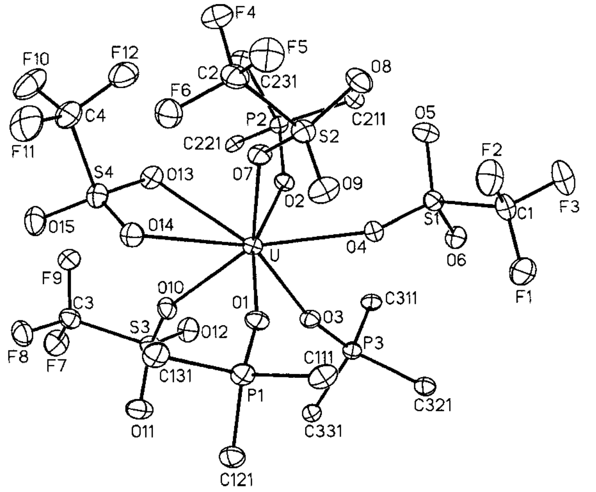
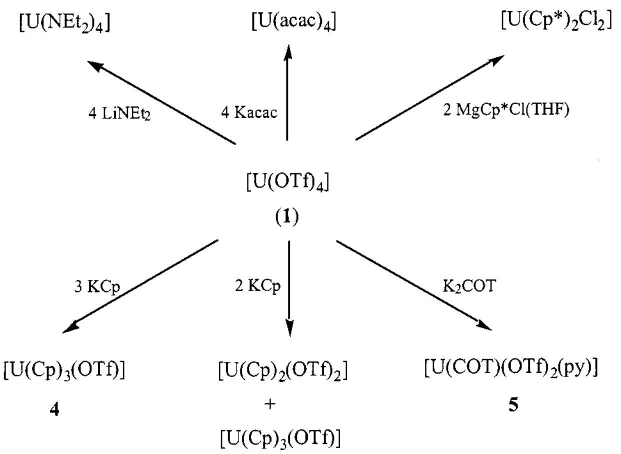


Figure 1. X-ray crystal structure of $[U(OTf)_4(OPPh_3)_3]$ with displacement ellipsoids at the 30% probability level; for clarity, only the *ipso*-carbon atoms of the phenyl rings are represented

Table 1. Selected bond lengths [Å] and angles [°] for $[U(OTf)_4(OPPh_3)_3]$

U−O(1)	2.207(3)	U−O(2)	2.252(3)
U−O(3)	2.318(3)	U−O(4)	2.403(3)
U−O(7)	2.371(3)	U−O(10)	2.418(3)
U−O(13)	2.563(3)	U−O(14)	2.593(3)
O(1)−U−O(2)	161.1(1)	O(3)−U−O(4)	74.9(1)
O(7)−U−O(10)	138.3(1)	O(13)−U−O(14)	54.5(1)

Homoleptic triflate complexes, like their halide counterparts, have been commonly used as starting materials for the synthesis of inorganic and organometallic derivatives;[2] in this context, it was of interest to evaluate the potential of **1**. The triflate groups of **1** can easily be substituted with anionic ligands (Scheme 1). For example, treatment of **1** with a slight excess of $LiNEt_2$ or Kacac (acac = MeCOCHCOMe) in tetrahydrofuran (THF) gave $[U(NEt_2)_4]$ or $[U(acac)_4]$ in almost quantitative yields (NMR experiments). In these syntheses, **1** proved to be as good a starting material as UCl_4.



Scheme 1. Reactions of $[U(OTf)_4]$

Attempts to prepare new organouranium(IV) triflates from **1** have been moderately successful. Reaction of **1** with 2 equiv. of KCp* in THF, pyridine, or toluene gave some unidentified products, while its treatment with MgCp*Cl(THF) in refluxing toluene afforded only the dichloride $[U(Cp^*)_2Cl_2]$ (Cp* = η-C_5Me_5).[11] Tris(cyclopentadienyl)uranium(IV) triflate $[U(Cp)_3(OTf)]$ (**4**) was synthesized in an almost quantitative yield by treatment of **1** with 3 equiv. of KCp in THF, followed by extraction with diethyl ether. However, a similar reaction of **1** with 2 equiv. of KCp afforded a mixture of $[U(Cp)_3(OTf)]$ and $[U(Cp)_2(OTf)_2]$ in a ratio of 73:27. Thus, pure bis(cyclopentadienyl)uranium(IV) compounds $[U(Cp^*)_2(OTf)_2]$ and $[U(Cp)_2(OTf)_2]$ could not be obtained by substitution of the triflate ligands of **1**.

Addition of 1 equiv. of $K_2C_8H_8$ to **1** in pyridine led to the immediate precipitation of a green powder, presumably $[U(COT)_2]$. The reaction mixture was heated under reflux for 15 h affording the (cyclooctatetraenyl)uranium(IV) triflate $[U(COT)(OTf)_2(py)]$ (**5**). In agreement with this observation, compound **5** was synthesized in an almost quantitative yield by direct comproportionation of **1** and $[U(COT)_2]$ in pyridine [Equation (2)]. Most notably, this ligand exchange reaction proceeded much less rapidly in THF. Such a remarkable solvent effect was also observed in the synthesis of $[U(COT)(BH_4)_2]$ from $[U(COT)_2]$ and $[U(BH_4)_4]$, which was effective in toluene but not in THF.[12] These results led us to re-examine the comproportionation reaction of UCl_4 and $[U(COT)_2]$ which, in refluxing pyridine, was found to readily afford the (cyclooctatetraenyl)uranium(IV) dichloride $[U(COT)Cl_2(py)_2]$ [Equation (3)].[13] It is ironical that this complex could so easily be obtained in pyridine whilst its synthesis in THF was difficult. This was a major obstacle in the development of the chemistry of mono(cyclooctatetraenyl) uranium compounds for a long time.[13] However, this situation favored the design of several $[U(COT)X_2]$ complexes (X = I,[14] BH_4,[12] NEt_2[15]) which were useful precursors for the synthesis of alkyl,[14b] alkoxide,[16] or thiolate[17] derivatives.

$$\underset{(\mathbf{1})}{[U(OTf)_4]} + [U(COT)_2] \xrightarrow{py} 2\,\underset{(\mathbf{5})}{[U(COT)(OTf)_2(py)]} \tag{2}$$

$$UCl_4 + [U(COT)_2] \xrightarrow{py} 2\,[U(COT)Cl_2(py)_2] \tag{3}$$

Synthesis of Organouranium(IV) Triflates from Alkyl or Amide Precursors − X-ray Crystal Structures of $[U(Cp)_2(OTf)_2(py)_2]$ and $[U(COT)(OTf)_2(OPPh_3)_2]\cdot0.5py$

The lack of success in the preparation of $[U(Cp^*)_2(OTf)_2]$ and $[U(Cp)_2(OTf)_2]$ from **1** forced us to envisage other synthetic routes. We first tried to prepare these complexes by treating chloride, alkyl or amide precursors with classical reagents like AgOTf, Me_3SiOTf, or TfOH that proved to be effective in the synthesis of main-group and d-transition metal triflates.[2] While reaction of $[U(Cp)_3X]$ (X = Cl, *n*Bu) with AgOTf in THF or toluene cleanly afforded **4**, similar treatment of $[U(Cp^*)_2X_2]$ (X = Cl, Me, NMe_2) failed to give any tractable product, and polymerization of THF was sometimes observed. Compounds **4** and **5** were prepared in quantitative yields by immersing the parent chlorides in pure Me_3SiOTf at 110 °C, but the same reaction with $[U(Cp^*)_2Cl_2]$ gave a mixture of unidentified products. Reactions of $[U(Cp)_3(NEt_2)]$ or $[U(Cp^*)_2Me_2]$ with stoichiometric amounts of triflic acid in benzene effectively produced the expected compounds **4** and $[U(Cp^*)_2(OTf)_2]$ (**6**). The X-ray crystal structures of the Lewis base adducts $[U(Cp)_3(OTf)(CN\textit{t}Bu)]$ and $[U(Cp^*)_2(OTf)_2(H_2O)]$ have been described in the preliminary communication.[3] However, difficulties were encountered when the above reactions were performed on a preparative scale; products resulting from protonation of the cyclopentadienyl ligands were also formed in variable yields, apparently depending on the concentration of the acid. Similar observations have previously been seen in the reaction of $[Zr(Cp)_4]$ and triflic acid.[2e]

The pyridinium triflate was then considered as a milder and more selective acidic reagent than triflic acid. Its use in the synthesis of uranium triflates was inspired by our previous studies on the protonolysis reactions of U−C and U−N bonds by means of the ammonium salt $[NHEt_3][BPh_4]$, which constitute an efficient route to cationic complexes.[18] Treatment of $[U(Cp)_3(NEt_2)]$ with [pyH][OTf] afforded **4** which was isolated with a 93% yield; **4** was similarly obtained from the alkyl precursor $[U(Cp)_3\textit{n}Bu]$. This synthetic method was found to have a general applicability, since **5** was prepared in a 92% yield from $[U(COT)(NR_2)_2]$ (R = Et, $SiMe_3$) and, most notably, the bis(cyclopentadienyl) complexes **6** and $[U(Cp)_2(OTf)_2(py)]$ (**7**) were obtained from $[U(Cp^*)_2X_2]$ (X = Me, NMe_2) and $[U(Cp)_2(NEt_2)_2]$ in a 78 and 60% yield, respectively. These syntheses, depicted in Equations (4) to (7), were reproducible.

$$[U(Cp)_3(NEt_2)] + [pyH][OTf] \xrightarrow{THF} \underset{(\mathbf{4})}{[U(Cp)_3(OTf)]} + HNEt_2 + py \tag{4}$$

$$\underset{R\,=\,Et,\ SiMe_3}{[U(COT)(NR_2)_2]} + 2\,[pyH][OTf] \xrightarrow{THF} \underset{(\mathbf{5})}{[U(COT)(OTf)_2(py)]} + 2\,HNR_2 + py \tag{5}$$

$$[U(Cp^*)_2Me_2] + 2\,[pyH][OTf] \xrightarrow{THF} \underset{(\mathbf{6})}{[U(Cp^*)_2(OTf)_2]} + 2\,CH_4 + 2\,py \tag{6}$$

$$[U(Cp)_2(NEt_2)_2] + 2\,[pyH][OTf] \xrightarrow{THF} \underset{(\mathbf{7})}{[U(Cp)_2(OTf)_2(py)]} + 2\,HNEt_2 + py \tag{7}$$

The synthesis of **7** from $[U(Cp)_2(NEt_2)_2]$ [Equation (7)] indicates that the formation of the tris(cyclopentadienyl) compound **4** as the major product in the reaction of **1** with 2 equiv. of KCp most likely occurs as a result of kinetic factors, and is not due to the decomposition of **7**, which is stable in coordinating solvents. This behavior of **7** is in contrast with that of the Lewis base adducts of $[U(Cp)_2Cl_2]$, which could not be isolated because of their rapid rearrangement into the equimolar mixture of $[U(Cp)_3Cl]$ and $[U(Cp)Cl_3L_2]$ (L = Lewis base or solvent).[19] As this disproportionation reaction was explained in terms of the great electron-rich nature of $[U(Cp)_2Cl_2L_x]$,[20] the stability of **7**, like that of the cationic complex $[U(Cp)_2(NEt_2)(THF)_x]^+$,[18a][18c] can clearly be related to the greater Lewis acidity of the metal center.

The acidic reagent [pyH][OTf] was also effective in the protonation of the aromatic ligand in $[U(COT)_2]$, since **5** was quantitatively obtained in refluxing THF or pyridine [Equation (8)]. Such syntheses of mono(cyclooctatetraenyl)uranium complexes by protonolysis of uranocene are not common; they are limited to the preparation of $[U(COT)(acac)_2]$ by reaction of $[U(COT)_2]$ with Hacac,[21] and to the non-selective formation of $[U(COT)Cl_2(THF)_x]$ by treatment of $[U(COT)_2]$ with HCl.[13] It is likely that the driving force of reaction (8) is the formation of a uranium−oxygen σ-bond, since $[U(COT)_2]$ failed to react with $[pyH][BPh_4]$ to give the dication $[U(COT)(THF)_x]^{2+}$.[22] A reaction was not observed between $[U(COT)_2]$ and NaOTf, while the uranocene was easily transformed into the anion $[U(COT)(O\textit{i}Pr)_3]^-$ in the presence of NaO*i*Pr;[23] this difference would simply reflect the weaker nucleophilic character of the triflate ligand.

$$[U(COT)_2] + 2\,[pyH][OTf] \xrightarrow{py\ or\ THF} \underset{(\mathbf{5})}{[U(COT)(OTf)_2(py)]} + C_8H_{10} \tag{8}$$

The pyridinium triflate thus proved to be very useful in the synthesis of organouranium(IV) triflates by protonolysis of alkyl or amide precursors. In addition to its selectivity and efficiency, this commercial reagent presents many advantages over triflic acid since it can be used in a greater variety of organic solvents, is not corrosive, can be stored for a long time and is easy to handle. Trialkylammonium triflates can also be used in such protonolysis reactions, as shown recently by the synthesis of (cyclopentadienyl)zirconium triflates by treatment of $[Zr(Cp)_4]$ with $[NBu_3H][OTf]$.[2e]

Compounds **2−7** were characterized by elemental analyses and ^1H NMR spectroscopy. Brown crystals of $[U(Cp)_2(OTf)_2(py)_2]$ (**8**) and orange crystals of a pyridine solvate of $[U(COT)(OTf)_2(OPPh_3)_2]$ (**9**) were obtained by slow diffusion of diethyl ether into a pyridine solution of **7**, or into a pyridine solution of **5** and excess $OPPh_3$. These crystals were suitable for X-ray diffraction analysis.

Other than the uranium borohydride $[U(Cp)_2(BH_4)_2]$[24] and the thorium complexes $[Th(Cp)_2X_2(DMPE)]$ (X = Cl, Me,[25a] CH_2Ph;[25b] DMPE = $Me_2PCH_2CH_2PMe_2$), **8** is one of the few mononuclear bis(cyclopentadienyl)actinide(IV) compounds to have been crystallographically characterized. The crystal structure is shown in Figure 2 and selected bond lengths and angles are listed in Table 2. The stereochemistry of this six-coordinate complex (if the Cp ring centroid is considered as occupying a single coordination site) strongly resembles that of the thorium derivatives $[Th(Cp)_2X_2(DMPE)]$; the two *cis* pyridine ligands can be thought of as replacing the bidentate phosphane ligand and the two *trans* monodentate triflate ligands can be thought of as replacing the X groups. The geometrical parameters of the $U(Cp)_2(py)_2$ and $Th(Cp)_2(DMPE)$ fragments are very similar, with the ring centroid−metal−ring centroid angles equal to 113.8(1) and 115(1)° (mean value) and the N(1)−U−N(2) and P−Th−P angles equal to 65.5(1) and 64.3(2)° (mean value), respectively. However, the O(1)−U−O(4) angle of 153.1(1)° is much greater than the C−Th−C or Cl−Th−Cl angles which average 140(1)°; this difference most likely reflects the greater steric size of the triflate ligands. The U−C bond lengths are unexceptional, with an average value of 2.73(4) Å, and the U−N bond lengths of 2.614(5) and 2.685(5) Å compare with those in $[U(S\mathit{i}Pr)_2I_2(py)_3]$[26] and $[U(COT)Cl_2(py)_2]$[13] [2.56(9) and 2.64(1) Å, respectively]. The U−O(1) and U−O(4) distances [2.395(4) and 2.385(4) Å, respectively] are similar to those found in the other uranium(IV) triflate compounds (vide infra).

Table 2. Selected bond lengths [Å] and angles [°] for $[U(Cp)_2(OTf)_2(py)_2]$

U−O(1)	2.395(4)	U−O(4)	2.385(4)
U−N(2)	2.685(5)	U−Cp(1)[a]	2.454(5)
U−N(1)	2.614(5)	U−Cp(2)[a]	2.466(5)
O(1)−U−O(4)	153.1(1)	N(1)−U−N(2)	65.5(1)
Cp(1)−U−Cp(2)	113.8(1)	Cp(1)−U−N(1)	155.5(1)
Cp(2)−U−N(2)	155.3(1)	Cp(1)−U−O(1)	94.1(1)
Cp(2)−U−O(1)	99.3(1)	Cp(1)−U−O(4)	98.5(1)
Cp(2)−U−O(4)	97.1(1)		

[a] Cp(1) and Cp(2) are the centroids of the C(1)−C(5) and C(6)−C(10) cyclopentadienyl rings.

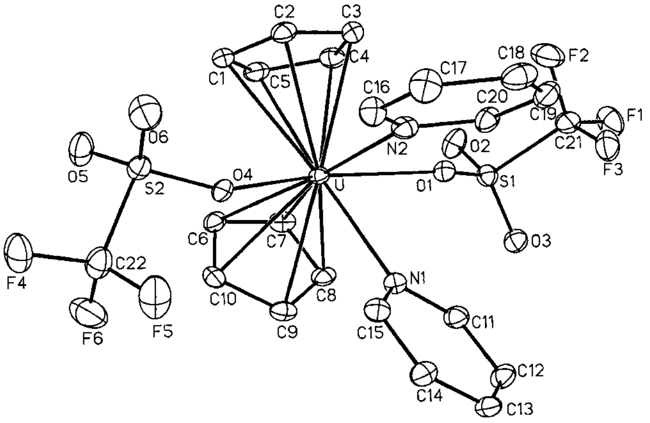


Figure 2. X-ray crystal structure of $[U(Cp)_2(OTf)_2(py)_2]$ with displacement ellipsoids at the 30% probability level

The crystal structure of one of the two independent and identical molecules of **9** is shown in Figure 3, and selected bond lengths and angles are listed in Table 3. The complex adopts a perfect square-pyramidal configuration, if the COT ligand is considered to be monodentate. The square base is defined by the oxygen atoms of the two $OPPh_3$ and the two monodentate OTf ligands, which are mutually in the *trans* positions; in the quadrilateral O(1)O(4)O(1′)O(4′), the O(1)−O(4) and O(1)−O(4′) distances are 2.923(4) and 2.763(4) Å, respectively, and the angles O(4)−O(1)−O(4′) and O(1)−O(4)−O(1′) have a value of 88.3(4) and 91.6(4)°, respectively. The square base is almost parallel to the planar COT ring, with a dihedral angle of 1.8(4)°, and the two planes are perpendicular to the two-fold axis. The U atom is 1.202(4) and 1.957(4) Å away from the square base and the COT ring, respectively. The COT ligation is similar to that found in uranocene and other mono(cyclooctatetraenyl)uranium(IV) compounds, with an average U−C bond length of 2.66(2) Å.[5a,13,27] The U−O($OPPh_3$) distances of 2.304(4) Å are unexceptional and the U−O(OTf) distances of 2.433(4) Å are within the range of the U−O bond lengths found in uranium(IV) monodentate triflates. These distances, which are equal to 2.371(3), 2.404(3) and 2.418(3) Å in $[U(OTf)_4(OPPh_3)_3]$ (vide supra), 2.36(1) and 2.40(1) Å in $[U(Cp^*)_2(OTf)_2(H_2O)]$,[3] 2.395(4) and 2.385(4) Å in $[U(Cp)_2(OTf)_2(py)_2]$ (vide supra), and 2.485(9) Å in $[U(Cp)_3(OTf)(NC\mathit{t}Bu)]$,[3] are significantly longer than the typical U−O bond length of the alkoxide ligand (2.0−2.3 Å),[28] thus indicating the much lower nucleophilic character of the OTf group. However, no dissociation and substitution of the triflate ligands were found to occur in these uranium(IV) compounds, even in the presence of strongly coordinating ligands like $OPPh_3$. In particular, it is worth noting that such a dissociation was not observed in $[U(OTf)_4(OPPh_3)_3]$, in contrast to the U^{III} derivative $[U(OTf)_2(OPPh_3)_4][OTf]$ which is composed of discrete cation−anion pairs in the solid state.[4] These features indicate that the uranium triflate bond is not as weak as is expected.

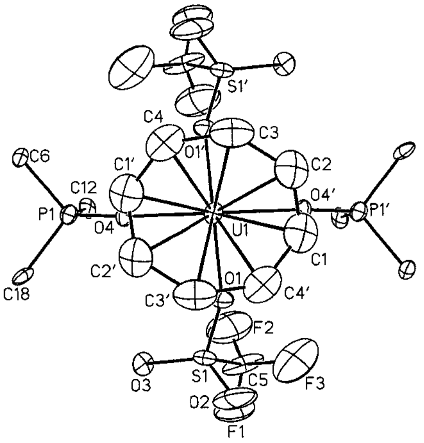


Figure 3. X-ray crystal structure of one of the two independent molecules of [U(COT)(OTf)$_2$(OPPh$_3$)$_2$] with displacement ellipsoids at the 30% probability level; view along the two-fold axis; for clarity, only the *ipso*-carbon atoms of the phenyl rings are represented; atoms labeled prime are related to the non-labeled ones by the two-fold axis (symmetry code: 0.75 − *x*, 1.75 − *y*, *z*)

Table 3. Selected bond lengths [Å] and angles [°] for [U(COT)(OTf)$_2$(OPPh$_3$)$_2$]

U(1)−O(1)[a]	2.382(4)	U(2)−O(5)[a]	2.433(4)
U(1)−O(4)	2.304(4)	U(2)−O(8)	2.296(4)
U(1)−COT[b]	1.957(4)	U(2)−COT	1.938(4)
O(1)−U(1)−O(1′)[c]	117.8(2)	O(5)−U(2)−O(5′)	117.4(2)
O(4)−U(1)−O(4′)	118.7(2)	O(8)−U(2)−O(8′)	116.5(2)
COT−U(1)−O(1)	121.2(2)	COT−U(2)−O(5)	121.3(2)
COT−U(1)−O(4)	120.7(2)	COT−U(2)−O(8)	121.7(2)

[a] The corresponding values in the two independent molecules [U(1) and U(2)] are given. [b] COT is the centroid of the cyclooctatetraenyl ring. [c] Atoms labeled prime are related to the non-labeled ones by the two-fold axis.

Conclusion

The uranium(IV) triflate [U(OTf)$_4$] (**1**) can be considered, like UCl$_4$, as a useful starting material for the synthesis of uranium complexes. We think that the preparation of **1**, although requiring the use of triflic acid, is more convenient and less hazardous than that of UCl$_4$ which necessitates the handling of harmful and volatile chlorinating agents.[29] However, there are some limitations associated with the use of **1** for the synthesis of organometallic compounds since the bis(cyclopentadienyl) complexes [U(Cp*)$_2$(OTf)$_2$] (**6**) and [U(Cp)$_2$(OTf)$_2$(py)] (**7**) could not be obtained by substitution of the triflate ligands. These compounds, as well as [U(Cp)$_3$(OTf)] (**4**) and [U(COT)(OTf)$_2$(py)] (**5**), the most representative examples of organouranium(IV) triflates, were prepared in good yields by protonolysis of the corresponding alkyl or amide precursors by means of pyridinium triflate. This synthetic method appears to have a general applicability, and [pyH][OTf] is a practical, effective and selective reagent which can be favorably used in place of TfOH or AgOTf. Of special interest is the synthesis of **5**, which was alternatively prepared by treatment of [U(COT)$_2$] with either [pyH][OTf] or [U(OTf)$_4$]; the solvent plays a major role in the comproportionation reactions of [U(COT)$_2$] and UX$_4$ (X = OTf, Cl), which were found to occur easily in pyridine. These results provide new and convenient findings for the chemistry of monocyclooctatetraenyl uranium compounds.

Experimental Section

General: All preparations were carried out under argon (less than 2 ppm of 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 before use. [D]$_8$THF was dried with Na/K alloy. The ^{1}H NMR spectra were recorded with a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ = 0). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). TfOH and Me$_3$SiOTf (Aldrich) were distilled before use, AgOTf (Aldrich) was used without purification, and the white powder of [pyH][OTf] was obtained by addition of pyridine to a solution of TfOH in diethyl ether. The uranium compounds UCl$_4$,[29] [U(OTf)$_4$],[4] [U(NEt$_2$)$_4$],[30] [U(N{SiMe$_3$}{CH$_2$SiMe$_2$})(N{SiMe$_3$}$_2$)$_2$],[31] [U(Cp)$_3$X] (X = Cl,[32] *n*Bu,[33] NEt$_2$[34]), [U(Cp*)$_2$X$_2$] (X = Cl,[11] Me,[35] NMe$_2$[36]), [U(Cp)$_2$(NEt$_2$)$_2$],[37] [U(COT)$_2$],[38] and [U(COT)(NR$_2$)$_2$] (R = Et,[18c] SiMe$_3$[39]) were synthesized as previously reported.

Syntheses of the Complexes

[U(OTf)$_4$(py)] (2): A 100-mL round-bottom flask was charged with [U(N{SiMe$_3$}{CH$_2$SiMe$_2$})(N{SiMe$_3$}$_2$)$_2$] (250 mg, 0.35 mmol) and [pyH][OTf] (319.1 mg, 1.39 mmol), and pyridine (20 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was heated for 20 h at 110 °C. After filtration, the volume of the green solution was reduced to 10 mL, and addition of pentane or diethyl ether (30 mL) led to the precipitation of a green powder of **2** which was filtered off, washed with diethyl ether and dried under vacuum (244 mg, 76%). ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 7.3, 7.85, and 8.8 (py). C$_9$H$_5$F$_{12}$NO$_{12}$S$_4$U (913): calcd. C 11.83, H 0.55, N 1.55; found C 12.07, H 0.72, N 1.59.

[U(NEt$_2$)$_4$]: An NMR tube was charged with [U(OTf)$_4$] (10.0 mg, 0.012 mmol) and LiNEt$_2$ (3.9 mg, 0.049 mmol) in [D$_8$]THF (0.4 mL). The tube was immersed in an ultrasound bath (80 W, 40 kHz) for 1.5 h, and the spectrum showed the quantitative formation of [U(NEt$_2$)$_4$].

[U(acac)$_4$]: An NMR tube was charged with [U(OTf)$_4$] (10.0 mg, 0.012 mmol) and Kacac (6.6 mg, 0.048 mmol) in [D$_8$]THF (0.4 mL). The tube was immersed in an ultrasound bath (80 W, 40 kHz) for 30 min, and the spectrum showed the quantitative formation of [U(acac)$_4$].

[U(Cp)$_3$(OTf)] (4)

From [U(Cp)$_3$(NEt$_2$)] and [pyH][OTf]: A 50-mL round-bottom flask was charged with [U(Cp)$_3$(NEt$_2$)] (209 mg, 0.41 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. At 20 °C, a solution of [pyH][OTf] (95 mg, 0.41 mmol) in THF (15 mL) was slowly added to the red solution of the uranium complex, which rapidly turned orange. After 45 min, the solution was filtered and its volume was reduced to 10 mL. Addition of pentane (20 mL) led to the precipitation of a brown powder of **4** which was filtered off, washed with pentane and dried under vacuum (225 mg, 93%). ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = -2.45$ (s, Cp). $C_{16}H_{15}F_3O_3SU$ (582): calcd. C 32.99, H 2.60; found C 32.86, H 2.70.

From [U(Cp)$_3$*n*Bu] and [pyH][OTf]: An NMR tube was charged with [U(Cp)$_3$*n*Bu] (10.0 mg, 0.02 mmol) and [pyH][OTf] (4.7 mg, 0.02 mmol) in [D$_8$]THF. After 15 h at 20 °C, the spectrum showed the quantitative formation of **4**.

From [U(Cp)$_3$X] (X = Cl, *n*Bu) and AgOTf: An NMR tube was charged with [U(Cp)$_3$Cl] (10.0 mg, 0.021 mmol) and AgOTf (6.6 mg, 0.025 mmol) in [D$_8$]THF (0.4 mL). The tube was immersed in an ultrasound bath for 10 min; the color of the solution turned brown and precipitation of AgCl was observed. The spectrum showed the quantitative formation of **4**. The same reaction with [U(Cp)$_3$*n*Bu] also gave **4** in a quantitative yield, with the precipitation of metallic silver.

From [U(Cp)$_3$Cl] and Me$_3$SiOTf: An NMR tube was charged with [U(Cp)$_3$Cl] (10.0 mg, 0.021 mmol) and Me$_3$SiOTf (0.1 mL, 0.55 mmol). The tube was immersed in an ultrasound bath for 1 h and left at 20 °C for 15 h. After concentration to dryness, the brown residue was washed with diethyl ether, dried under vacuum and dissolved in [D$_8$]THF. The spectrum showed the quantitative formation of **4**.

From [U(Cp)$_3$(NEt$_2$)] and TfOH: An NMR tube was charged with [U(Cp)$_3$(NEt$_2$)] (10.0 mg, 0.021 mmol) in benzene (0.4 mL), and TfOH (1.7 µL, 0.02 mmol) was added via a microsyringe. After vigorous shaking by hand, a brown powder was deposited from the red solution. After concentration to dryness, the residue was dissolved in [D$_8$]THF and the spectrum showed the formation of the unique product **4**.

From [U(OTf)$_4$] and KCp: An NMR tube was charged with [U(OTf)$_4$] (10.0 mg, 0.012 mmol) and KCp (3.8 mg, 0.036 mmol) in [D$_8$]THF (0.4 mL). After 1 h at 20 °C, the spectrum showed a large signal at $\delta = -4.7$. The solvent was evaporated and the residue extracted with diethyl ether. After concentration to dryness, the spectrum of the brown powder in [D$_8$]THF showed the formation of the unique product **4**.

[U(COT)(OTf)$_2$(py)] (5)

From [U(COT)(N{SiMe$_3$}$_2$)$_2$] and [pyH][OTf]: A 50-mL round-bottom flask was charged with [U(COT)(N{SiMe$_3$}$_2$)$_2$] (250 mg, 0.38 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. At 20 °C, a solution of [pyH][OTf] (174 mg, 0.76 mmol) in THF (15 mL) was introduced and the resulting dark red solution was stirred for 30 min. After filtration and concentration to dryness, the residue was extracted with diethyl ether or toluene (30 mL). The solvent was evaporated and the brown powder of **5** was dried under vacuum (250 mg, 92%). ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = -37.5$ (s, 8 H, COT), 6.9, 7.4 and 7.6 (s, 5 H, py). $C_{15}H_{13}F_6NO_6S_2U$ (719): calcd. C 25.04, H 1.82, N 1.94; found C 24.98, H 1.92, N 2.08. Complex **5** was similarly prepared in an almost quantitative yield from [U(COT)(NEt$_2$)$_2$] (10.0 mg, 0.02 mmol) and [pyH][OTf] (9.3 mg, 0.04 mmol).

From [U(COT)$_2$] and [pyH][OTf]: An NMR tube was charged with [U(COT)$_2$] (10.0 mg, 0.022 mmol) and [pyH][OTf] (10.3 mg, 0.45 mmol) in [D$_8$]THF (0.4 mL). After 15 min at 80 °C, the spectrum of the red solution showed the quantitative formation of **5**. The same reaction in refluxing pyridine required 15 h to go to completion.

From [U(COT)Cl$_2$(py)$_2$] and Me$_3$SiOTf: An NMR tube was charged with [U(COT)Cl$_2$(py)$_2$] (25 mg, 0.044 mmol) (prepared from [U(COT)$_2$] and UCl$_4$, see below) and Me$_3$SiOTf (0.4 mL, 2.2 mmol). The suspension was heated for 15 h at 110 °C, and after concentration to dryness, the brown residue was dissolved in [D$_8$]THF. The spectrum showed the formation of [U(COT)(OTf)$_2$(THF)$_x$] ($\delta = 37.3$) and [PySiMe$_3$][OTf].

From [U(OTf)$_4$] and K$_2$C$_8$H$_8$: An NMR tube was charged with [U(OTf)$_4$] (10.0 mg, 0.012 mmol) and K$_2$C$_8$H$_8$ (2.2 mg, 0.012 mmol) in pyridine. Precipitation of a green powder of [U(COT)$_2$] was immediately observed. After heating at 110 °C for 15 h, the dark green solution was concentrated to dryness and the residue dissolved in [D$_8$]THF. The spectrum showed the formation of **5** as a unique product.

From [U(OTf)$_4$] and [U(COT)$_2$]: A 50-mL round-bottom flask was charged with [U(OTf)$_4$] (100 mg, 0.12 mmol) and [U(COT)$_2$] (53.5 mg, 0.12 mmol), and pyridine (20 mL) was condensed into it under vacuum at −78 °C. The mixture was heated at 110 °C for 20 h and the resulting dark green solution was concentrated to dryness. The residue was extracted with diethyl ether and the brown powder of **5** was obtained after evaporation of the solvent (155 mg, 90%). Under the same conditions, reaction of **2** and [U(COT)$_2$] in [D$_8$]THF did not reach completion, as only ca. 20% of the green crystalline powder of uranocene was transformed into **5**.

[U(COT)Cl$_2$(py)$_2$]: A 25-mL round-bottom flask was charged with [U(COT)$_2$] (50 mg, 0.11 mmol) and UCl$_4$ (42.5 mg, 0.11 mmol) in pyridine (10 mL). The mixture was heated for 24 h at 110 °C; the color of the solution turned from green to red. The solvent was evaporated and the residue extracted with THF (10 mL). After concentration to dryness, the product was dissolved in pyridine (5 mL) and was then precipitated on addition of diethyl ether (10 mL). The red powder was filtered, washed with toluene (10 mL) and dried under vacuum (88 mg, 70%).

[U(Cp*)$_2$(OTf)$_2$] (6)

From [U(Cp*)$_2$X$_2$] (X = Me, NMe$_2$) and [pyH][OTf]: A 100-mL round-bottom flask was charged with [U(Cp*)$_2$Me$_2$] (257 mg, 0.47 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. A solution of [pyH][OTf] (219 mg, 0.95 mmol) in THF (20 mL) was slowly added to the solution of the uranium complex at −70 °C; vigorous evolution of gas was observed. After 1 h at 20 °C, the brown solution was concentrated to dryness and the residue extracted with toluene (30 mL). The solvent was evaporated and a red brown powder of **6** was washed with pentane and dried under vacuum (300 mg, 78%). ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = 20.1$ (s, Cp*). $C_{22}H_{30}F_6O_6S_2U$ (806): calcd. C 32.75, H 3.75, S 7.95; found C 32.81, H 3.73, N 7.84. An NMR tube was charged with [U(Cp*)$_2$(NMe$_2$)$_2$] (10.0 mg, 0.017 mmol) and [pyH][OTf] (7.7 mg, 0.034 mmol) in [D$_8$]THF (0.4 mL). The tube was immersed in an ultrasound bath and after 30 min, the spectrum showed that **6** was formed in an almost quantitative yield.

From [U(Cp*)$_2$Me$_2$] and TfOH: An NMR tube was charged with [U(Cp*)$_2$Me$_2$] (10.0 mg, 0.018 mmol) in [D$_8$]toluene (0.4 mL), and TfOH (1.6 µL, 0.018 mmol) was introduced via a microsyringe. Evolution of gas was immediately observed and the spectrum showed the formation of **6** with variable amounts of side products.

[U(Cp*)$_2$Cl$_2$]: An NMR tube was charged with **1** (10.0 mg, 0.012 mmol) and MgCp*Cl(THF) (6.4 mg, 0.024 mmol) in [D$_8$]toluene (0.4 mL). After 3 h at 110 °C, the spectrum of the red solution showed the formation of $[U(Cp^*)_2Cl_2]$ as the unique product.

$[U(Cp)_2(OTf)_2(py)]$ (7)

From $[U(Cp)_2(NEt_2)_2]$ and [pyH][OTf]: A 100-mL round-bottom flask was charged with $[U(Cp)_2(NEt_2)_2]$ (300 mg, 0.58 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. A solution of [pyH][OTf] (268 mg, 1.17 mmol) in THF (20 mL) was slowly added into the solution of the uranium compound at −40 °C. After stirring for 1 h at −30 °C and 3 h at 20 °C, the orange solution was filtered, concentrated to dryness and the orange powder of **7** was washed with diethyl ether and dried under vacuum (260 mg, 60%). Compound **7** may be contaminated with traces (2−3%) of **4**. ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = 6.9$, 8.8 and 8.85 (s, 5 H, py), 11.2 (s, 10 H, Cp). $C_{17}H_{15}F_6NO_6S_2U$ (745): calcd. C 27.39, H 2.02, N 1.88; found C 26.66, H 1.99, N 2.05.

From $[U(OTf)_4]$ and KCp: An NMR tube was charged with $[U(OTf)_4]$ (10.0 mg, 0.012 mmol) and KCp (2.5 mg, 0.024 mmol) in [D$_8$]THF (0.4 mL). After 12 h at 20 °C, the spectrum of the yellow solution showed the formation of **4** and **7** in a ratio of 73:27.

X-ray Crystallography of $[U(OTf)_4(OPPh_3)_3]\cdot 0.5py\cdot 0.5Et_2O$: Diffraction data collection was carried out with a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 2° Φ-scans and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz polarization and absorption[40] effects. The structure was solved by the heavy-atom method and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-solvent atoms. H atoms were introduced at calculated positions and constrained to ride on their parent C atom with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. One pyridine and one diethyl ether solvent molecules were found on the same position and were refined disordered on two positions with 0.5 occupation factor. All calculations were performed with an O2 Silicon Graphics Station using the SHELXTL package.[41] Crystal data and summary of data collection and refinement are given in Table 4. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171474. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

X-ray Crystallography of $[U(Cp)_2(OTf)_2(py)_2]$: Diffraction collection was carried out with a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 2° Φ-scans and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 30 mm. Data were corrected for Lorentz polarization and absorption[40] effects. The structure was solved by the heavy-atom method and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were introduced at calculated positions and constrained

Table 4. Crystal data and structure refinement for the complexes

	3·0.5py·0.5Et$_2$O	**8**	**9**·0.5py
Empirical formula	$C_{62.5}H_{52.5}F_{12}N_{0.5}O_{15.5}P_3S_4U$	$C_{22}H_{20}F_6N_2O_6S_2U$	$C_{48.5}H_{40.5}F_6O_8P_2S_2U$
M [g·mol^{-1}]	1745.73	824.55	1229.40
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$Fddd$
a [Å]	12.879(3)	10.804(2)	13.376(3)
b [Å]	13.475(3)	9.924(2)	45.169(9)
c [Å]	19.917(4)	24.660(5)	66.273(13)
α [°]	84.78(3)	90	90
β [°]	88.31(3)	99.95(3)	90
γ [°]	79.35(3)	90	90
V [Å^3]	3382.6(12)	2604.2(9)	40041(14)
Z	2	4	32
$\rho_{calcd.}$ [g·cm^{-3}]	1.714	2.103	1.632
μ(Mo-K_α) [mm^{-1}]	2.693	6.478	3.463
Crystal size [mm]	0.20 × 0.15 × 0.10	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.10
T_{min}/T_{max}	0.633/0.766	0.830/0.974	0.550/0.698
F(000)	1728	1568	19312
2θ range [°]	4−50	4−50	4−46
T [K]	123(2)	123(2)	123(2)
No. of data collected	18318	16307	26890
No. of unique data	10662	4378	6152
Observed data [$I > 2\sigma(I)$]	9700	3677	3275
R_{int}	0.036	0.052	0.084
No. of parameters	903	352	596
R_1[a]	0.031	0.033	0.064
wR_2[b]	0.072	0.073	0.120
S	1.008	1.015	0.972
$\Delta\rho_{min}$ [e·Å^{-3}]	−1.341	−1.288	−0.786
$\Delta\rho_{max}$ [e·Å^{-3}]	0.668	0.726	0.654

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ (observed reflections). [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma(w|F_o^2|)^2]^{1/2}$ (observed reflections).

to ride on their parent C atom with an isotropic displacement parameter equal to 1.2 (CH) times that of the parent atom. All calculations were performed with an O2 Silicon Graphics Station using the SHELXTL package.[41] Crystal data and summary of data collection and refinement are given in Table 4. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171475. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

X-ray Crystallography of $[U(COT)(OTf)_2(OPPh_3)_2]\cdot 0.5py$: Diffraction collection was carried out with a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 2° Φ-scans and later refined on all data. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 35 mm. Data were corrected for Lorentz polarization and absorption[40] effects. The structure was solved by the heavy-atom method and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Two independent and similar molecular complexes were found in the unit cell, with the two uranium atoms lying on a two-fold axis. H atoms (except those of the solvent molecules) were introduced at calculated positions and constrained to ride on their parent C atom with an isotropic displacement parameter equal to 1.2 (CH) times that of the parent atom. The pyridine solvent molecule lies on a two-fold axis and all atoms were assigned as C atoms. All calculations were performed with an O2 Silicon Graphics Station using the SHELXTL package.[41] Crystal data and summary of data collection and refinement are given in Table 4. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171476. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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