Identification of the U(V) Complex $(C_5Me_5)_2U^{VI}(=NSiMe_3)$ in the Reaction of $(C_5Me_5)_2U^{III}I(THF)$ with N_3SiMe_3

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Identification of the U(V) Complex $(C_5Me_5)_2U^V I(=NSiMe_3)$

in the Reaction of $(C_5Me_5)_2U^{III}I(THF)$ with N_3SiMe_3

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Abstract

The U(V) imido complex $(C_5Me_5)_2U^V I(=NSiMe_3)$, **1**, was crystallographically characterized from the reaction of $(C_5Me_5)_2U^{III}I(THF)$ with N_3SiMe_3 which demonstrates that it can be an intermediate in the reaction which ultimately forms $(C_5Me_5)_2U^{VI}(=NSiMe_3)_2$ and $(C_5Me_5)_2U^{IV}I_2$. U(V) intermediates have been proposed in such reactions, but have not been previously observed. The direct observation of **1** provides insight into the reaction mechanisms of U(III) compounds with azide reagents.

Introduction

Reactions of uranium complexes with azides and oxygen-transfer reagents have been heavily studied due to interest in actinide-ligand multiple bonding.[1–6] Additionally, uranium oxo and imido species are of interest for theoretical and reactivity studies.[7–13] To generate uranium-nitrogen multiple bonds, often a uranium complex is reacted with an organic azide reagent, RN_3, or azobenzene, PhN=NPh, to oxidize the metal center and install an NR imido ligand or NPh.

For example, U(III) compounds containing the $[(C_5Me_5)_2U^{III}]^{1+}$ bent metallocene framework react with azide and azo reagents to generate U(VI) products. This is exemplified by the reaction of $(C_5Me_5)_2U^{III}Cl_2Na$ with adamantyl azide and azobenzene which led to the isolation of $(C_5Me_5)_2U^{VI}(=NR)_2$ (R = Ad, Ph)[14] (eqn 1).

1

$$R = Ad, Ph \qquad (1)$$
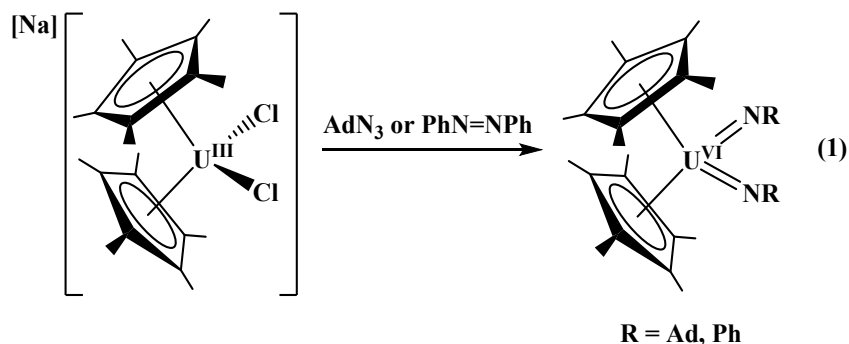
Other reports include the reaction of $(C_5Me_5)_3U^{III}$ with azobenzene which formed $(C_5Me_5)_2U^{VI}(=NPh)_2$ with a byproduct of $(C_5Me_5)_2,[15]$ the reaction of $(C_5Me_5)_2U^{III}[P(SiMe_3)(Mes)](THF)$ (Mes = $C_6H_2Me_3$-2,4,6) with organoazides to form $(C_5Me_5)_2U^{VI}(=NR)_2$ (R = SiMe$_3$, Ad) and dimeric $[P(SiMe_3)(Mes)]_2,[16]$ and the reaction of $(C_5Me_5)_2U^{III}(hpp)$ (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidinato) with N_3SiMe_3 to form $(C_5Me_5)_2U^V(hpp)(=NSiMe_3).[17]$ In the latter case, the isolation of the U(V) species $(C_5Me_5)_2U^V(hpp)(=NSiMe_3)$ rather than a U(VI) product is likely due to the inability of the hpp ligand to oxidatively dimerize in contrast to the C_5Me_5 and $P(SiMe_3)(Mes)$ examples.

In the initial report of $(C_5Me_5)_2U^{III}Cl_2Na$ reacting with AdN$_3$ (Ad = 1-adamantyl), a mechanism was proposed in which an unobserved U(V) intermediate $(C_5Me_5)_2U^V(=NAd)(Cl)$ underwent reduction by the U(III) starting material to an unobserved U(IV) intermediate that subsequently reacted with a second equivalent of AdN$_3$ to generate the observed U(VI) product $(C_5Me_5)_2U^{VI}(=NAd)_2[14]$ (Scheme 1).
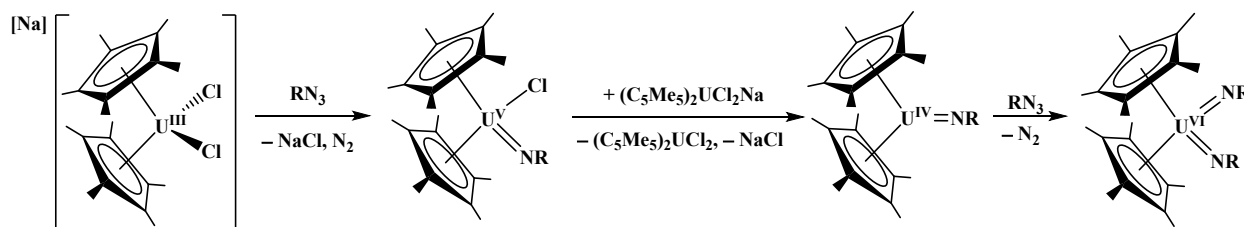
Scheme 1: Original proposed mechanism for the reaction of $(C_5Me_5)_2U^{III}Cl_2Na$ with adamantyl azide (R = Ad).[14]

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Although neither the U(V) nor U(IV) intermediates were isolated in the study in Scheme 1, they are quite reasonable. U(V) imido species can be generated in other systems in addition to the $(C_5Me_5)_2U^V(hpp)(=NSiMe_3)$ example described above.[17] Examples include $Cp''_2U^V(=NSiMe_3)Cl$, [$Cp'' = C_5H_3(SiMe_3)_2$],[18] $Cp^{Me}_3U^V(=NR)$ [$Cp^{Me} = C_5MeH_4$; R = SiMe_3, Ph],[19] $U^V[N(SiMe_3)_2]_3(=NR)$ [R = SiMe_3, CPh_3, naphthyl],[20,21] [$(^{Ad,tBu}ArO)_3tacn]U^V(=NSiMe_3)$,[22] and [K(18-crown-6)][$U^V(OSiR_3)_4(=NR')$] [R = O^{t}Bu; R' = SiMe_3, Ad].[8] Furthermore, the U(IV) imido complex $(C_5Me_5)_2U^{IV}(=NAr)(THF)$ reacts with CuX and PhE–EPh to form $(C_5Me_5)_2U^V(=NAr)(X)$ (Ar = 2,6-^{i}Pr_2C_6H_3; X = F, Cl, Br, I, OTf, C≡CPh, SPh, SePh, TePh)[23–26] and the $(C_5Me_5)_2U^V(=NAr)(X)$ complexes can be further derivatized with MX' (M = Li, K; X' = NPh_2, OPh, Me, Ph) via salt metathesis reactions to form $(C_5Me_5)_2U^V(=NAr)(X')$.[25]

Although many U(V) imido complexes have been reported, no examples have been found in reactions of U(III) metallocenes that form U(VI) bis(imido) products. Here, we present results on a $(C_5Me_5)_2U^{III}I(THF)$ reaction with RN_3 that led to the isolation of a U(V) complex, which could form the U(VI) product by disproportionation. The U(V) compound, $(C_5Me_5)_2U^VI(=NSiMe_3)$, appears to be unstable with respect to disproportionation into $(C_5Me_5)_2U^{VI}(=NSiMe_3)_2$ and $(C_5Me_5)_2U^{IV}I_2$ which explains why these intermediates were not observed before.

Results and Discussion

Initially, the reaction of $(C_5Me_5)_2U^{III}I(THF)$ and Me_3SiN_3 was performed in an attempt to generate a species such as "$(C_5Me_5)_2U^{III}(N_3)$"[27,28] by elimination of Me_3SiI. However, the U(III) reduction of the organic azide took place. The first time this reaction was performed, brown X-ray quality crystals were isolated from hexane upon workup. These were identified as the U(V) mono-imido species $(C_5Me_5)_2U^VI(=NSiMe_3)$, **1**, by X-ray crystallography (Fig. 1).

Reduction of the azide by the U(III) center is not surprising, but isolation of the mono-imido species was unexpected given that previous reactions of $[(C_5Me_5)_2U^{III}]^{1+}$ complexes with organic azides typically afford U(VI) bis(imido) species. Complex **1** crystallizes in the $P2_1/m$ space group with two independent molecules in the unit cell. It maintains the bent metallocene motif with the iodide and imido ligand occupying the metallocene wedge positions. Although the crystallographic data were not high quality, a brief metrical analysis is presented in the next paragraph.
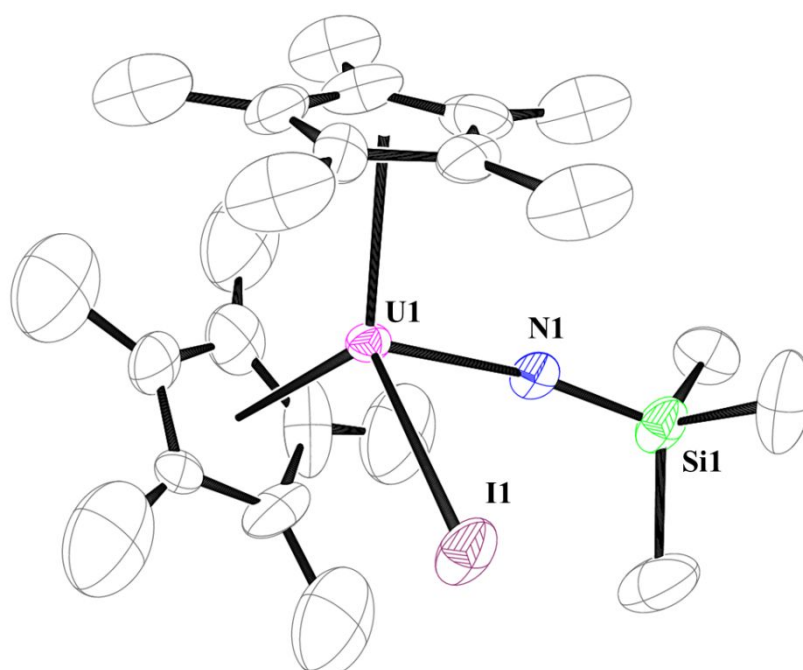

Fig 1: Molecular structure of **1** with selective atom labelling. Hydrogen atoms are omitted for clarity.

Modeling the X-ray data gave U–Cnt distances of 2.513 and 2.525 Å and the U–I distances of 3.1074(14) and 3.1137(14) Å. The U–N distances obtained from the crystal, 2.061(10) and 2.100(13) Å, are long for a U(V) imido species. For example, the U–N distance in $(C_5Me_5)_2U^V(hpp)(=NSiMe_3)$ is 1.969(2) Å. The U–N distances in $(C_5Me_5)_2U^V(X)(=NAr)$ (Ar = $C_6H_3{}^iPr_2$-2,6; X = OTf, SPh, F, Cl, Br, I) range from 1.957(5) to 1.976(4) Å.[24–26,29,30] However,

the 163.7(7) and 164.0(7)° U–N–Si angles in **1** are not close to U–N–Si angles of M–NHSiMe$_3$ moieties. For example, the Ti–N–Si angle in (C$_5$Me$_5$)[SiMe$_3$NS(=NSiMe$_3$)NSiMe$_3$-κ^2-*N,N*]Ti(NHSiMe$_3$) is significantly more acute at 137.3(1)°[31] and the Ge–N–Si angles in {HC[C=CH$_2$C(Me)NAr]$_2$}Ge(NHSiMe$_3$)$_2$ (Ar = C$_6$H$_3$^{i}Pr$_2$-2,6) are 134.7(1) and 138.0(1)°.[32] In comparison, the U–N–Si angles in the (C$_5$Me$_5$)$_2$U^V(X)(=NAr)[24–26,29,30] complexes are 168.3(5) to 172.2(9)° and (C$_5$Me$_5$)$_2$U^V(hpp)(=NSiMe$_3$) has a 173.64(12)° angle.[17]

Despite numerous efforts, reproducible isolation of compound **1** proved difficult. All further attempts at the reaction led to the isolation of the U(VI) compound (C$_5$Me$_5$)$_2$U^{VI}(=NSiMe$_3$)$_2$.[16] During these reactions, a second signal was identified in the ^{1}H NMR spectrum arising from the U(IV) product, (C$_5$Me$_5$)$_2$U^{IV}I$_2$,[23,33] which is formed in nearly equal amounts to (C$_5$Me$_5$)$_2$U^{VI}(=NSiMe$_3$)$_2$. The presence of the U(IV) complex can be explained by the disproportionation of **1** into (C$_5$Me$_5$)$_2$U^{VI}(=NSiMe$_3$)$_2$ and (C$_5$Me$_5$)$_2$U^{IV}I$_2$. In other words, compound **1** can be an intermediate in the reaction of (C$_5$Me$_5$)$_2$U^{III}I(THF) and Me$_3$SiN$_3$ (eqn 2).
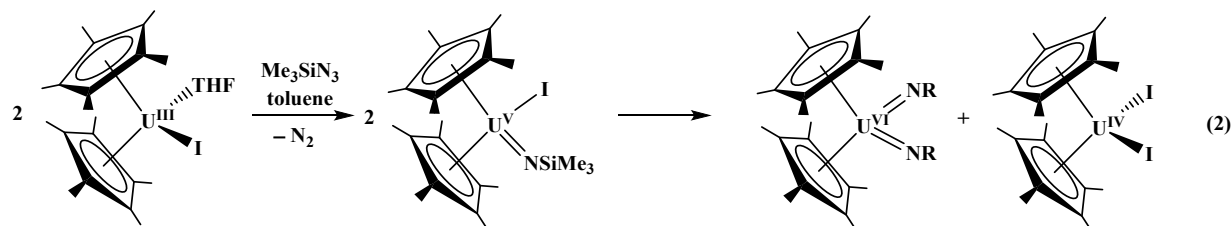
The reaction in eqn 2 was followed by NMR with excess (C$_5$Me$_5$)$_2$U^{III}I(THF) in hopes of identifying the resonances attributable to **1**. Multiple new resonances were observed, but definitive assignment of the spectrum was not possible.

The reactivity of (C$_5$Me$_5$)$_2$U^{III}I(THF) with adamantyl azide was investigated to determine if the reaction above was unique to a trimethylsilyl azide and if an analogous U(V) compound to **1** could be identified. However, only (C$_5$Me$_5$)$_2$U^{VI}(=NAd)$_2$[14] and (C$_5$Me$_5$)$_2$U^{IV}I$_2$ were isolated

from this reaction (eqn 3), and no U(V) intermediate could be definitively identified. However,

the formation of $(C_5Me_5)_2U^{IV}I_2$ suggests that a disproportionation reaction is active as in eqn 2.

$$[RN_3] = Me_3SiN_3, AdN_3, PhN=NPh$$
$$R = SiMe_3, Ad, Ph$$
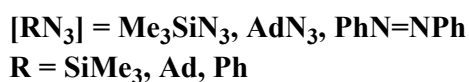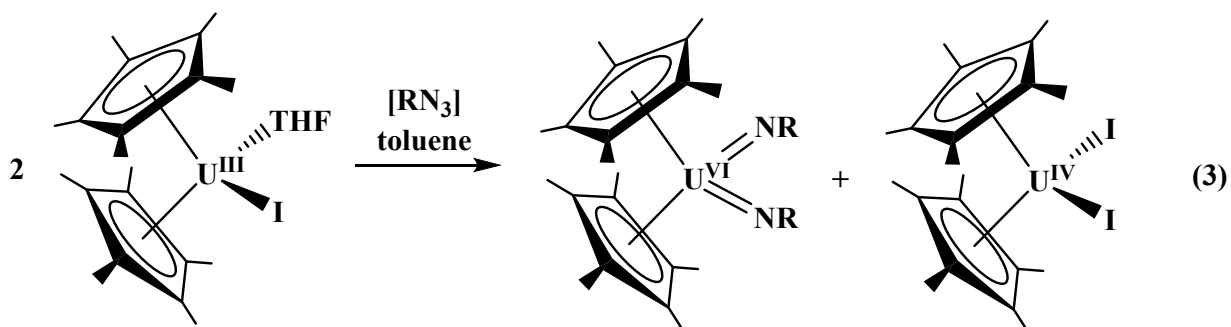
Similar results were observed in the reaction of $(C_5Me_5)_2U^{III}I(THF)$ with azobenzene.

$(C_5Me_5)_2U^{VI}(=NPh)_2$[14,34] and $(C_5Me_5)_2U^{IV}I_2$ were isolated from the reaction mixture (eqn 3).

Although azobenzene is not formally an azide reagent, the reaction is proposed to again follow a

disproportionation mechanism due to the formation of the U(IV) byproduct $(C_5Me_5)_2U^{IV}I_2$.

Conclusions

In summary, reaction of $(C_5Me_5)_2U^{III}I(THF)$ with azide reagents can form a U(V)

intermediate, $(C_5Me_5)_2U^{VI}(=NR)$, which was crystallographically identified in the case of

$(C_5Me_5)_2U^{VI}(=NSiMe_3)$. It is likely that this intermediate undergoes disproportionation to form

the U(VI) product $(C_5Me_5)_2U^{VI}(=NR)_2$ and a U(IV) co-product, $(C_5Me_5)_2U^{IV}I_2$, which was

identified in this system. This disproportionation mechanism allows the net three electron

oxidation of U(III) to U(VI) to be accomplished by a two electron U(III) to U(V) process, followed

by disproportionation.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

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