Project title: UNIQUE ADVANTAGES OF ORGANOMETALLIC SUPPORTING LIGANDS FOR URANIUM COMPLEXES

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UNIQUE ADVANTAGES OF ORGANOMETALLIC SUPPORTING LIGANDS FOR URANIUM COMPLEXES: Final Report

Overview: We focused on uranium complexes supported by ferrocene-based ligands because they provide an interesting platform to study the electronic interaction between iron and uranium. Understanding the electronic communication between iron and uranium in ferrocene-based complexes allowed the uncovering of new properties and reactivity behaviors. We studied the following:

(1) *Reactions of uranium alkyl complexes supported by 1,1'-ferrocene diamide ligands toward aromatic heterocycles.* The relevance of aromatic heterocycles to natural products and pharmaceuticals has prompted a concerted research effort toward their synthesis and functionalization. Aromatic heterocycles also appear as unwanted impurities in carbon-based fuels and, recently, processes that fragment them are becoming prominent. Interestingly, d^{0}f^n metal-carbon bonds show diverse reactivity toward aromatic heterocycles: functionalization as well as ring opening have been reported. Specific to actinide chemistry, since aromatic N-heterocycles are used in separation columns for actinide processing, understanding the interactions between the actinides and materials/molecules is also critical to a number of applications within the Department of Energy complex. Expertise in the production, processing, purification, characterization, analysis, and disposal of actinide elements is essential to the U.S. national security. In this way, our studies add to the intense field of research focused on inert molecule activation and functionalization reactions and to actinide chemistry relevant to radioactive waste processing.

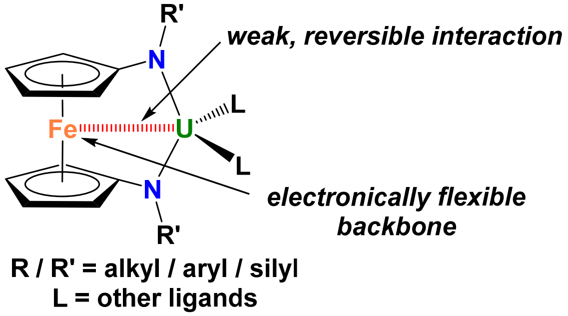


Figure 1. Ferrocene diamide complexes of uranium

(2) *Importance of f orbitals in determining interactions between iron and uranium in bis(1,1'-ferrocene diamide) complexes.* Uranium complexes containing two ferrocene-based ligands allowed us to study the electronic interaction between iron and uranium and how uranium mediates the electronic coupling of the two iron centers. In addition, this study offerred insight into the question of the participation of f orbitals in covalent bonding, which is still a hotly debated topic. By designing a system in which uranium interacts directly with a transition metal, we created a unique class of compounds to use as a basis to address this question.

(3) *Inverse sandwiches of arene-bridged diuranium complexes*. We expanded our studies on the reactivity of a diuranium toluene-bridged complex supported by a ferrocene diamide ligand reported previously by our group. In addition, unique examples of quadruply reduced biphenyl-bridged uranium and thorium complex were isolated and characterized.

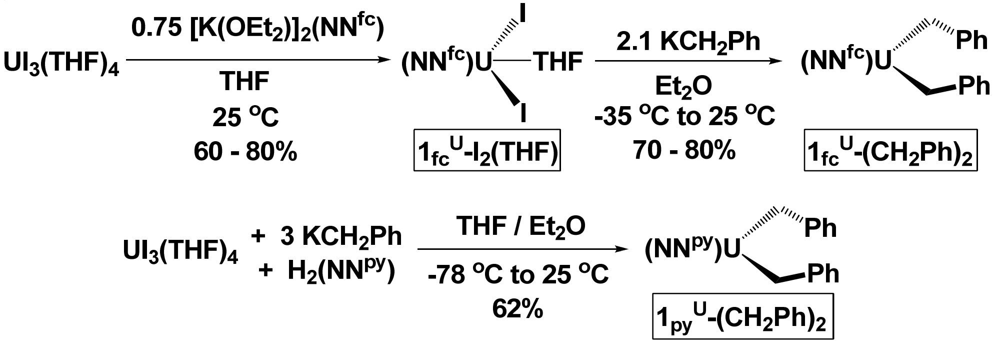
The objective of our research project was to study the reactivity of uranium complexes supported by ferrocene-based ligands. In addition, this research provides training of graduate students as the next generation of actinide scientists. A description of our results is provided here with details in references that have been published or submitted since the beginning of the funding period,[1-16] although a large body of work is still unpublished.[17]

1. Uranium-iron electronic communication

We have been pursuing the study of 1,1'-disubstituted, ferrocene-based chelating ligands as versatile frameworks in supporting uranium complexes (**Figure 1**).[9] Such ligands have the following characteristics: (i) the 1,1'-disubstituted ferrocene enforces *cis*-coordination of the two donors, thus one side of the metal center is blocked; (ii) the ferrocene backbone has the ability to accommodate changes in the electronic density at the metal center by varying the geometry around iron; (iii) the other ligands and incoming substrates coordinate in a plane perpendicular to the plane formed by the two donors, iron, and uranium, thus the access to the electrophilic center is unrestricted; (iv) a weak interaction of donor-acceptor type could occur between iron and the metal that might influence the reactivity of the corresponding complex; (v) the ligand backbone is redox active.

1.1 Synthesis and characterization of uranium benzyl complexes. Ferrocene-diamide uranium dialkyl complexes (Scheme 1) were synthesized by salt-metathesis reactions between the corresponding diiodide, **$1_{fc}{}^{U}$-I_2(THF)**, and various alkyl sources (benzyl potassium, *neo*-pentyl lithium).[18] The synthesis of **$1_{py}{}^{U}$-$(CH_2Ph)_2$** was accomplished in situ[10] since the salt metathesis route did not lead to the desired pyridine-diamide diiodide complex. The in situ method proved general and allowed not only the isolation of pyridine-diamide dialkyl uranium(IV) complexes, but also the isolation of other ferrocene-diamide complexes that had not been accessible by the salt metathesis method.[10]

Scheme 1. Syntheses of uranium dibenzyl complexes supported by ferrocene- and pyridine-diamide ligands.



The dibenzyl **$1_{fc}{}^{U}$-$(CH_2Ph)_2$** and the benzyl cation **[$1_{fc}{}^{U}$-$(CH_2Ph)(OEt_2)$][BPh_4]** complexes were structurally characterized as well as the pyridine-diamide complex **$1_{py}{}^{U}$-$(CH_2Ph)_2$**. The iron−uranium distance is smaller than the sum of the covalent radii for iron and uranium[19] in both complexes (Table 1).

Table 1. Comparison of iron-metal distances in uranium benzyl complexes

Complex	X-ray Fe-M distance (Å)	Sum of covalent radii (Å)	Δ_{Fe-M} (Å)
$1_{fc}{}^{U}$-$(CH_2Ph)_2$	3.19	3.28	- 0.09
$1_{fc}{}^{U}$-$(CH_2Ph)(OEt_2)$	3.07	3.28	- 0.20

DFT calculations were employed to probe the iron−metal interaction. Initial calculations were carried out on models in which the Si^tBu_2Me group was replaced by SiH_3.[18, 20] Calculations were repeated on the full structures.[9] The validity of the calculations was established by comparing metrical parameters obtained from geometry optimizations with those from the corresponding X-ray crystal structures. The optimized iron-uranium distances compare well to the experimental parameters (Table 2).

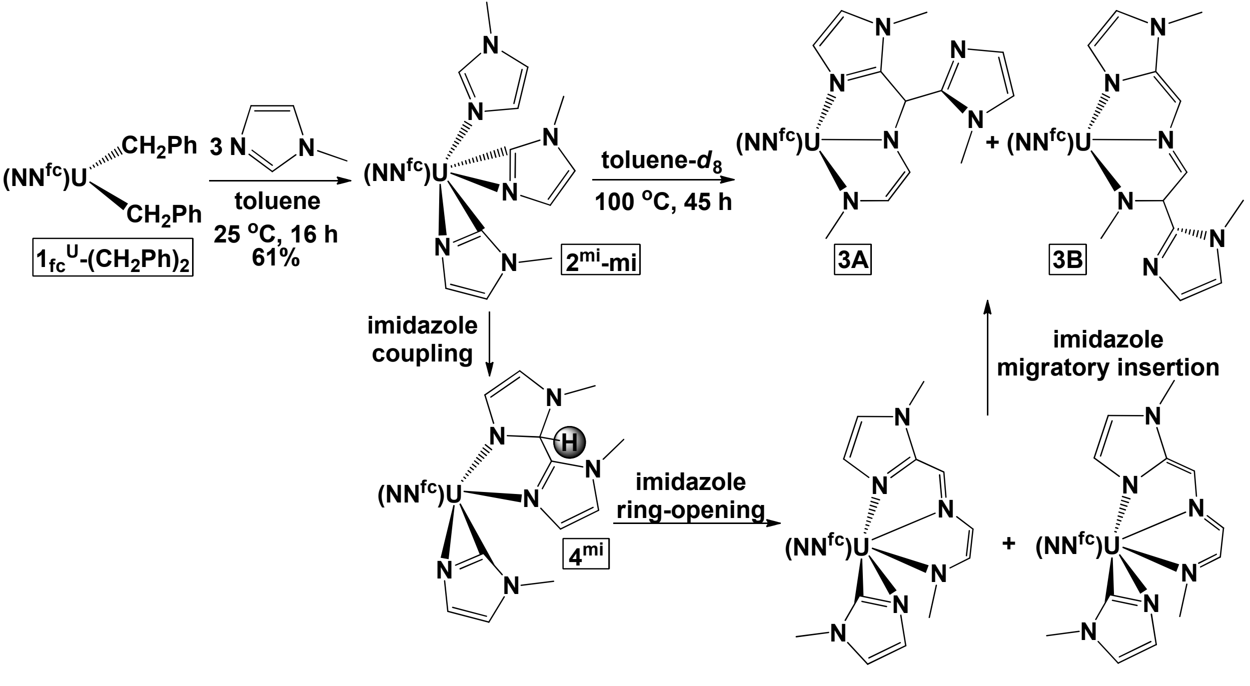
Table 2. DFT calculated parameters for uranium benzyl complexes

Complex	Calculated Fe-M (X-ray) distance (Å)	Fe-M Mayer bond order	Hirshfeld charge of M	Hirshfeld charge of C_{Bz}
1_{fc}^{U}-(CH$_2$Ph)$_2$	3.20 (3.19)	0.39	0.64	-0.22 -0.21
1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)	3.12 (3.07)	0.49	0.71	-0.21

Mayer bond orders for the uranium-iron interaction are significant (Table 2). It is interesting to point out that these values are larger than those calculated for the bond between uranium and the ether-oxygen donor (ca. 0.2). The bond order is dependent on the nature of the ligands present: the more electron-donating the ligands, the weaker the metal-iron interaction (0.49 for **1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)** and 0.39 for **1_{fc}^{U}-(CH$_2$Ph)$_2$**). Although the charge of uranium is different (0.71 for **1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)** and 0.64 for **1_{fc}^{U}-(CH$_2$Ph)$_2$**), the charge on the benzyl carbon atom is invariable between the two uranium complexes (Table 2).

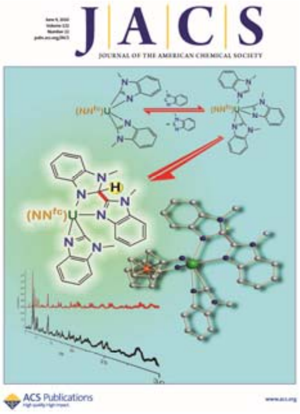
1.2 Reactions with aromatic N-heterocycles. The two ferrocene-diamide uranium benzyl complexes as well as other dialkyl complexes did not show C–H activation of hydrocarbons. Because of the high electrophilicity of uranium inferred from DFT calculations and the fact that **1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)** coordinates OEt$_2$, the reaction of **1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)** with 1-methylimidazole, which can displace the coordinated ether, was studied. That substrate was chosen in order to compare the reactivity of the uranium complexes with that of reported zirconium compounds because [Cp*$_2$ZrMe(THF)]$^+$ did not C−H activate 1-methylimidazole (only coordination was observed).[21]

Scheme 2. Reactions of 1-methylimidazole mediated by the uranium dibenzyl complex **1_{fc}^{U}-(CH$_2$Ph)$_2$**.



The complex **1_{fc}^{U}-(CH$_2$Ph)(OEt$_2$)** reacts with 1-methylimidazole; more interestingly, **1_{fc}^{U}-(CH$_2$Ph)$_2$** mediated the C−H activation of two heterocycles in the case of 1-methylimidazole (to give **2^{mi}-mi**) or 1-methylbenzimidazole (to give **2^{mbi}-mbi**). That process was followed by an unprecedented reaction cascade leading to the ring opening and functionalization of imidazoles (Scheme 2).[7] This double C−H activation and the sequence of transformations succeeding it are unique to uranium and has been observed for other aromatic heterocycles as well.[11]

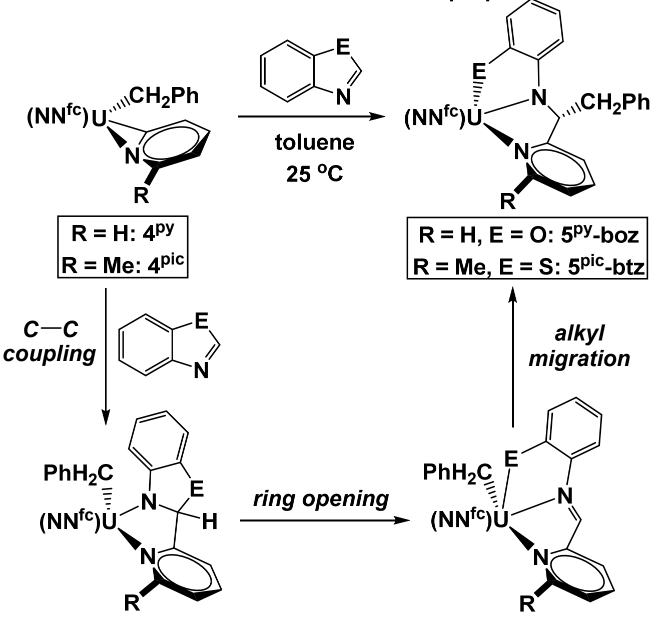
Two isomeric products, **3A** and **3B**, were isolated and characterized (Scheme 2). Complexes **3A** and **3B** feature a new ligand formed from the coordinated imidazole and the two imidazolyl fragments initially present in **2**$^{\mathbf{mi}}$**-mi**: one C−N bond in the coordinated imidazole ring was broken, while the other two rings resemble the original imidazolyl entities. Conducting a reaction between **1-(CH**$_{\mathbf{2}}$**Ph)**$_{\mathbf{2}}$ and 1-methylbenzimidazole allowed the isolation and characterization of **4**$^{\mathbf{mbi}}$, which is analogous to **4**$^{\mathbf{mi}}$, suggesting that, prior to the ring-opening event, C–C coupling of two imidazole rings likely occurred.[22] This coupling reaction dearomatizes one of them and poises it for ring opening, which takes place, presumably, because structures with delocalized double bonds can be obtained and are more stable.[23] It was proposed that the ring-opening reaction led to two intermediate isomer structures, which differ by the alternation of their double bonds. The novelty of the present process results from the ability of uranium to mediate an additional reaction compared to corresponding group 3 metal benzyl complexes, the migratory insertion of an imidazolyl ligand.



Interestingly, the C−C coupling between the two imidazole rings in **4**$^{\mathbf{mbi}}$ was found to be reversible.[13] This finding was supported by single-crystal and powder X-ray diffraction, ^{1}H and ^{2}H variable-temperature NMR spectroscopy, and DFT calculations. Reversible bond formation has been invoked as the basis for developing switchable molecular systems, and C−C bonds of heterocycles have been recently identified as a fruitful area for exploration. In general, such systems switch between two states in response to an external stimulus. The two states coexist in solution for **4**$^{\mathbf{mbi}}$. The uranium system is a rare example of reversible bond formation that involves organometallic complexes and that work was highlighted by being chosen as the cover for the June 9, 2010 issue of the *Journal of American Chemical Society* (see figure above).

Mechanistic support was obtained by investigating the ring opening of other aromatic N-heterocycles (Scheme 3).[11] The complex **1**$_{\mathbf{fc}}$$^{\mathbf{U}}$**-(CH**$_{\mathbf{2}}$**Ph)**$_{\mathbf{2}}$ mediated the C−H activation of pyridines to give the corresponding ortho-metalated products (**4**$^{\mathbf{py}}$ and **4**$^{\mathbf{pic}}$). Those complexes reacted with benzoxazole or benzothiazole by the same cascade of reactions proposed for 1-methylimidazole to give uniquely functionalized heterocyclic structures (**5**$^{\mathbf{py}}$**-boz** and **5**$^{\mathbf{pic}}$**-btz**).

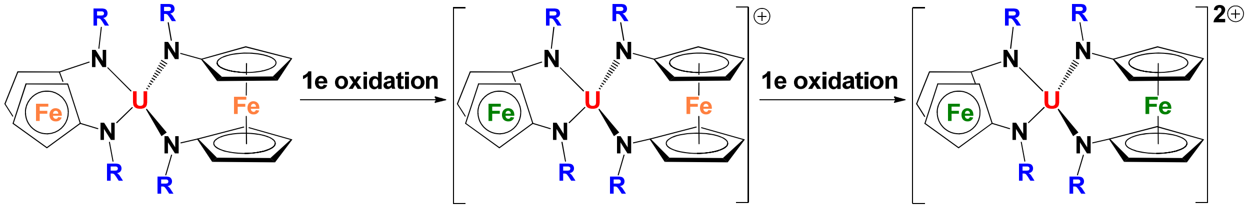
Scheme 3. Reactions of uranium η^2-N,C-pyridyl complexes with benzoxazole and benzothiazole and proposed mechanism



Based on the reactions discussed herein and on isolated examples drawn from the literature, it is proposed that ferrocene diamides represent a versatile ligand framework for uranium. DFT calculations performed by the Maron group (personal communication) indicated that the ferrocene diamide ligand NN^{fc} is unique in supporting a more electrophilic uranium center than a bis-diamide or bis-cyclopentadienyl framework. It is likely that the privileged status of these organometallic ancillary ligands is a consequence of iron’s ability to accommodate changes in the electronic density at the metal center more readily than classical supporting ligands.

2. Uranium-iron electronic communication

Uranium complexes containing two ferrocene-based ligands provide an interesting platform to study the electronic interaction between iron and uranium. In 2007, we reported that the characterization of the mixed-valent bisferrocene compound **[(NN^{TBS})$_2$U][BPh$_4$]**[24] (**Figure 2**) supports a uranium-mediated electronic communication between the two iron centers. As described below, further characterization of these compounds indicates that uranium may engage the ligand in redox activity. These results open new avenues for using such metal complexes for processes that require two and more electrons.



mixed-valent uranium complexes

R = SiMe$_3$: NN^{TMS}; SitBuMe$_2$: NN^{TBS}; SiMe$_2$Ph: NN^{DMP}; 2,4,6-Me$_3$C$_6$H$_2$: NN^{Mes}

Figure 2. Bis(ferrocene diamide) complexes of uranium.

Electrochemistry. One of the most accessible methods used to investigate the existence of electronic communication between two redox-active centers is cyclic voltammetry. To probe the electrochemical behavior of the corresponding **(NN^R)$_2$U** compounds, voltammetric and chronoamperometric experiments were carried out in various electrolyte media using a standard three-electrode cell.

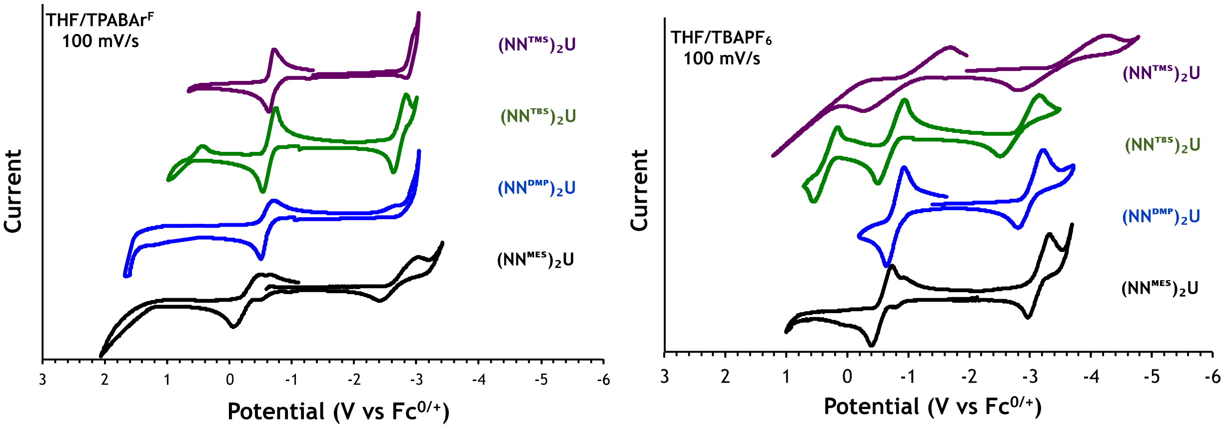


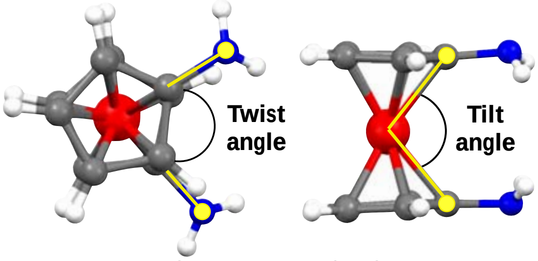
Figure 3. Cyclic voltammetry of **(NN^R)$_2$U** complexes measured with a 2-mm platinum disk as the working electrode.

At least two redox events were observed for all **(NN^R)$_2$U** complexes. Reduction potentials vary from –2.3 V to –3.0 V in TPABAr^F (TPA = ^{i}Pr$_4$N) and –2.83 V to –3.64 V in TBAPF$_6$ (**Figure 3**). At negative potentials, the observed event is assigned to reduction of uranium. Oxidation potentials vary from –0.27 V to –0.86 V in TPABAr^F and –0.56 V to –0.79 V in TBAPF$_6$. An additional one-electron oxidative event is revealed at a more positive potential for **(NN^{TBS})$_2$U** and is better resolved in a THF solution of TBAPF$_6$. Assuming that the two oxidation events correspond to ferrocene/ferrocenium couples, a comproportionation constant of 1.2 x 10^{18} is calculated for **$(NN^{TBS})_2U$**. This value indicates that there is strong electronic coupling between the two ferrocene moieties in **$(NN^{TBS})_2U$** (class III mixed-valent compound).

The first anodic events are attributed to oxidation of iron. We initially hypothesized that, in a THF solution of $TBAPF_6$, the first oxidation event may be a two-electron process for all uranium bis(1,1'-ferrocene diamide) complexes, except for **$(NN^{TBS})_2U$**. In order to determine the number of electrons consumed in each oxidative event, a combination of transient and steady state methods was employed.[25-31] Chronoamperometric measurements of **$(NN^{TBS})_2U$** in THF with $TBAPF_6$ and $TPABAr^F$ indicated that both oxidations are one-electron processes. Measurements of **$(NN^{TMS})_2U$** in THF with $TPABAr^F$ reveal that the oxidation is also a one-electron event. In the same type of medium, quantifying the electrons involved in oxidation of **$(NN^{MES})_2U$** was impeded by the presence of a small oxidative wave slightly overlapping the main event. Analogous measurements of **$(NN^{DMP})_2U$** in two different media (namely, THF solutions of $TBAPF_6$ and $TPABAr^F$) reveal that the sole oxidation event is actually a two-electron process. Differential pulse voltammetry (DPV) measurements of **$(NN^{DMP})_2U$** in a dichloromethane solution of TBABr clearly show two oxidation events. This is a significant piece of evidence for a simultaneous transfer of two electrons and is consistent with crystallographic results (see below).

Chemical Oxidation and Decomposition. Our attempts to grow single crystals of the oxidation products (**Figure 2**) led us to the observation that only **$[(NN^{TBS})_2U][I_3]$** is stable. For example, allowing the reaction mixture to stir for 15 min, collecting the resulting powder by filtration onto a medium-porosity frit, then washing it with copious amounts of a hydrocarbon solvent resulted in analytically pure triiodide salts. Elemental analysis confirmed the formation of **$[(NN^{TBS})_2U][I_3]$**, **$[(NN^{MES})_2U][I_3]$**, **$[(NN^{TMS})_2U][I_3]$**, and **$[(NN^{DMP})_2U][I_3I]$**. However, subsequently dissolving the powder in THF or dichloromethane decomposes the products. For example, the color of **$[(NN^{MES})_2U][I_3]$** changes from black to orange after several minutes in solution and the neutral species is regenerated. Unlike **$[(NN^{MES})_2U][I_3]$**, singly oxidized **$(NN^{TMS})_2U$**, **$[(NN^{TMS})_2U]^+$**, and doubly oxidized **$(NN^{DMP})_2U$**, **$[(NN^{DMP})_2U]^{2+}$**, are relatively stable in dichloromethane, but decompose in THF at room temperature after several minutes. However, **$[(NN^{TMS})_2U][I_3]$** decomposes to the analogous tetraiodoferrate salt, **$[(NN^{TMS})_2U][FeI_4]$** (structure determined crystallographically).

Structural Features. Direct examination of the structural features of neutral, monooxidized, and dioxidized complexes can offer insight into the potential interaction between iron and uranium centers.



	$(NN^{TMS})_2U$	$(NN^{TBS})_2U$	$(NN^{DMP})_2U$	$(NN^{MES})_2U$
Tilt (°)	120.8	121.9	117.0	115.6
Twist (°)	22.7	37.2	1.4	5.1
Fe–U–Fe (°)	178.3	177.1	178.5	135.2
$Fe–U_{avg}$ (Å)	3.33	3.21	3.51	3.47

Figure 4. Left: Twisting (defined by the NC-CN dihedral angle) and tilting (defined by C-Fe-C angle). Right: Relevant structural parameters of **$(NN^R)_2U$** complexes.

For neutral **$(NN^R)_2U$** complexes (**Figure 4**), as the torsion angle (twist) between Cp rings increases, the distance between iron and uranium decreases. For example, **$(NN^{MES})_2U$** contains two structurally distinct ferrocene moieties. The ligand whose Cp rings are twisted by only 2.1° relative to each other features an iron-uranium distance of 3.5 Å. In the ligand with rings twisted by 8.0°, the iron-uranium distance is 3.4 Å. This effect is also evident across the ligand series. For example, average torsion angles of 22.7° and 37.2° in **$(NN^{TMS})_2U$** and **$(NN^{TBS})_2U$** correlate with average iron-uranium distances of 3.3 Å and 3.2 Å, respectively. Like **$(NN^{MES})_2U$**, the torsion of

Cp rings in **(NN$^{\mathrm{DMP}}$)$_2$U** is very small. Moreover, the rings in both ferrocene backbones are perfectly eclipsed. As a result, the distance between iron and uranium is long.

Table 3. Relevant structural parameters of **[(NN$^{\mathrm{R}}$)$_2$U]$^{n+}$** (n = 1, 2) complexes.

	[(NN$^{\mathrm{TMS}}$)$_2$U]$^{+}$		**[(NN$^{\mathrm{TBS}}$)$_2$U]$^{+}$**		**[(NN$^{\mathrm{DMP}}$)$_2$U]$^{2+}$**	
Tilt (°)	124.7		126.6		126.9	
Twist (°)	29.4	27.4	39.4	41.7	31.4	38.5
Fe–U–Fe (°)	177.8		178.6		179.1	
Fe–U (Å)	3.04		2.95		2.95	

In order to accommodate further decrease of this distance upon oxidation, both angular distortions expand even more. For example, when **(NN$^{\mathrm{TBS}}$)$_2$U** is oxidized, the Cp rings twist and tilt relative to each other even more, and, in turn, push the iron center closer to uranium. That is, the average iron-uranium distance in **(NN$^{\mathrm{TBS}}$)$_2$U** decreases by 0.26 Å upon oxidation. These structural parameters are consistent with previous studies of geometrical distortions in multinuclear iron complexes[32-36] and support the existence of a weak interaction between iron and uranium. More importantly, no significant difference in the iron-uranium distance is observed between ferrocene and ferrocenium moieties in **[(NN$^{\mathrm{TBS}}$)$_2$U][BPh$_4$]** (**Table 3**), further supporting its valence-delocalized nature.

Within the cation of the oxidized **(NN$^{\mathrm{TMS}}$)$_2$U**, **[(NN$^{\mathrm{TMS}}$)$_2$U][FeI$_4$]**, the metal-metal distances are slightly longer, while both angular distortions are greater than those in **[(NN$^{\mathrm{TBS}}$)$_2$U][BPh$_4$]**. These structural parameters indicate that the mixed-valent **[(NN$^{\mathrm{TMS}}$)$_2$U][FeI$_4$]** exhibits weaker electronic communication between the ferrocene and ferrocenium moieties than **[(NN$^{\mathrm{TBS}}$)$_2$U][BPh$_4$]**. For **(NN$^{\mathrm{DMP}}$)$_2$U**, only the doubly oxidized species could be isolated and structurally characterized. Interestingly, while both iron-uranium distances in **[(NN$^{\mathrm{DMP}}$)$_2$U][I$_3$I$_5$]**, as well as the corresponding tilt angles, are essentially identical, considerable difference is observed in the torsion angles. Specifically, both Fe^{3+} centers are 2.95 Å away from uranium, but the twisting in each pair of Cp rings differs by 7.1°.

Concluding remarks on redox processes in bis(1,1'-diamidoferrocene) uranium complexes. Using nuclear magnetic resonance, electrochemistry, optical and vibrational spectroscopy, as well as crystallography and magnetometry, our investigation of four uranium bis(1,1'-diamidoferrocene) complexes and their oxidized counterparts shows the following:

(1) Ligands bearing a bulky *tert*-butyl group on the silylamido substituents impose greater torsion and tilt angles at the ferrocene backbone, creating shorter distances between uranium and iron centers, and in turn, enhancing their interaction. In addition to a single one-electron reduction of uranium, electrochemical data reveal two one-electron anodic processes, which we attribute to oxidation of the iron centers. Indeed, chemical oxidation of **(NN$^{\mathrm{TBS}}$)$_2$U** generates a tetravalent uranium center supported by both ferrocene and ferrocenium diamide ligands. This cationic complex can be isolated as a triiodide and tetraphenylborate salt, and is shown by ^{1}H NMR spectra to be stable in solution at room temperature indefinitely. Electronic absorption spectra of these mono-oxidized complexes show an intense band ascribed to charge transfer between Fe^{2+} and Fe^{3+} moieties. The two ligands are structurally indistinguishable, corroborating the valence delocalized nature of **[(NN$^{\mathrm{TBS}}$)$_2$U]**$^{+}$.

(2) Although they strictly enforce a staggered conformation of the Cp rings in 1,1'-ferrocene diamine, mesityl substituents create considerably less torsion strain when the ligands coordinate to uranium, resulting in greater iron-uranium distances in **(NN$^{\mathrm{MES}}$)$_2$U** than in **(NN$^{\mathrm{TBS}}$)$_2$U**. In addition, in **(NN$^{\mathrm{MES}}$)$_2$U**, the ferrocene fragments are structurally distinct. More remarkably, the intensity and position of the inter-valence charge transfer band observed upon oxidation indicate that **[(NN$^{\mathrm{MES}}$)$_2$U]$^{+}$** is valence trapped. This is attributed to the non-linear path of travel (as defined by

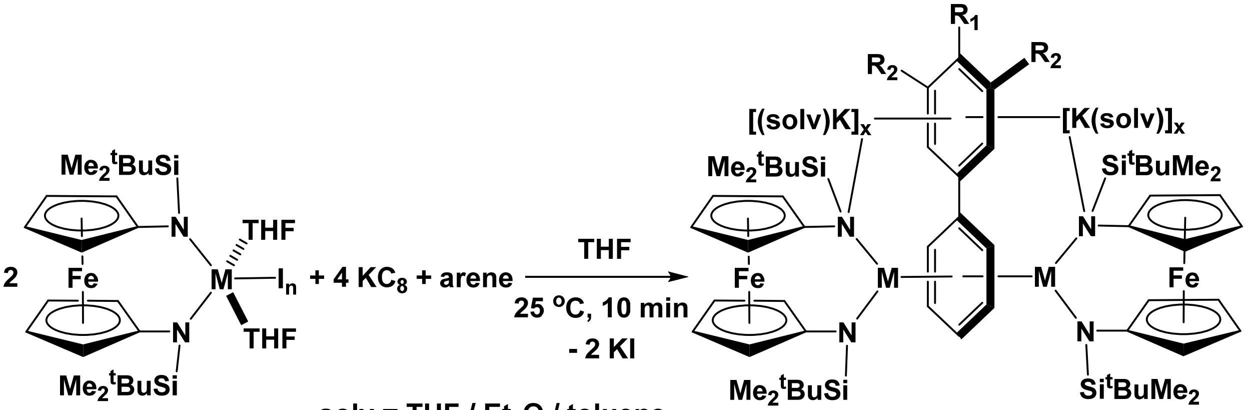
the Fe-U-Fe angle), which provides support for the notion that the uranium center is directly involved in mediation of electron transfer between ferrocene and ferrocenium ligands.

(3) The uranium complex supported by two ferrocene diamide ligands bearing dimethylphenylsilyl substituents, **(NN^{DMP})$_2$U**, represents an anomaly. As confirmed by voltammetric and amperometric methods, **(NN^{DMP})$_2$U** undergoes a two-electron oxidation, whose product does not exhibit an inter-valence charge transfer band in the near IR region.

3. Inverse sandwiches of arene-bridged diuranium complexes

Metal complexes involving the π system of benzene and related aromatic hydrocarbons have been of long-standing interest because of the fundamental nature of such species.[37] Arene-bridged diuranium complexes constitute a general bonding motif for low-valent organouranium compounds featuring benzene/toluene,[3, 38-44] naphthalene,[45] biphenyl,[46] cycloheptatrienyl,[47-48] or cyclooctatetraene,[45] as the bridging arene ligand.

Our work with **[(NN^{TBS})U]$_2$(η^6-toluene)**[3] inspired a separate project with group 3 metal complexes, namely the reduction of metal iodides, **(NN^{TBS})MI(THF)$_2$**, with KC_8 in the presence of aromatic hydrocarbons. While the isolation of inverse sandwiches of naphthalene and anthracene[49] was reminiscent of previously reported yttrium and lutetium complexes,[50] the reduction in the presence of non-fused aromatic hydrocarbons (biphenyl, terphenyl, 1,3,5-triphenylbenzene) gave surprising results and led to the isolation of **[(NN^{TBS})Y]$_2$[K(toluene)]$_2$(*μ*-biphenyl)**, as determined by X-ray crystallography (**Figure 5**).[4] Importantly, similar compounds of uranium and thorium could be isolated and characterized (Figure 5). Current efforts are focused on understanding the electronic structure of the actinide complexes.



solv = THF / Et$_2$O / toluene
arene = biphenyl, R$_1$ = R$_2$ = H, M = Sc / Y / La / Lu (n = 1, x = 1);
M = U / Th (n = 2, x = 0)
arene = terphenyl, R$_1$ = phenyl, R$_2$ = H, M = Y
arene = 1,3,5-triphenylbenzene, R$_1$ = H, R$_2$ = phenyl, M = Lu

Figure 5. Synthesis of quadruply reduced biphenyl complexes of group 3 metals and actinides (uranium and thorium).

4. Graduate and Undergraduate Education in f Element Chemistry

Graduate students who received training as part of this grant are: Marisa J. Monreal, Ph.D. 2011 (postdoctoral fellow, Los Alamos National Laboratory); Erin M. Broderick, Ph.D. 2011; Selma Duhović, Ph.D. 2012; Wenliang Huang, Ph.D. 2013; Kevin L. Miller, M.Sc. 2014; Michael Lopez, M.Sc. 2014; Jeremy Oria, M.Sc. 2014.

Undergraduate students who received training as part of this grant are: Nathaniel P. Gutzwiller, M.Sc. 2009 (assistant nuclear chemistry technician, San Onofre Nuclear Generating Station, CA); Peter S. Thuy-Boun, B.Sc. 2010; Andrew Elliott, B.Sc. 2011; Jason Lee, B.Sc. 2012; Brian Lydon, M.Sc. 2013.

5. List of publications supported by this grant

1. **Beyond C−H Activation with Uranium: Imidazole Ring-Opening Mediated by a Uranium Dialkyl Complex**. Monreal, Marisa J.; Khan, S.; Diaconescu, Paula L. *Angew. Chem. Int. Ed.* **2009**, *48*(44), 8352-8355.
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