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Reaction of the *N*-heterocyclic carbene, 1,3-dimesityl-imidazol-2-ylidene, with a uranyl triflate complex, $UO_2(OTf)_2(thf)_3$

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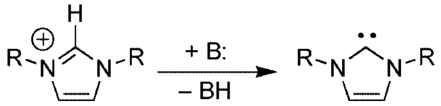
The N-heterocyclic carbene, 1,3-dimesityl-imidazol-2-ylidene (IMes) reacts with tetrahydrofuran (THF) in the presence of an oxidizing uranyl triflate complex, $UO_2(OTf)_2(thf)_3$ ($^-OTf = {}^-OSO_2CF_3$), to give 1,4-bis(1,3-dimesityl-2-imidazolium)-1,3-butadiene bis(trifluoromethanesulfonate), formally understood as the coupling product of two equivalents of IMes with [CH=CH–CH=CH]$(OTf)_2$. Copyright © 2005 John Wiley & Sons, Ltd.

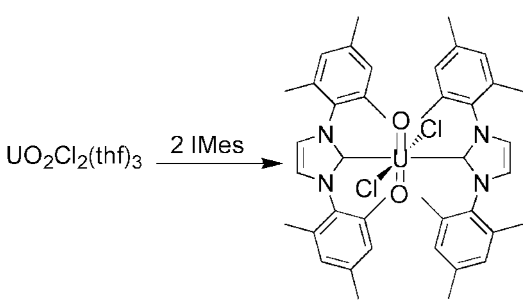
KEYWORDS: uranyl; triflate; tetrahydrofuran; *N*-heterocyclic carbene (NHC); oxidation

INTRODUCTION

N-heterocyclic carbenes (NHCs) derived from the deprotonation reaction of 1,3-disubstituted imidazolium salts [eqn (1)] are of much current interest as ancillary ligands in a variety of metal-mediated catalytic reactions[1–5] and as reactive intermediates generated in organic and room temperature ionic liquid solvents.[6–13] While NHCs have been shown to function as extremely robust ligands for low valent metal complexes, their reactions with highly valent, electrophilic metal species are significantly less developed.



(1)



(2)

The NHC, 1,3-dimesityl-imidazol-2-ylidene (IMes) has previously been shown to react cleanly with $UO_2Cl_2(thf)_3$ to give the first organometallic uranyl complex, $UO_2Cl_2(IMes)_2$ [eqn (2)].[14] (Since this report a few additional complexes containing uranyl–carbon bonds have been described.[15–18])

A direct carbon-to-uranium(VI) bond length of 2.626(7) Å was determined for this complex by single crystal X-ray diffraction. As bonding in the equatorial plane of uranyl complexes is generally regarded as being almost purely ionic in character, the successful isolation of $UO_2Cl_2(IMes)_2$ indicates that a significant coulombic attraction must be obtained between the $[UO_2]^{2+}$ moiety and the σ-electron pair of the NHC ligand. In an effort to further define the chemistry of NHC nucleophiles with highly electrophilic metal systems, the reaction of $UO_2(OTf)_2(thf)_3$ with IMes was attempted. In this case the uranyl triflate complex promotes an unexpected, and previously unknown oxidation reaction.

RESULTS AND DISCUSSION

Preparation of $UO_2(OTf)_2(thf)_3$

Synthetic entry and general exploration of uranium triflate reaction chemistry has been led by the work of Berthet and coworkers.[19–23] Compared with analogous halide species, uranium triflates have been shown to behave as even more highly polarizing electrophiles. A versatile uranium(VI) starting material, $UO_2(OTf)_2$, can be readily prepared upon treatment of UO_3 with pure triflic acid or triflic anhydride.[21]

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Potential difficulty in handling large volumes of these highly corrosive reagents and possible contamination of the product with HOTf can be alleviated by reaction of $UO_2Cl_2(thf)_3$ with two equivalents of AgOTf in THF to give $UO_2(OTf)_2(thf)_3$ (**1**) in good yield [eqn (3)].

$$UO_2Cl_2(thf)_3 \xrightarrow[-2\ AgCl]{+2\ AgOTf} UO_2(OTf)_2(thf)_3 \qquad (3)$$

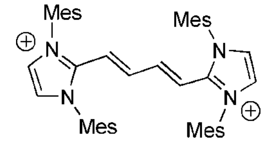
Complex **1** adopts a nearly ideal pentagonal bipyramidal structure with the equatorial plane defined by three oxygen atoms of the thf ligands and two oxygen atoms of the triflate groups that are monodentate and non-adjacent (Fig. 1). The structural parameters of **1** are unexceptional and compare well with closely related complexes such as $UO_2Cl_2(thf)_3$[24] and $UO_2(OTf)_2(pyridine)_3$[21] (Table 1). The THF ligands in complex **1** seem to be held more tightly compared with $UO_2Cl_2(thf)_3$. The uranyl dichloride complex readily loses a THF ligand at ambient temperature to give $[UO_2Cl_2(thf)_2]_2$, whereas elemental analysis of vacuum dried samples of **1** remain consistent with the mononuclear formulation.

Table 1. Selected bond lengths and angles for compound **1**

Bond lengths (Å)		Bond angles (°)	
U(1)–O(1)	1.754(5)	O(1)–U(1)–O(2)	179.5(2)
U(1)–O(2)	1.746(5)	O(1)–U(1)–O(6)	87.3(3)
U(1)–O(6)	2.372(6)	O(1)–U(1)–O(3)	91.2(2)
U(1)–O(3)	2.386(5)	O(1)–U(1)–O(9)	91.9(2)
U(1)–O(9)	2.386(5)	O(1)–U(1)–O(4)	89.3(2)
U(1)–O(4)	2.410(5)	O(1)–U(1)–O(5)	91.9(2)
U(1)–O(5)	2.420(5)	O(6)–U(1)–O(3)	72.78(19)
		O(3)–U(1)–O(9)	72.2(2)
		O(9)–U(1)–O(4)	71.65(18)
		O(4)–U(1)–O(5)	70.73(17)
		O(5)–U(1)–O(6)	72.92(19)

Reaction of $UO_2(OTf)_2(thf)_3$ with IMes

Dropwise addition of two equivalents of IMes[25] in THF to a pale yellow solution of **1** in THF causes a slight darkening of the solution. Upon layering with hexane and allowing the reaction flask to stand undisturbed in a −20 °C freezer for several days, a limited collection of bright fluorescent yellow needles contained within a heterogeneous matrix of off-white and brown powder separated from solution. As uranyl complexes frequently appear as fluorescent yellow crystals, one of these was selected for crystallographic characterization. Unexpectedly, the yellow needles proved to be the organic salt, 1,4-bis(1,3-dimesityl-2-imidazolium)-1,3-butadiene bis(trifluoromethanesulfonate) (**2**) shown below and in Fig. 2.



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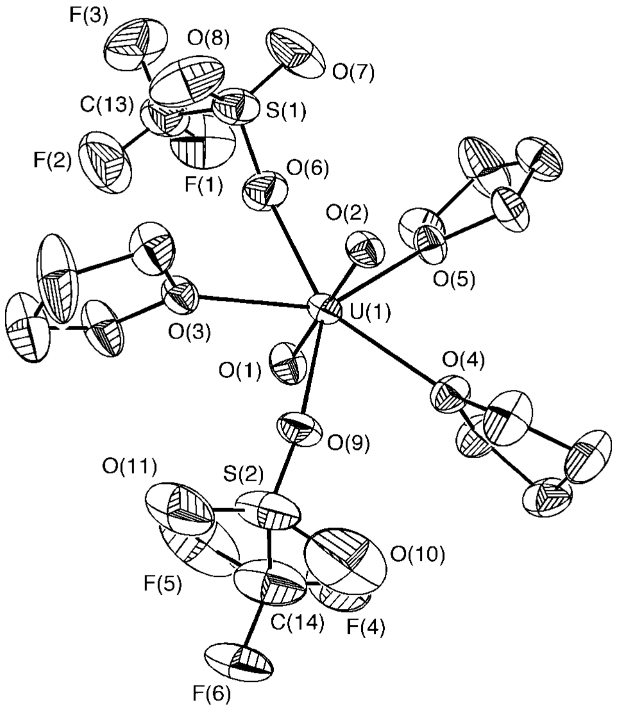


Figure 1. Thermal ellipsoid plot of $UO_2(OTf)_2(thf)_3$ (**1**).

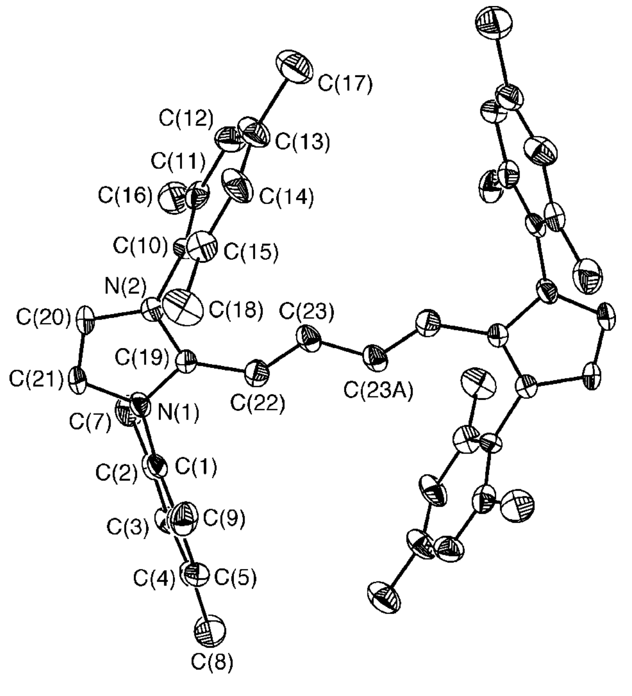
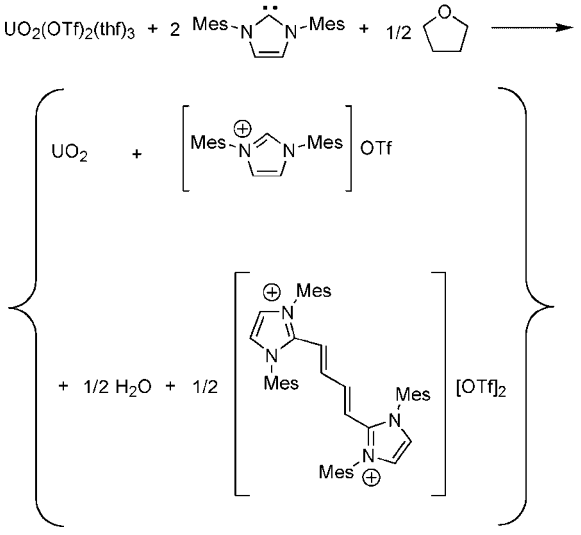


Figure 2. Thermal ellipsoid plot of **2**. Hydrogen atoms and triflate counter anions have been omitted for clarity.

Compound **2** can be rationalized as the triflate salt resulting from the coupling reaction of two equiv. of IMes with $[CH{=}CH{-}CH{=}CH]^{2+}$, presumably derived from THF. Formation of the butadiene dication from ring-opened THF is a four-electron oxidation reaction. Thus a balanced equation that accounts for the formation of compound **2** is shown in eqn 4. The uranyl triflate complex, **1**, is proposed to act as the oxidant and is ultimately reduced in the process to a uranium(IV) oxide. Within this scheme, IMes is converted in a 2 : 1 ratio to its conjugate acid, [HIMes]OTf, and **2**.

It should be noted that **1** shows no tendency to react with THF in the absence of added IMes, suggesting that the oxidation reaction proceeds via initial formation of the radical cation, $[IMes]^+$, considered to be a potent hydrogen atom acceptor. Previous studies by Clyburne and coworkers of the oxidation chemistry of IMes have shown that the ultimate reaction products depend markedly on the particular oxidant used.[26] For example, reaction of THF solutions of IMes with equimolar solutions of tetracyanoethylene (TCNE) or ferrocenium salts $[Cp_2Fe][A]$ ($A = PF_6$ or BF_4) yield imidazolium cations, **3** or **4**, respectively. The dication **3** results from rapid coupling of two $[IMes]^+$ radical cations, whereas a simple imidazolium cation, **4**, is obtained if hydrogen atom abstraction from solvent (THF) predominates. Rationalization of these two products rests on the relative rate of formation of $[IMes]^+$. In the first case, rapid oxidation gives a high radical concentration favoring the symmetrical dimer. However, if the concentration of $[IMes]^+$ is low, then hydrogen atom abstraction from solvent dominates. In contrast to these outer sphere oxidation reactions, we speculate that formation of **2** may occur within the coordination sphere of the uranyl ion, which facilitates the unusual C–C coupling reaction. Unfortunately, the complex mixture of products that is generated in the reaction of **1** with IMes has hindered complete characterization of **2**.



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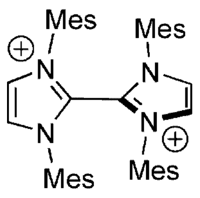

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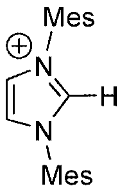

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Table 2. Selected bond lengths and angles for compound **2**

Bond lengths (Å)		Bond angles (°)	
C(19)–C(22)	1.459(9)	C(22)–C(23)–C(23A)	122.2(9)
C(22)–C(23)	1.330(9)	C(19)–C(22)–C(23)	130.3(7)
C(23)–C(23A)	1.440(13)	N(1)–C(19)–N(2)	105.8(6)
C(19)–N(1)	1.341(8)	C(19)–N(2)–C(20)	110.2(6)
N(1)–C(21)	1.383(8)	N(2)–C(20)–C(21)	107.6(6)
C(21)–C(20)	1.342(9)	C(20)–C(21)–N(1)	106.4(6)
C(20)–N(2)	1.359(8)	C(21)–N(1)–C(19)	110.0(6)
N(2)–C(19)	1.347(8)		
N(1)–C(1)	1.458(9)		
N(2)–C(10)	1.473(9)		

Molecular structure of 2

The molecular structure of **2** determined by single crystal X-ray diffraction is shown in Fig. 2. The butadiene linker adopts an *E,E* conformation with localized single and double bonds [C(19)–C(22) = 1.459(9), C(22)–C(23) = 1.330(9), C(23)–C(23A) = 1.440(13)] that are identical within experimental error to structural data reported for (*E,E*)-1,4-diphenylbutadiene.[27] The terminal imidazolium units lie in the same plane as the butadiene linker [dihedral angle C(23)–C(22)–C(19)–N(1) = 4.56°] and the *N*-mesityl groups are each rotated approximately orthogonal to the imidazolium plane [C(19)–N(1)–C(1)–C(2) = 102.2° and C(19)–N(2)–C(10)–C(11) = 91.6°]. The bond lengths and angles that define the imidazolium heterocycles of **2** compare well with structural parameters reported for simple 1,3-disubstituted imidazolium salts.[28–30] Selected bond lengths and angles for **2** can be found in Table 2.

EXPERIMENTAL

Synthesis

Reagents and solvents were obtained from Aldrich and used as received unless noted otherwise. IMes[25] and $[UO_2Cl_2(thf)_2]_2$[24] were prepared following published procedures. Anhydrous solvents, THF and hexane, were purified as described by Grubbs.[31]

$UO_2(OTf)_2(thf)_3$ (1)

To a stirred suspension of AgOTf (318 mg, 1.24 mmol) in THF (3 mL) was added dropwise a solution of $[UO_2Cl_2(thf)_2]_2$

Table 3. Crystallographic data for compounds **1** and **2**

Compound	**1** • (thf)$_2$	**2**(hexane)$_2$
Empirical formula	$C_{22}H_{40}F_6O_{13}S_2U$	$C_{60}H_{80}F_6N_4O_6S_2$
Crystal system	Trigonal	Monoclinic
Space group	R–3	C2/c
Unit cell		
a (Å)	33.7605(13)	24.792(5)
b (Å)	33.7605(13)	8.7428(11)
c (Å)	13.7465(8)	26.9665(5)
α (°)	90	90
β (°)	90	103.760(2)
γ (°)	120	90
V (Å^3)	13 568.8(11)	5677.1(17)
Z	18	4
D_{calc} (g cm^{-3})	2.046	1.324
Absorption coefficient (mm^{-1})	5.621	0.168
F (0 0 0)	8172	2408
Crystal size (mm^3)	0.21 × 0.21 × 0.21	0.21 × 0.08 × 0.04
θ range (°)	1.21–28.46	1.55–20.83
Index range	$-43 \leq h \leq 22, 0 \leq k \leq 44, 0 \leq l \leq 18$	$-24 \leq h \leq 24, -8 \leq k \leq 5, -26 \leq l \leq 26$
Reflections collected	6947	6482
Independent reflections (R_{int})	6947 (0.0000)	6482 (0.0802)
Completeness (%)	99.8; $\theta = 25.00°$	96.6; $\theta = 20.83°$
Data/restraints/parameters	6947/0/307	2880/0/298
GOF on F^2	1.182	1.033
Final R indices [$I > 2\square(I)$]	$R_1 = 0.0558, wR_2 = 0.1210$	$R_1 = 0.0838, wR_2 = 0.1993$
R indices (all data)	$R_1 = 0.0889, wR_2 = 0.1290$	$R_1 = 0.1480, wR_2 = 0.2282$
Largest difference peak and hole (e^- Å^{-3})	2.392 and −1.316	0.355 and −0.342

(300 mg, 0.309 mmol) in THF (10 mL). The resulting pale yellow solution containing a copious amount of insoluble AgCl was stirred at room temperature for 2 h, then filtered into a clean flask. The volume of the solution was reduced to ca. 5 mL and was carefully layered with hexane and allowed to crystallize at −20 °C in a low-temperature freezer. The pale yellow crystalline product was filtered and washed with hexane. The yield was 435 mg (90%). IR (Nujul): ν (cm^{-1}) 1335 (m), 1235 (m), 1202 (s, br), 1006 (s), 963 (m), 946 (m), 921 (w), 885 (w), 892 (m). Anal. calcd for $C_{14}H_{24}F_6O_{11}S_2U$: C, 21.43; H, 3.08. Found: C, 20.74; H, 3.43%.

$(C_3H_2N_2(C_9H_{11})_2CHCH)_2(OTf)_2$ (**2**)

To a pale yellow solution of **1** (100 mg, 0.127 mmol) in THF (8 mL) was added a second THF (5 mL) solution of IMes (80 mg, 0.263 mmol) with stirring. The solution became a deeper yellow color and was allowed to stir for 2 h, then layered with hexane and placed in a −20 °C freezer for several days. From the heterogeneous solids that were deposited, a bright yellow needle was selected for single crystal X-ray analysis.

X-ray crystallography

Crystals of compound **1** suitable for X-ray analysis were grown from THF layered with hexane at −20 °C. Crystals of compound **2** were obtained from a THF reaction mixture of **1** with two equivalents of IMes that was subsequently layered with hexane and stored at −20 °C.

The reflection data for both structures were collected on a Bruker P4/CCD using a combination of ϕ and ω scans. The structures were solved using standard direct method techniques (SHELXS-97),[32] and refined using full-matrix least squares based on F^2 (SHELXL-97).[32] Hydrogen atom positions were idealized, and all non-hydrogen atoms were refined anisotropically. Disordered lattice THF molecules in crystals of **1** • (thf)$_2$ and lattice hexane molecules in crystals of **2** • (hexane)$_2$ were eliminated from the refinement using PLATON/SQUEEZE.[33] A summary of crystallographic data is presented in Table 3.

Acknowledgments

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