Novel Uranium-Small Molecule Interactions, and X-ray Spectromicroscopy for Nuclear Forensics

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Nuclear Science & Security Consortium

Poster 7

Introduction

Dihydrogen complexes are mainstays of transition metal chemistry

- Homogeneous hydrogenations
- Biomimetic chemistry
- Hydrogen storage

Since discovery in 1984, dihydrogen complexes have been implicated in main group as well as lanthanide chemistry

No counterpart in the actinides

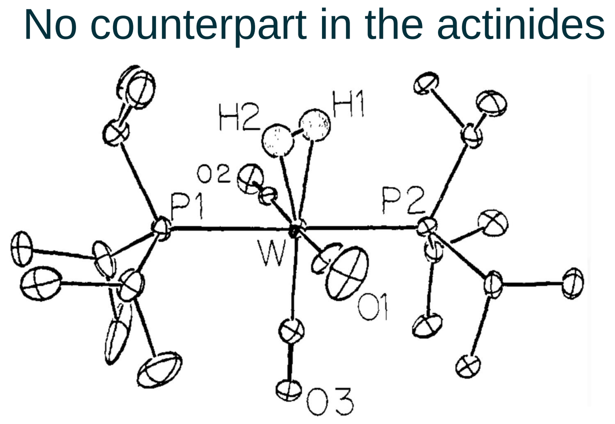


Fig 1. Structure of the "Kubas" complex.[1]

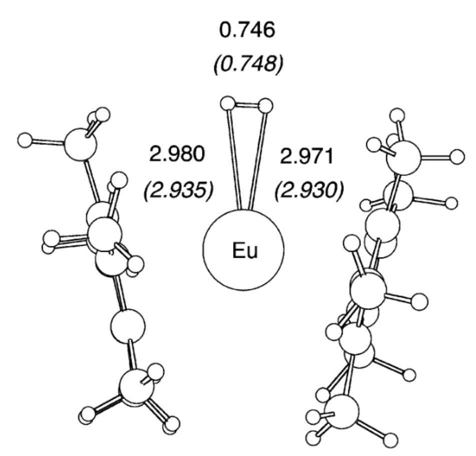


Fig 2. Structure of $Cp^*_2Eu\text{-}H_2$.[2]

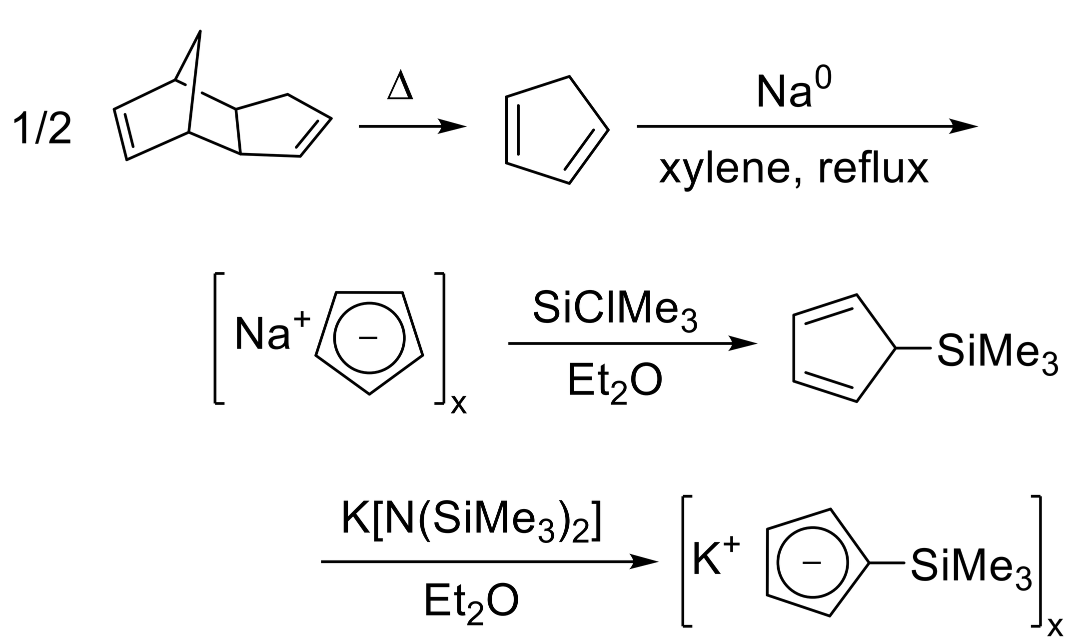
Design and Synthesis

Target: electron-rich uranium complex with vacant coordination site

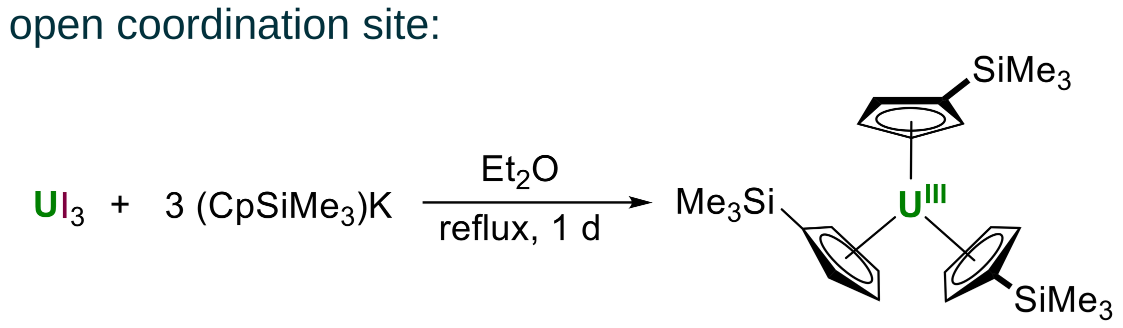
Start synthesis from uranium turnings:

$$U^0 + 3/2\ I_2 \xrightarrow[\text{sonication, 7 d}]{Et_2O} UI_3$$

Separately, synthesize bulky, multihaptic "Cp" ligand:



Combine ligand and UI_3 to yield uranium(III) complex with open coordination site:



Experimental Results

[1]H nuclear magnetic resonance ([1]H NMR) spectroscopy very sensitive to paramagnetic ion interactions[3]:

$$\Delta_L = \Delta v / v_0 = \Delta_{CFS} + \Delta_{CS} + \Delta_{PCS}.$$

Titration experiment shows linear dependence of H_2 chemical shift on $[(C_5H_4SiMe_3)_3U]$:

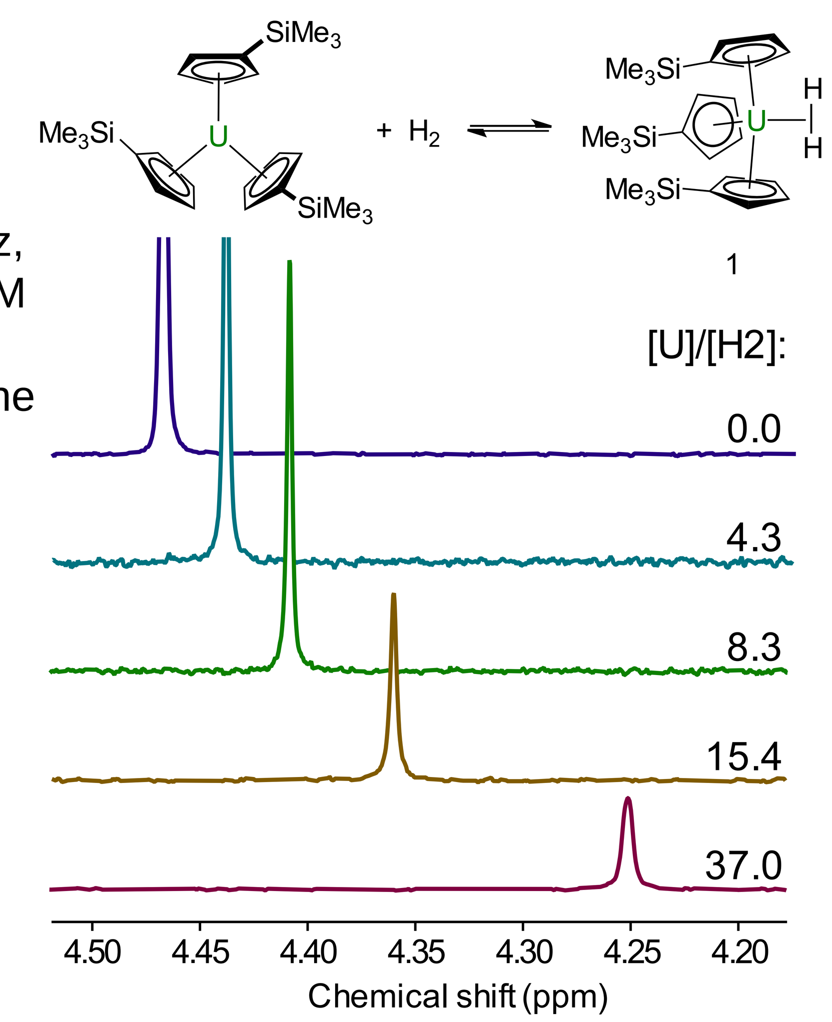


Fig 3. [1]H NMR spectra (500 MHz, 296 K) of a ~3 mM solution of H_2 in C_6D_6 containing the indicated equivalents of $(C_5H_4SiMe_3)_3U$. Concentrations calibrated to internal hexamethylbenzene.

Temperature dependence deviates from Curie-Weiss behavior:

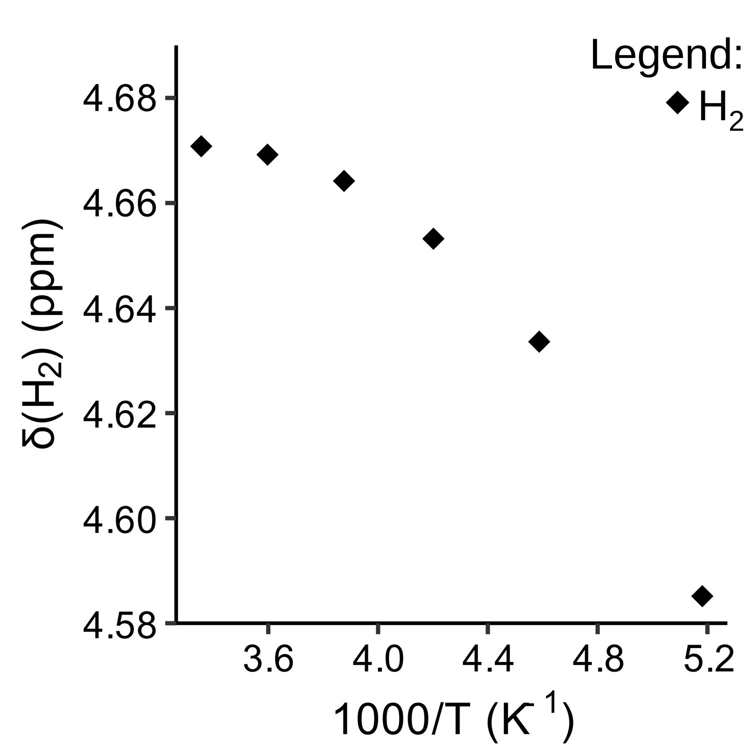
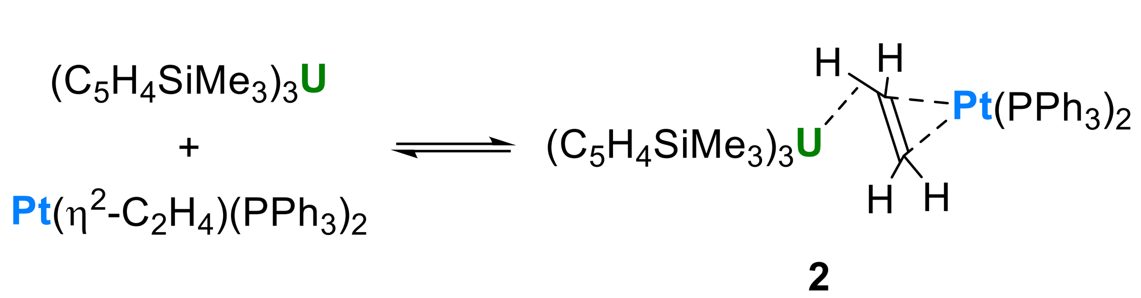


Fig 4. Plot of chemical shift vs. 1000/T for a methylcyclohexane-d14 solution of H_2, $(C_5H_4SiMe_3)_3U$, and hexamethylbenzene.

Similar [1]H NMR evidence suggests a uranium-olefin interaction is possible with $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$:



Theoretical Modeling

Density functional theory calculations:

- Geometry similar to $Cp^*_2Eu\text{-}H_2$, but very close U-H contacts
- U-H_2 bonding orbital shows f-electron involvement

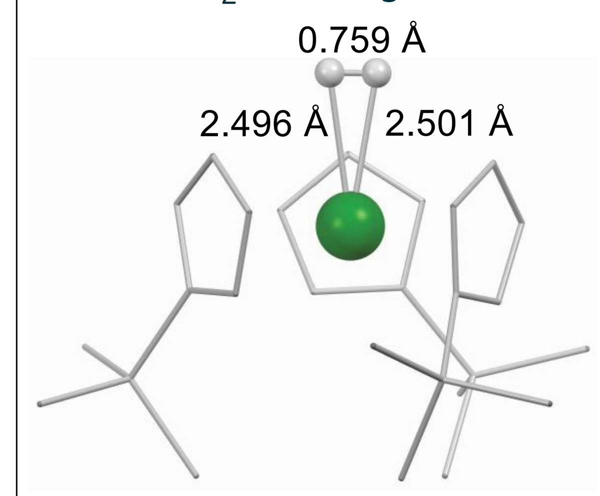


Fig 5. Optimized structure of complex **1**.

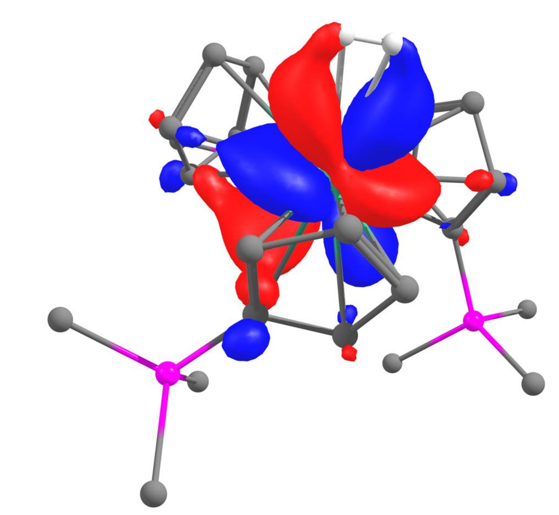


Fig 6. U-H_2 bonding orbital in complex **1**.

Mission Relevance

The NNSA's understanding of actinide chemistry informs its development of technologies capable of characterizing and analyzing nuclear materials. As such, continuing to study new actinide-based materials is critical to maintaining a current and effective detection and analysis protocol. This research expands the community's knowledge base in fundamental actinide-element interactions, relevant to the structure and properties of materials such as actinide carbides, silicides, and post-transition-metal alloys.

The detection of trace elements in taggant samples greatly facilitates material accounting. Furthermore, the application of synchrotron X-ray techniques to actinide material analysis can yield information as to material origin and refinement method(s) for nuclear forensics purposes.

Acknowledgments

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References

(1) *J. Am. Chem. Soc.* **1984**, *106*, 451–452. (2) *Organometallics* **2003**, *22*, 5447–5453. (3) *Progress in Nuclear Magnetic Resonance Spectroscopy* **1980**, *14*, 67–111.

Internship Highlight: Nuclear Forensics at the Advanced Light Source *via* Soft and Tender X-ray Spectromicroscopy

Background:

- Robust nuclear forensics program part of preventing the use and proliferation of nuclear weapons
- X-ray fluorescence elucidates elemental composition of a sample by measuring spectrum of characteristic X-ray emissions

Metallic uranium doped with other metals to facilitate "intentional forensics":

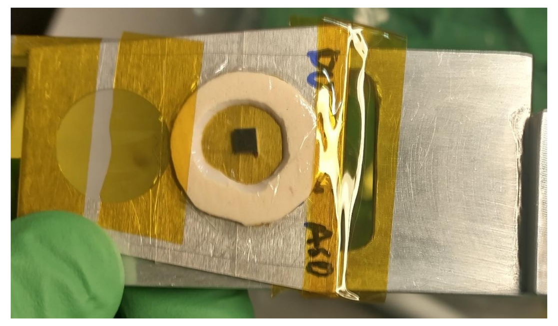

Fig 7. Uranium taggant monolith in containment system of polypropylene and Kapton.

Analysis at ALS BL 10.3.2 allows detection of trace (tens of ppm) elements in the taggants and element mapping:

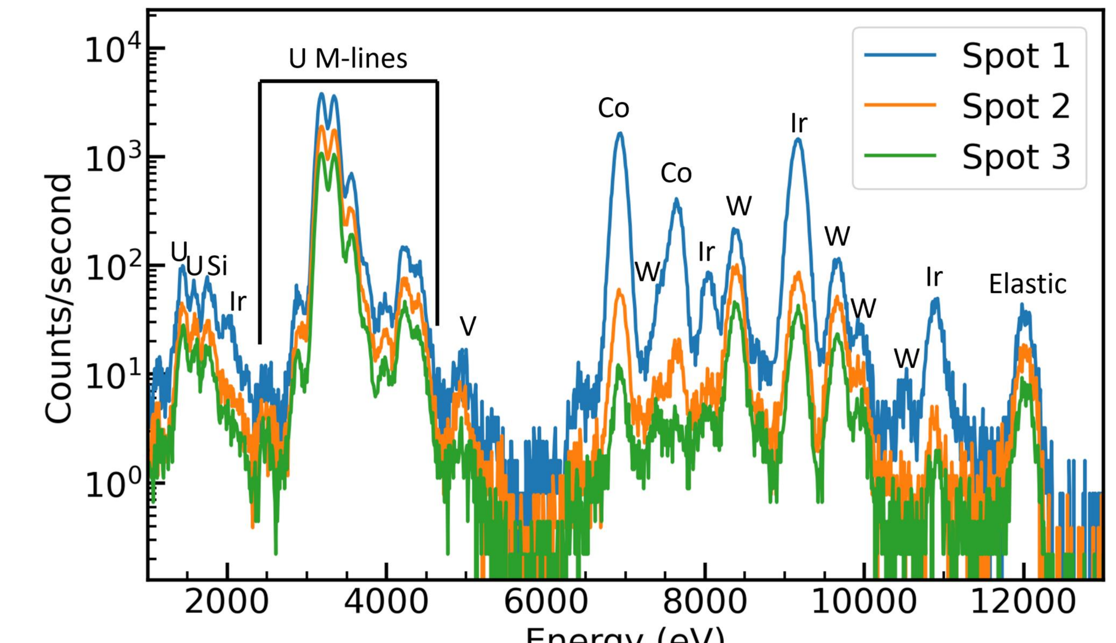

Fig 8. X-ray fluorescence spectrum of the uranium taggant monolith. Spectra are offset for clarity.

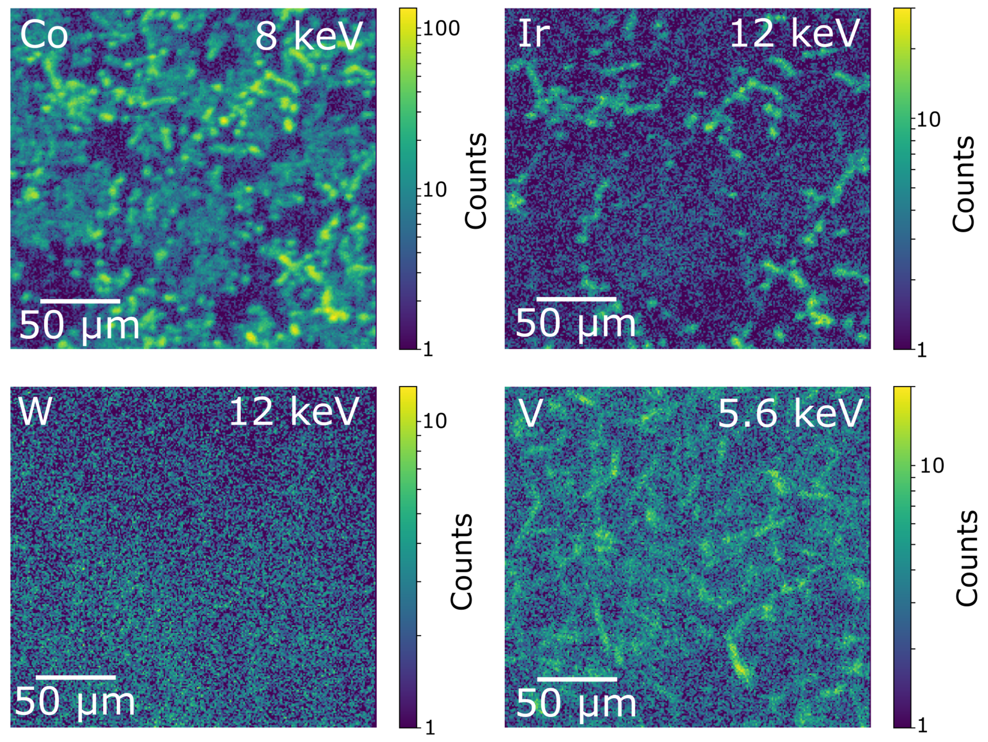

Fig 9. X-ray fluorescence element maps.

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