4306 *Organometallics* **2002,** *21,* 4306−4308

$[(C_5Me_5)_2U(Me)(OTf)]_2$: A New Reagent for Uranium Metallocene Chemistry. Preparation of the First Actinide Hydrazonato Complexes

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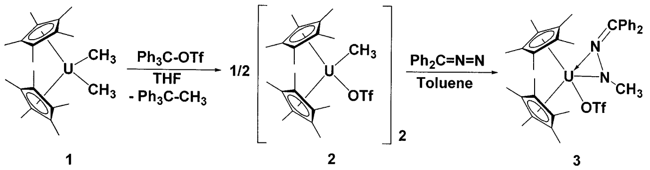
Received July 19, 2002

Summary: The synthesis and characterization of the first actinide hydrazonato complex, $(C_5Me_5)_2U(\eta^2(N,N')\text{-}CH_3\text{-}NN{=}CPh_2)(OTf)$ (**3**)*, has been made possible by use of the organouranium(IV) trifluoromethanesulfonate (triflate) complex* $[(C_5Me_5)_2U(CH_3)(OTf)]_2$ (**2**; $OTf = OSO_2CF_3$)*, which is derived from the reaction between* $(C_5Me_5)_2U(CH_3)_2$ *and* Ph_3COTf*. The related chemistry for* $(C_5Me_5)_2U(CH_3)(Cl)$ *is also reported. All new complexes have been structurally characterized.*

Transition-metal and lanthanide triflate complexes and their respective chemistry have been known for some time, and in recent years these compounds have enjoyed considerable utility as Lewis acid catalysts in organic chemistry,[1] as important precursors in inorganic chemistry,[2] and as building blocks in supramolecular chemistry.[3] In contrast, molecules possessing actinide−triflate bonds are quite scarce and until recently have been limited to a handful of thorium(IV)[4] and uranyl (UO_2^{2+})[5] triflate complexes. The paucity of available starting materials has clearly hampered the development of chemistry involving organoactinide triflate complexes. Recently, Berthet and Ephritikhine demonstrated that organouranium(IV) triflate complexes can be prepared by protonolysis of metal−alkyl and metal−amide bonds with either triflic acid or pyridinium triflate.[6] In a separate report, these authors showed that pure triflic acid reacts with U and UCl_3 to give $U(OTf)_3$ and with UCl_4 to afford $U(OTf)_4$.[7] To the best of our knowledge, there have been no reports regarding the reaction chemistry of these uranium triflate systems.

Scheme 1



Our interest in the synthesis and reactivity of uranium complexes containing multiply bonded functional groups[8] now leads us to explore the use of organometallic uranium triflate complexes as potential entries into this chemistry. Herein we describe the synthesis, properties, and chemical reactivity of a well-defined organometallic uranium(IV) methyl triflate complex, $[(C_5Me_5)_2U(CH_3)(OTf)]_2$. This complex represents the only organouranium system with both a triflate ligand and an alkyl ligand at the same metal center and offers the opportunity for further elaboration of the uranium−methyl bond in the presence of the triflate moiety within the uranium coordination sphere. The ability of this complex to participate in reaction chemistry with diphenyldiazomethane has enabled the preparation of the first actinide hydrazonato complex and illustrates the utility of this complex as a useful starting material for organometallic uranium triflate chemistry.

Our investigation takes advantage of trityl triflate, Ph_3COTf, which serves as an efficient methide-abstracting agent.[9] As illustrated in Scheme 1, reaction of $(C_5Me_5)_2U(CH_3)_2$ (**1**) with 1 equiv of Ph_3COTf in tetrahydrofuran at ambient temperature affords $[(C_5Me_5)_2U(CH_3)(OTf)]_2$ (**2**) and Ph_3CCH_3. Filtration and recrystallization from THF/hexanes at −30 °C furnishes **2** as a red crystalline solid in 80% isolated yield. The conversion of **1** to **2** is essentially quantitative, as evidenced by ^1H and ^{19}F NMR spectroscopy. The ^1H NMR spec-

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Publication on Web 09/19/2002

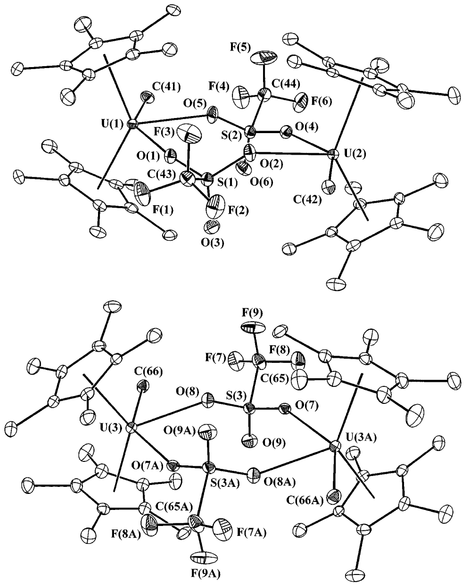

Figure 1. Molecular structures of **2a** (top) and **2b** (bottom) with thermal ellipsoids at the 20% probability level.

trum of complex **2** is characterized by a broad singlet at δ −68.65 ppm integrated to three protons (relative to the 30-proton C_5Me_5 resonance at δ 7.23 ppm) and corresponding to the remaining methyl ligand on the uranium metal center. The ^{19}F NMR spectrum of complex **2** features a resonance at δ −77.44 ppm corresponding to the triflate ligand. The solid-state infrared spectrum of **2** displays absorption bands at 1315, 1236, and 1218 cm^{-1}, consistent with the presence of bridging triflate ligands (vide infra).[2a,4c] The electronic absorption spectrum for **2** in toluene solution compares well with those typically observed for actinide complexes with f^2 electronic configurations: rich with narrow line width, low molar absorptivity (<100 M^{-1} cm^{-1}) transitions in the near-infrared region derived from the $^3H_4$ ground state.[10] Addition of excess trityl triflate affords the previously reported bis(triflate) complex $(C_5Me_5)_2U(OTf)_2$ [6] and is signaled by a singlet in the ^1H (δ 20 ppm) NMR spectrum and ultimately results in the polymerization of tetrahydrofuran.

The identity of **2** as a uranium(IV) methyl triflate complex was confirmed by a single-crystal X-ray diffraction study. As illustrated in Figure 1, complex **2** crystallizes as a dimer in the solid state and consists of two $(C_5Me_5)_2U(CH_3)$ units joined by means of two bridging triflate ligands. The molecular structure reveals that two conformers exist for **2** in the unit cell and these two conformers differ only by the orientation of the bridging triflate ligands. For example, conformer **2a** possesses C_{2v} symmetry, while **2b** contains a center of inversion. In both systems, the uranium metal centers feature a typical bent-metallocene framework with the triflate and methyl ligands positioned in the equatorial girdle. The bonding of the triflate ligands to the uranium is symmetric, with one triflate ligand forming a σ bond to the metal center and the second triflate ligand coordinating to the metal by means of a dative bond. Thus, for conformer **2a**, U(1)−O(5) = 2.516(5) Å, U(1)−O(1) = 2.519(5) Å, U(2)−O(2) = 2.496(5) Å, and U(2)−O(4) = 2.544(5) Å; for conformer **2b**, U(3)−O(8) = 2.533(5) Å and U(3)−O(7A) = 2.543(5) Å. The most salient metrical parameters, namely the $U-CH_3$ bond lengths (**2a**, U(1)−C(41) = 2.403(7) Å, U(1)−C(42) = 2.405(7) Å; **2b**, U(3)−C(66) = 2.441(7) Å) compare well with the U−C distances reported for other structurally characterized uranium(IV) alkyl complexes (e.g. $[(3,5\text{-}C_6H_3Me_2)N(^tBu)]_3UMe$, $U-CH_3$ = 2.446(7) Å;[11] $[1,3\text{-}^tBu_2C_5H_3]_2UMe_2$, $U-CH_3$ = 2.42(2) Å;[12] $(C_5Me_5)_2U[P(SiMe_3)SiMe_2CH_2]$, $U-CH_2$ = 2.415(20) Å;[13] Cp_3UBu, $U-CH_2$ = 2.43(2) Å;[14] $(Me_2PCH_2CH_2PMe_2)U(Me)(CH_2C_6H_5)_3$, $U-CH_3$ = 2.41(1) Å).[15]

Diazoalkanes were chosen to probe the reactivity of the new organouranium triflate system. As depicted in Scheme 1, treatment of a toluene solution of **2** with 1 equiv of diphenyldiazomethane affords the unprecedented uranium(IV) hydrazonato complex $(C_5Me_5)_2U(\eta^2(N,N')\text{-}CH_3NN{=}CPh_2)(OTf)$ (**3**) in 68% isolated yield. The reaction is accompanied by a marked color change from red to magenta. The ^1H NMR spectrum of **3** is sharp and paramagnetically shifted, which suggests that the complex is a U(IV) species. The room-temperature electronic absorption spectrum, recorded in tetrahydrofuran solution from 1600 to 300 nm, shows several narrow line width, low molar absorptivity (<150 M^{-1} cm^{-1}) transitions, which is consistent with the assignment of an f^2 U(IV) metal center.[10] Inspection of the ^{19}F NMR spectrum of **3** reveals that the triflate ligand is still coordinated to the uranium metal center and undergoes a marked upfield shift to δ −100.63 ppm, which is consistent with a more electron-rich metal center sustained by the η^2(N,N′)-bound hydrazonato moiety, $Ph_2C{=}NNCH_3$.[16] Interestingly, absorption bands at 1331, 1233, and 1201 cm^{-1} in the solid-state IR spectrum of **3** suggest the presence of a bridging triflate ligand in the solid state.[2a,4c]

That the uranium−methyl bond in complex **2** had been elaborated was verified by a single-crystal X-ray diffraction study (Figure 2). The molecular structure of complex **3** shows that the diphenyldiazomethane molecule has been inserted into the uranium−methyl linkage and forms two new nitrogen bonds to the uranium metal center: a U−N σ bond (U(1)−N(1) =

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(16) The ability of the hydrazonato ligand to stabilize the U(IV) metal center was also evaluated by comparing the electrochemistry of complexes **2** and **3**. Complex **2** exhibits a single reversible U(IV/III) couple at $E_{1/2} = -1.83$ V (vs $[Cp_2Fe]^{0/+}$) and irreversible oxidative chemistry associated with C_5Me_5 ligands. In contrast, complex **3** shows both a reversible reduction process at $E_{1/2} = -2.01$ V and a reversible oxidation step at $E_{1/2} = +0.18$ V. Thus, the metal center in complex **3** has become more difficult to reduce and easier to oxidize (both the U(IV/III) and U(V/IV) couples are shifted to more negative potentials), which is consistent with a more electron-rich U(IV) metal center supported by donation of electron density from the hydrazonato ligand.

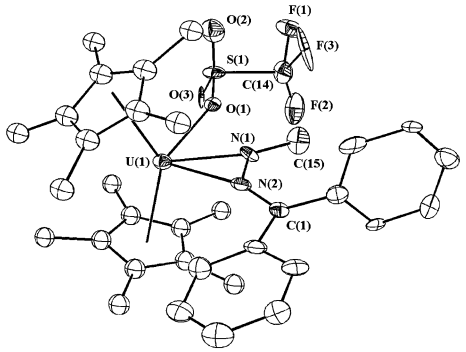

Figure 2. Molecular structure of **3** with thermal ellipsoids at the 25% probability level.

2.25(2) Å) and a second U−N dative interaction (U(1)−N(2) = 2.46(2) Å). The N(2)−C(1) bond length of 1.32(3) Å is characteristic of an N=C double bond,[17] but the N(1)−N(2) bond length of 1.41(3) Å is intermediate between an N−N single and an N=N double bond[17] and implies some electronic delocalization over the C−N−N unit. The coordinated triflate ligand features a U−O bond distance of 2.395(14) Å.

Efforts were made to extend this chemistry to the known[18] uranium chloride complex $(C_5Me_5)_2U(Me)(Cl)$ (**4**), and reaction of **4** with diphenyldiazomethane does afford the corresponding hydrazonato complex, $(C_5Me_5)_2U(\eta^2(N,N')\text{-}CH_3NN{=}CPh_2)(Cl)$ (**5**). However, in contrast to the triflate complex **2**, the chemistry observed for the chloride derivative **3** was problematic, suffering from low yields (39%) and redistribution processes to give $(C_5Me_5)_2UCl_2$ in addition to the desired hydrazonato product **5**. Clearly, the difficulties encountered using the known uranium chloride complex **4**, which are absent for the triflate system, further underscores the utility of complex **2** as an alternative starting material for organoactinide chemistry.

Despite the complications discussed above, a few X-ray-quality crystals of **5** could be obtained from cold hexanes. Complex **5** was subjected to scrutiny by X-ray crystallography, pertinent metrical parameters being the U−NMe distance of 2.212(7) Å, the $U{-}NCPh_2$ distance of 2.473(7) Å, the $N{=}CPh_2$ distance of 1.310(11) Å, and the $MeN{-}NCPh_2$ distance of 1.370(9) Å, all of which are similar to those presented by the triflate derivative **3**.[19] The U−Cl bond length of 2.632(2) Å lies within the range of U−Cl distances reported for other structurally characterized U(IV) chloride complexes.[20]

Knowledge regarding the reaction chemistry of uranium triflate complexes is lacking. Thus, the most interesting aspect of this work is the ability of the uranium triflate complex **2** to participate in further reaction chemistry with diphenyldiazomethane to afford the uranium(IV) hydrazonato complex **3**; the diazoalkane does not lose N_2 to give an uranium alkylidene complex but instead inserts into the U−C bond of complex **2**. Related migratory insertion chemistry involving isocyanides,[21] CO,[22] CO_2,[23] and SO_2 [24] has been noted for other uranium(IV) alkyl complexes. To the best of our knowledge, complex **3** represents the first example of an f-element hydrazonato complex. However, our results find interesting parallels to group IV chemistry. For example, Floriani and co-workers demonstrated that diphenyldiazomethane reacts with both Cp_2ZrMe_2 and $Cp_2Zr(H)(Cl)$, inserting into the Zr−C and Zr−H bonds, to give the hydrazonato complexes $Cp_2Zr(\eta^2(N,N')\text{-}CH_3NN{=}CPh_2)(Me)$ and $Cp_2Zr(\eta^2(N,N')\text{-}HNN{=}CPh_2)(Cl)$, respectively.[25] Likewise, Santarsiero and Moore reported that $(C_5Me_5)_2Zr(Me)(Cl)$ reacts with bis(*p*-tolyl)diazomethane to generate the hydrazonato complex $(C_5Me_5)_2Zr(\eta^2(N,N')\text{-}(CH_3)NN{=}C(p\text{-}tol)_2)(Cl)$.[26] A related example was provided by Royo and coworkers, who showed that diphenyldiazomethane inserts into two of the Ti−C bonds of the dimer $[(C_5Me_5)TiMe_2]_2(\mu\text{-}O)$ to give the corresponding hydrazonato system $[(C_5Me_5)Ti(\eta^2(N,N')\text{-}CH_3NN{=}CPh_2)(Me))]_2(\mu\text{-}O)$.[27]

In summary, a new reagent for uranium(IV) metallocene chemistry, $[(C_5Me_5)_2U(CH_3)(OTf)]_2$ (**2**), has been prepared from the reaction between $(C_5Me_5)_2U(CH_3)_2$ and Ph_3COTf. The synthetic utility of this complex has been validated by the synthesis of the first actinide hydrazonato complex, $(C_5Me_5)_2U(\eta^2(N,N')\text{-}CH_3N\text{-}N{=}CPh_2)(OTf)$. Importantly, we have also shown that complex **2** provides an alternative to the known $(C_5Me_5)_2U(Me)(Cl)$, since the latter complex can suffer from undesirable redistribution chemistry. We anticipate that the distinct structure and reactivity patterns displayed by complex **2** will enable the preparation of a variety of new organouranium complexes that are not currently accessible using the chloride system. We are exploring this chemistry further.

Acknowledgment. For financial support of this work, we acknowledge the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (C.J.B.) and the LANL Laboratory Directed Research and Development Program (D.E.M.). J.L.K. is the recipient of a Frederick Reines fellowship at Los Alamos National Laboratory. Finally, we thank Prof. Paul B. Duval (University of Missouri, Columbia, MO) for helpful discussions.

Supporting Information Available: Text giving full synthesis and characterization data for compounds **2**, **3**, and **5**, figures displaying an ORTEP diagram for complex **5** and UV−vis−near-IR spectra for complexes **2**, **3**, and **5**, and X-ray crystallographic information given as CIF files for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205804

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