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Exploiting the Reactivity of Actinide Fluoride Bonds for the Synthesis and Characterization of a New Class of Monometallic Bis(azide) Uranium Complexes.

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	A B S T R A C T	
Keywords:	The terminal actinide fluoride bonds	in $(C_5Me_5)_2ThF_2(py)$ (py = pyridine) and
	$(C_5Me_5)_2UF_2(O=PR_3)$ (R = Me, Ph) react with	h two equivalents of Me ₃ SiN ₃ in toluene to form the
Thorium	polymeric thorium bis(azide), $[(C_5Me_5)_2Th($	$[N_3)_2]_{\infty}$, and a new class of monometallic uranium
Uranium	bis(azide) complexes, $(C_5Me_5)_2U(N_3)_2(O=P)$	R ₃), respectively. Full characterization of the novel
Fluoride	complexes $(C_5Me_5)_2$ ThF ₂ (py) and $(C_5Me_5)_2$ U	$F_2(O=PR_3)$ (R = Me, Ph) are reported, including the
Azide	solid-state structures of $(C_5Me_5)_2ThF_2(py)$ a	nd $(C_5Me_5)_2U(N_3)_2(O=PPh_3)$. Electronic absorption
Electronic absorption	spectral data are also reported for $(C_5Me_5)_2A$	$AnF_2(py)$ (An = Th, U) and (C ₅ Me ₅) ₂ U(N ₃) ₂ (O=PR ₃)
spectroscopy	(R = Me, Ph) to confirm metal oxidation sta	ate and enable elucidation of the fluoride and azide
X-ray crystallography	ligand bonding in these complexes.	

This article is dedicated to Professor William J. Evans, inspirational mentor and friend, in honor of his tremendous scientific contributions to the field of f-element chemistry.

1. Introduction

Developing new routes for the safe synthesis of actinide nitride complexes has become part of a greater global effort towards crafting accident-tolerant nuclear fuel cycles.[1, 2] Over the past 20 years, several examples of bridging or capped molecular uranium nitride complexes have been reported[2, 3] as well as a variety of uranium nitride compounds identified through spectroscopic and matrix-isolation experiments.[2, 4, 5] The first terminal actinide nitride was reported by our group in 2010, where photolysis of the uranium azide complex, $(C_5Me_5)_2U(N_3)[N(SiMe_3)_2],$ afforded the transient uranium(VI) nitride $(C_5Me_5)_2U(\equiv N)[N(SiMe_3)_2]$; the reactive U≡N fragment inserts into a ligand C-H bond to N–H and N–C bonds, yielding generate new $(C_5Me_5)(C_5Me_4CH_2NH)U[N(SiMe_3)_2].[6]$ The first isolable terminal uranium(V) nitride, [tren^{TIPS}U \equiv N][Na(12- $(rown-4)_2$] $(tren^{TIPS} = N(NCH_2CH_2NSi^iPr_3)_3)$, was isolated by Liddle and co-workers in 2012.[7] The steric protection provided by the tren^{TIPS} ligand prevented the formation of bridging nitrides, while the chelating crown ether sequestered the sodium ion to preclude capping. Subsequently, the Liddle group has reported the

preparation of a suite of terminal uranium nitride complexes. [8, 9]

Although salt metathesis chemistry using NaN₃ represents the most commonly used method for installing azide ligands on actinide metal centers, [2, 10-17] we have been exploring additional routes for accessing actinide azide complexes. One promising avenue our group has discovered capitalized on the nucleophilic chemistry displayed by terminal uranium fluoride ligands.[18] Specifically, $(C_5Me_5)_2UF_2(py)$ reacted with Me₃SiN₃ to afford Me₃SiF and the uranium bis(azide) trimetallic complex, $[(C_5Me_5)_2U(N_3)_2]_3$, which was previously prepared by Evans and co-workers using salt metathesis.[11]

Herein, we expand upon this chemistry to prepare a new class of monometallic uranium bis(azide) complexes. Specifically, we show that the formation of multimetallic uranium complexes with bridging azide ligands can be thwarted in the presence of phosphine oxide ligands. We also report the synthesis of a new thorium terminal fluoride complex and demonstrate that ionic Th–F bonds also react cleanly with Me₃SiN₃ to prepare a thorium bis(azide) polymer. Finally, we use electronic absorption spectroscopy to assess the metal oxidation states in these bent metallocene complexes and to compare coordination

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