

# Exploring the border of the periodic table: new concepts in uranium chemistry

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## Abstract

The activation of small molecules is a paramount challenge in modern chemistry. The use of cheap and abundant molecules such as N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, or CO as energy supplies or precursors for fine chemicals production is highly desirable. In particular, the only industrial process which uses the ubiquitous molecule N<sub>2</sub> is the Haber-Bosch process to produce NH<sub>3</sub>, consuming approximately 2% of the world energy yearly. Low valent uranium complexes have been proven to be ideal candidates in the field of small molecule activation such as N<sub>2</sub>. Despite its relative abundance in the earth crust and its widespread use in the nuclear industry, the chemistry of uranium compounds is relatively underdeveloped and poorly understood. Actinides and uranium possess accessible 5*f* orbitals, making their chemical properties unique and lying between those of transition metals and lanthanides. The radial extension of 5*f* orbitals allows uranium to engage in the formation of multiple bonds. Amongst multiply bonded species, uranium nitrides, long-sought intermediates in the activation of N<sub>2</sub> by uranium complexes, are extremely important considering their potential use in N-functionalization processes.

The current seminar is about recent advances in the chemistry of uranium compounds in the context of small molecule activation. Initially, the synthesis and reactivity of uranium nitrides in different oxidation states and binding modes will be presented. Their ability to undergo N-functionalization processes through the activation of industrially relevant small molecules such as CO, CO<sub>2</sub>, and H<sub>2</sub> will be shown. The impact of the coligands, oxidation state, and the binding mode on the reactivity of the uranium-nitride moiety will be highlighted and demonstrated. The extension of actinide-nitride bonds to thorium complexes will also be presented, featuring the first reactive thorium nitride moiety. Despite the report of several uranium bridging nitride complexes, a paucity of uranium terminal nitrides is, instead, isolable. The first photochemical synthesis of a remarkably stable uranium terminal nitride and its N-functionalization will be presented here.

The ability of low valent uranium species to activate N<sub>2</sub> will then be showcased. A dimeric U(III) complex featuring an oxo-bridging ligand and its ability to activate N<sub>2</sub> with 4 electrons will be presented. The nature of the bridging atom link will be shown to greatly affect the magnetic properties and the N-functionalization chemistry of the compound. Further reduction of the oxo-hydrazido bridging complex allows the full splitting of the N<sub>2</sub> triple bond yielding an unprecedented uranium tetranitride cluster able to activate CO to produce N<sub>2</sub>-derived CN<sup>-</sup> and NCO<sup>-</sup>.

Given the outstanding ability of U(III) complexes to reduce small molecules, the identification of more reactive uranium compounds in lower oxidation states is a staple in actinide chemistry. Although, since their identification in 2013, very little has been reported about the reactivity of divalent U(II) compounds. Recent work on the reactivity of a neutral divalent uranocene showed its remarkable stability towards oxidation. Here, the unprecedented synthesis of a monovalent uranium complex by reduction of a U(II) metallocene will be presented. This represents the first complex of uranium in +1 oxidation state. Its reactivity, stability, and magnetic properties were investigated and will be presented here. The chemistry of super-reduced uranium is a milestone in actinide chemistry and paves new avenues for the activation of small molecules through uranium complexes.