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Metal-Ligand "Multiple" Bonding: Revelations in the Electronic Structure of Complexes of High-Valent f-Elements

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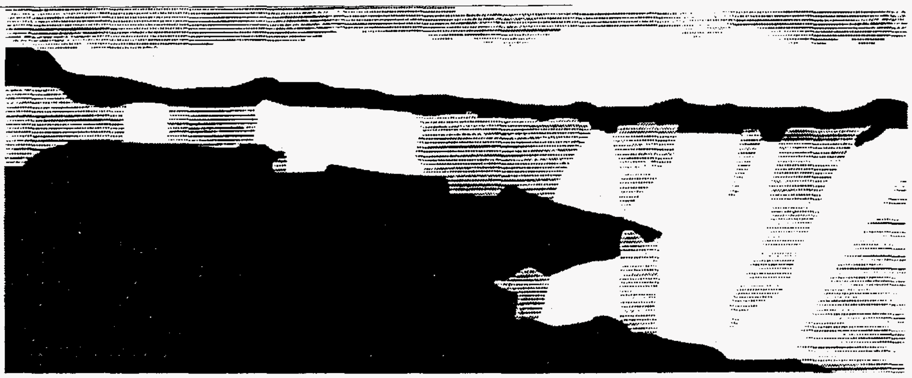

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Metal-Ligand "Multiple" Bonding: Revelations in the Electronic Structure of Complexes of High-Valent f-Elements

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The goal of this project has been to extend our understanding of the nature of interactions between f-metals and first row elements (important both in natural systems and in ceramics), as well as providing important new information regarding basic differences in the chemical nature of d- and f-metals. By developing preparative routes to novel classes of early actinide and lanthanide complexes in which metal-ligand bonding is formally unsaturated, this project has provided the means to study orbital interactions and charge distribution in these species by physical, chemical, and theoretical means. Evaluation of the physical and chemical characteristics of these species is providing dramatic evidence for the involvement of valence metal orbitals [nf and (n+1)d] in bonding, and is yielding new insights into the factors influencing stability of related species.

1. Background and Research Objectives

The goal of this project is to extend the development of the field of metal-ligand multiple bonding to include organo-f-element analogs. Understanding of the electronic structure in these and first row elements has far-reaching impact in the evaluation and prediction of interactions between f-metals and chalcogenide and pnictide elements (important both in natural systems and in ceramics). In addition, characterization of this class of compounds is providing important new information regarding basic differences in the chemical nature of d- and f-metals. We are

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developing new preparative routes to the formation of high-valent early actinide and lanthanide complexes in which metal-ligand bonding is formally unsaturated, and are studying the orbital interactions and charge distribution in these species by physical, chemical, and theoretical means. Evaluation of the physical and chemical characteristics of these species is providing dramatic evidence for the involvement of valence metal orbitals [nf and (n+1)d] in bonding, and is yielding new insights into the factors influencing stability of related species.

The preparation and reactivity of complexes containing multiply-bonded functional groups such as alkylidene ($=CR_2$), alkylidyne ($\equiv CR$), imido ($=NR$), nitrido ($\equiv N$), and oxo ($=O$) ligands is an area of keen interest in modern synthetic chemistry [1]. These complexes fill an increasingly important role in the design of synthetic homogeneous processes both in the laboratory and at production scale. Intense study of the reactivity, electronic spectroscopy, and dynamics of these complexes has provided an understanding of the metal-ligand bonding which has proven invaluable in the rational design of practical applications. Complexes of the f-elements containing related ligands are relatively rare, however, and they can often exhibit complex chemical behavior that defies prediction. Actinyl ions (AnO_2^{n+}) are the best known examples of this class of molecules (the uranyl ion is the dominant form of uranium in aerobic media) [2]. Hydrolysis and redox reactions of these species can give rise to complicated distribution of species in solution; the equilibrium between solution oxo complexes and precipitated oxides is central in the environmental behavior of these elements. Even these relatively simple equilibria currently can only be investigated empirically. Currently, we have *no* basis for understanding the electronic factors, which dominate the physicochemical behavior of these systems. Theoretical investigations in the area have been restricted primarily to examinations of the bonding in the uranyl ion, and much controversy exists even regarding this simple system [3].

It is also important to ascertain the chemical reactivity of this type of functional groups at organo-f-element centers. As discussed previously, transition metal organometallic complexes are often employed as well-defined homogeneous reagents because of the high degree of selectivity they introduce in stoichiometric and catalytic chemical transformations including oxidation, polymerization, and amination. Of particular current interest is metal-ligand multiple bonding in the chemistry of the early transition metals (Groups 4 and 5). These functional groups display unusually high reactivity in C-H activation reactions, and as such may be highly useful in organic synthesis. It is anticipated that similar functional groups in organo-f-element chemistry may possess an even higher degree of reactivity, owing to the greater degree of ligand charge localization inherent in these species.

In order to clarify the chemical and physical properties of complexes of the f-elements containing these ligands, it is necessary to develop new representatives of the class. We have been able to extend important new methodologies to the development of oxo- and imido-containing f-element complexes in a variety of oxidation states. Physical and theoretical investigations have begun to reveal an unexpected picture of the electronic structure in these complexes.

2. Importance to LANL's Science and Technology Base and National R&D Needs

The chemistry of the actinide elements has always been of prime importance at LANL, providing the basis for the development of process and separation chemistry related to the weapons mission of the Laboratory. The superb facilities available at Los Alamos for the safe handling of radioactive materials provided the catalyst for the development of a storehouse of knowledge relating to the phase behavior, metallurgy, structural chemistry, solid state chemistry, and analytical chemistry of the 5f-elements. Nuclear and Advanced Materials remains one of the core competencies of the Laboratory. Recently, interest in the chemistry of the actinides at Los Alamos and elsewhere within the DOE complex has taken on new significance in the arenas of environmental remediation, residue stabilization, and process waste minimization. These programmatic areas have been recognized as requiring a sound base of expertise in actinide molecular science, as suggested by the recent awarding of resources to an LDRD competency development proposal in this area.

In order to address these challenges, the Laboratory must maintain its technology base in the fundamental chemistry of these elements, and lead the way in exploring the unique chemical properties of these elements. This project sought to address this need by examining the preparation and characterization of actinide complexes in unusual ligand environments as a means of extending our understanding of the comparative chemistry of actinides and lanthanides. Past results from this and related efforts have found immediate application in other programs within the Laboratory. Basic nonaqueous coordination chemistry developed in this project has been adapted to processes designed to treat uranium scrap waste at the Laboratory, and related dissolution chemistry is currently being explored for application in material recovery efforts associated with core weapons programs. This project has also established the inorganic chemistry effort at LANL as home of one of the premier programs in synthetic actinide chemistry, producing an extensive list of invited seminars and peer-reviewed publications. The high visibility of this effort serves as an excellent recruiting tool for quality postdoctoral fellows (many of whom are now staff members at LANL), and serves for many as their first introduction to handling radioactive materials. This project also maintained a high degree of synergy with other projects in the Laboratory, both in applied actinide chemistry and in general basic inorganic chemistry.

3. Scientific Approach and Accomplishments

Development of an understanding of the electronic structure of this new class of organo-f-element complexes (and its ramifications in reactivity and physical behavior) relies upon an approach integrating synthesis, characterization, and theoretical interpretation. The project concentrated on developing new synthetic methodologies for the introduction of unsaturated functional groups, and examining the chemical reactivity of the species as a probe of the stability of molecules.

Physical characterization often provided the most direct probe of the bonding characteristics of these novel species. Vibrational spectroscopy was conducted to yield information on relative bond energetics and coupling, while optical probes verified oxidation states and reveal unusual electronic transitions. New complexes were structurally characterized in order to examine bond variances as a function of oxidation state and ligand environment (as well as to determine coordination geometries). NMR spectroscopy was utilized to examine solution dynamics and to determine kinetic parameters for chemical reactions. External collaborations facilitated study of the unusual chemical properties of these complexes. Dr. Jennifer Green (Oxford U.) examined the valence photoelectron spectroscopy of high-valent organo-f-element complexes. Combined with the results of electronic structure calculations being conducted in the group of Prof. Bruce Bursten (Ohio State U.), these experiments could be used to interpret the extent of electronic stabilization of imido- and oxo-based orbitals by interaction with the metal center. Prof. Tobin Marks (Northwestern U.) examined the thermochemistry of metal-oxo bond formation as a direct measure of the energetics of metal-ligand interaction. Most recently, we developed a collaboration with Prof. Steven Buchwald (MIT), examining the reactivity of high-valent organocerium complexes and their potential utility as synthetic reagents.

Initial synthetic efforts in the project focused on examining ligand elimination reactions in the synthesis of unsaturated functional groups. It had previously been determined that reaction of $(Me_5C_5)_2AnMeCl$ (An = U, Th) with potassium or lithium anilide salts in the presence of a coordinating solvent results in the elimination of methane, and the formation of the complex $[M(L)]-[(Me_5C_5)_2UCl(NPh)]$ (M = Li, K). This elimination takes place readily at room temperature. We extended these studies to a survey of direct reactions of $(Me_5C_5)_2AnMe_2$ with substituted anilines. While reaction of relatively small anilines (H_2NPh, $H_2N(2,6\text{-}Me_2C_6H_3)$) with $(Me_5C_5)_2AnMe_2$ has previously been shown to yield the bisamide products, the use of more sterically demanding ligands disfavored the bis(anilide) complexes, and gave rise to monoimido derivatives (Eq. 1). The solvation state of the isolated product was also found to be a function of

$$(Me_5C_5)_2UMe_2 + H_2NAr \xrightarrow[L]{-MeH} (Me_5C_5)_2U(NAr)(L)_x \qquad (1)$$

$$(Ar = 2,6\text{-}R_2C_6H_3,\ L = THF,\ x = 0,1)$$

the steric bulk of the aniline. Protonation of $(Me_5C_5)_2UMe_2$ with $H_2N(2,6\text{-}i\text{-}Pr_2C_6H_3)$ yielded $(Me_5C_5)_2An[N(2,6\text{-}i\text{-}Pr_2C_6H_3)](THF)$ when the reaction was conducted in THF. Protonation by the slightly larger aniline $H_2N(2,6\text{-}t\text{-}Bu_2C_6H_3)$ yielded only the base-free derivative, however, regardless of the reaction medium.

Prior to commencing the project, we demonstrated the synthesis of the first true organometallic complexes of uranium(VI), i.e. supporting metal-carbon bonding. Complexes of the formula $(Me_5C_5)_2U(NR)_2$ and $(Me_5C_5)_2U(NR)(O)$ were prepared by 2-electron oxidation of monoimido precursors, or by unprecedented reductive cleavage of substrates such as hydrazines at uranium(IV) centers. The stability of uranium(VI) in the presence of ligands as electron-rich as cyclopentadienyl groups was unexpected; the few known complexes of hexavalent uranium are notoriously unstable with respect to reduction via heterolytic bond cleavage. Further, these complexes also displayed highly unusual geometries, with a *nonlinear* arrangement of the E=U=E core. In the course of the project, we extended the range of known mono-oxo complexes of uranium to include complexes of uranium(V). By utilizing analogous steric control measures, we were able to isolate the mixed oxo-aryloxide complex $(Me_5C_5)_2U(OAr)(O)$ by oxidation of the trivalent precursor (Eq. 2). This complex has been identified as a pentavalent product on the basis of its paramagnetic NMR spectrum and its UV-vis-NIR spectrum. The product was also structurally characterized for comparison with its U(VI) analog $(Me_5C_5)_2U(NAr)(O)$. The uranium-oxo bond distance in this complex (U(1)-O(2) = 1.859 (6) Å) deviated significantly

$$(Me_5C_5)_2U(OAr)(THF) + py{\longrightarrow}O \longrightarrow (Me_5C_5)_2U(OAr)(O) \qquad (2)$$

$$(Ar = 2,6\text{-}i\text{-}PrC_6H_3)$$

from a typical uranyl U-O bond length (1.70-1.76 Å) [4], and was found to be comparable to that found in the α-phase of UOF_4 (1.84(2) Å) [5]. By analogy with related early d-transition metal complexes, it might be expected that the oxo and imido functional groups would behave in a nucleophilic manner in subsequent reactions. Surprisingly, these complexes were not found to be reactive. No reaction was observed with olefins, acetylenes, phosphines, silanes, or electrophiles (such as methyl iodide). This points to an unusual stabilization of these electron rich functional groups by interaction with the metal center. The only reactivity that is observed is very slow reduction by dihydrogen or silanes to yield bis(amide) complexes.

Most recently, we extended the available synthetic routes to include sequential multiple electron transfer reactions from "U(II)" synthons produced by reduction or disproportionation of U(III) precursors (Figure 1). Bis(imido) derivatives can be produced from direct 4-electron reduction of azo compounds, and imido-oxo analogs can be prepared by reduction of organic nitroso compounds. Further, reaction of these "U(II)" precursors with two sequential equivalents of organic azides resulted in the isolation of asymmetrically substituted bis(imido) complexes $(Me_5C_5)_2U(NR)(NR')$. These new synthetic pathways have been important in providing entry into a wider variety of organoimido compounds for subsequent reactivity studies (e.g. complexes in which R is a saturated alkyl substituent). Complexes containing alkylimido groups are slightly more reactive than their arylimido counterparts. The reduction by dihydrogen or silanes (*vide supra*) is faster in these complexes; this reduction reaction has potential utility in metal-catalyzed hydrogenation or hydrosilylation of substrates, when coupled with the electron-transfer cleavage reactions. Alkylimido complexes also undergo reaction upon heating to generate a novel "ring activated" product, in which a methyl group on the ancillary ligand has been activated (Figure 2).

In order to examine the electronic effect of the ancillary ligand on the course of these reactions, we prepared a series of uranium(IV) precursors employing "tied-back" cyclopentadienide groups, in which the hydrocarbon rings are bridged by a linking silyl group. This permits variation of the degree of alkylation of the ligands, while inhibiting ring redistribution reactions common to this system. It was found that while permethylated versions of these compounds similarly displayed electron-transfer reactions leading to U(VI) organoimido products, less electron rich analogs (Figure 3) gave rise only to tetravalent organoimido products. The probable cause for the difference in this reactivity is a shift in the metal redox potential; electrochemical investigations of the complexes $[(\eta^5\text{-}Me_4C_5)(\eta^5\text{-}C_5R_4)SiMe_2]UCl_4^{2-}$ (R = Me, H) demonstrate that the oxidation potential of the metal center can shift by as much as 250 meV.

We examined the extent of f-orbital participation in the bonding in the novel hexavalent uranium complexes through collaborative interactions with both experimental and theoretical scientists. Prof. Bruce Bursten has conducted theoretical investigations on the model complex $Cp_2U(NH)_2$, initially using non-relativistic DV-Xα methods, and more recently employing density functional methods (this represents one of the first applications of density functional approaches to f-element chemistry). His results demonstrate that 5f orbital involvement can contribute to the stabilization of in-plane nitrogen 2p-lone pair combinations for which no appropriate symmetry match exists for d-transition elements. He is now attempting to develop quasi-relativistic approximations to improve upon these results. The N-2p stabilization was also assessed by Dr. Jennifer Green by examination of the UV-photoelectron spectra a number of the actinide imido complexes. Spectra of the bis(phenylimido) complex revealed an ionization at 6.27 eV, corresponding to ionization of electrons from the in-plane nitrogen 2p-lone pair / f-orbital hydrid molecular orbitals. This result indicates a small (but significant) f-orbital based bonding interaction.

No terminal phosphinidene complex of an actinide has previously been isolated. The diffuse nature of the 6d-orbitals precludes significant stabilization of phosphorus 3p-lone pair electrons through metal π-acceptance, and the large ionic radii exhibited by the actinide ions makes it difficult to introduce sufficient steric stabilization of a terminal "PR" ligand. Indeed, the only previously reported example of an actinide phosphinidene complex is $[(\eta^5\text{-}C_5Me_5)_2U(OMe)]_2(\mu\text{-}PH)$,[6] in which the phosphinidene ligand is capable of bridging even the relatively sterically hindered "$(\eta^5\text{-}C_5Me_5)_2U$" moieties.

Utilizing a combination of bulky substituents on the phosphinidene and stabilization by an additional coordinated Lewis base, we successfully isolated the first terminal phosphinidene complex of an f-element. Reaction of $KPH\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2$ with $(\eta^5\text{-}C_5Me_5)_2UMeCl$ at room temperature in the presence of trimethylphosphine oxide generated the complex $(\eta^5\text{-}C_5Me_5)_2U(=P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(O=PMe_3)$ (Eq. 3). In the absence of added base, intractable product mixtures result, presumably due to reaction of the phosphinidene with solvent or

$$(\eta^5\text{-}C_5Me_5)_2UMeCl + KPH\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2 \xrightarrow{O=PMe_3} (\eta^5\text{-}C_5Me_5)_2U(P\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)(OPMe_3) \qquad (3)$$

ancillary ligand by intra- or intermolecular C-H activation.

The phosphine oxide adduct was structurally characterized (Figure 4). The U-P distance was found to be 2.562(3) Å and the angle about the phosphorus atom is 143.7(3)°. This bond distance is significantly shorter than those found in the bridging phosphinidene complex $[(\eta^5\text{-}C_5Me_5)_2U(OMe)]_2(\mu\text{-}PH)$ (U-P = 2.743(1) Å) [6] or in tetravalent phosphide complexes [7]. While testing the redox stability of uranium(VI) in reducing environments, we also found it possible to extend the chemistry of hexavalent uranium to include heavier chalcogenides by oxidation of uranium(IV) monoimido precursors. While we have attempted to use a variety of reagents in the preparation of sulfido analogs, reaction with elemental sulfur proved the cleanest method for the introduction of a sulfido ligand into the coordination sphere of uranium.

Reaction of $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)$ with a stoichiometric amount of elemental sulfur results in the formation of a black complex which analyzes for "$(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(S)$" (Eq. 4). It appears that the complex behaves in solution in

$$(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF) + 1/8\ S_8 \longrightarrow \text{"}(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(S)\text{"} \quad (4)$$

an analogous fashion to the previously characterized U(VI) derivatives, i.e. as a temperature independent paramagnet (the complex is monomeric by solution molecular weight measurements). Chemically, the compound is significantly less robust than the imido-oxo compounds. Reaction with excess trimethylphosphine results in reduction of the uranium center to give the phosphine sulfide adduct $(\eta^5\text{-}C_5Me_5)_2U(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(S{=}PMe_3)$.

Reaction of the monoimido precursor complexes with excess sulfur produced a second product, identified as the disulfido-uranium(VI) derivative. The complex is an unusual example of an η^2-disulfido ligand coordinated to a high-valent metal center. Although η^2-dichalcogenide derivatives of uranium have been characterized [8], they generally involve lower formal metal oxidation states. Again, the compound behaves in solution as a complex of uranium(VI). Curiously, this species now proves unreactive to trimethylphosphine; no reduction is observed even after prolonged reaction times. This is in contrast to similar d-transition metal systems which contain reactive disulfido groups [9].

The aforementioned multiple-electron transfer capability of "U(II)" synthons has been harnessed in examining the reductive coupling of alkynes, a reaction well known in the chemistry of Group 4 metallocenes [10]. Reduction of U(III) precursors in the presence of alkynes produces metallocyclopentadiene products. When the two alkynes are sterically "linked" by a silyl or phenyl unit, products are isolated which may be described as intermediates in the coupling process (Figure 5). Similar products may be derived containing thorium, utilizing the previously unknown precursor $(Me_5C_5)_2ThMe(H)$. This complex will undergo insertion of one equivalent of alkyne. Subsequent elimination of methane from the vinyl intermediate leads to the formation of a metallocyclopropene intermediate, which will insert another equivalent of alkyne to produce the metallocyclopentadiene product. The stability of hexavalent uranium had suggested that additional electron transfer into the unsaturated hydrocarbon unit might be possible, but all physical measurements suggest that the uranium products derived in these coupling reactions are rigorously U(IV). We most recently have explored the possibility of oxidizing the tetravalent products with atom transfer reagents (amine N-oxides, organic azides), in hopes that atom extrusion reactions might make these systems useful in the production of heterocyclic products; this question remains unresolved.

The final area investigated under the context of this project was attempted stabilization of tetravalent cerium products with multiply-bonded ligands. We have examined both the oxidation of cerium(III) precursors, and the introduction of these functional groups at preexisting cerium(IV) centers through elimination routes. Neither of these routes has been succesful in producing an cerium(IV) imido complex. Initial attempts focused on producing metallocene complexes analogous to the previously discussed tetravalent uranium complexes $(Me_5C_5)_2U(=NR)$. Reaction of potassium anilide salts with the known precursor $(Me_5C_5)_2Ce(Cl)_2^-$ yielded dark green to dark red complexes of the formula $(Me_5C_5)_2Ce(NHAr)$ ($Ar = 2,6\text{-}R_2C_6H_3$). These species could in some instances be isolated as THF solvates depending on the bulk of the aryl group. Reaction of these species with butyllithium yields yellow salts which may be formulated as $[Li(tmeda)][(Me_5C_5)_2Ce(NAr)]$ (Eq. 5). These species

$$(Me_5C_5)_2Ce(NHAr) + BuLi \xrightarrow{\text{tmeda}} [Li(tmeda)][(Me_5C_5)_2Ce(NAr)] \qquad (5)$$

appear to be quite reactive and decompose slowly in THF. Addition of tetramethylethylenediamine (tmeda) appears to inhibit decomposition. These complexes are still under investigation. Attempts to chemically oxidize these species resulted only in decomposition.

Attempts have also been made to generate organoimido derivatives by ligand elimination from tetravalent precursors. While we have not yet been successful in generating a multiply-bonded species, these studies have begun to develop a previously unexplored area of lanthanide chemistry: complexes of Ce(IV) containing amide ligands. Tetravalent cerium amide complexes can be prepared through the use of judiciously substituted trimethylsilyamides to help stabilize the high oxidation state metal center in the presence of a bis-*tertiary*-butoxide framework. The bisamide complexes $(^tBuO)_2Ce(N(TMS)_2)_2$ and $(^tBuO)_2Ce(N(TMS)(o\text{-}MeOC_6H_4))_2$ have been prepared and structurally characterized by direct metathetical routes from the reaction between the cerium(IV) precursor $(^tBuO)_2Ce(NO_3)_2(THF)_2$ and the requisite lithium amide salts. The arylamide complex is isolated much more cleanly, presumably due to the influence of the methoxy substituents on aryl ring, which are shown to be chelating in the solid-state structure. The bis(alkoxide)-bis(trimethylsilylamide) complex may also be prepared by the reaction of $Cp_2Ce(OR)_2$ with the appropriate lithium salt. Conversely, the trialkoxide amide complex $(^tBuO)_3Ce(N(TMS)(2,6\text{-}^iPr_2C_6H_3))$ is the major species generated as a result of redistribution processes initiated by the bulky amide $LiN(TMS)(2,6\text{-}^iPr_2C_6H_3)$ (≥ 1 equiv). Although isolable bisamide species have been prepared, efforts so far to prepare synthetically appealing amide nitrate complexes have so far proven unsuccessful owing to rapid redistribution and/or reduction processes.

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Four-Electron Reduction of Substrates

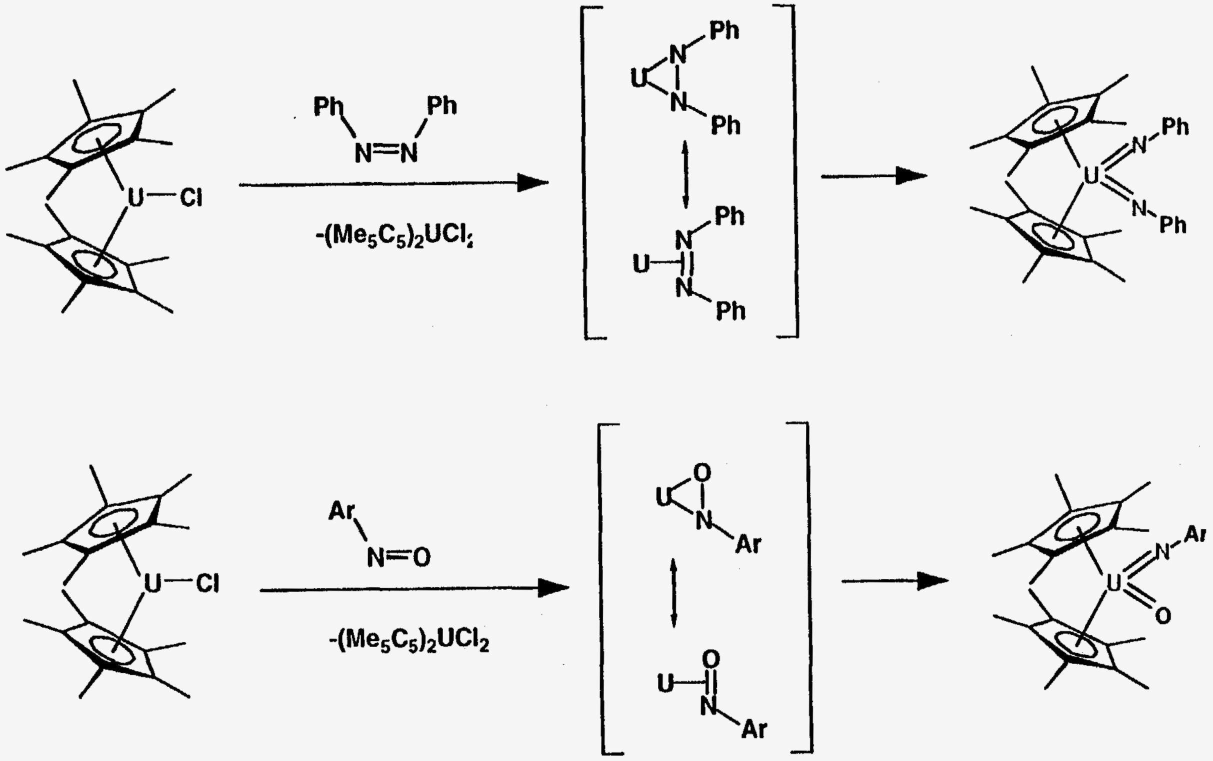


Figure 1. Four-electron reduction of organic substrates provides a direct route to uranium(VI) products.

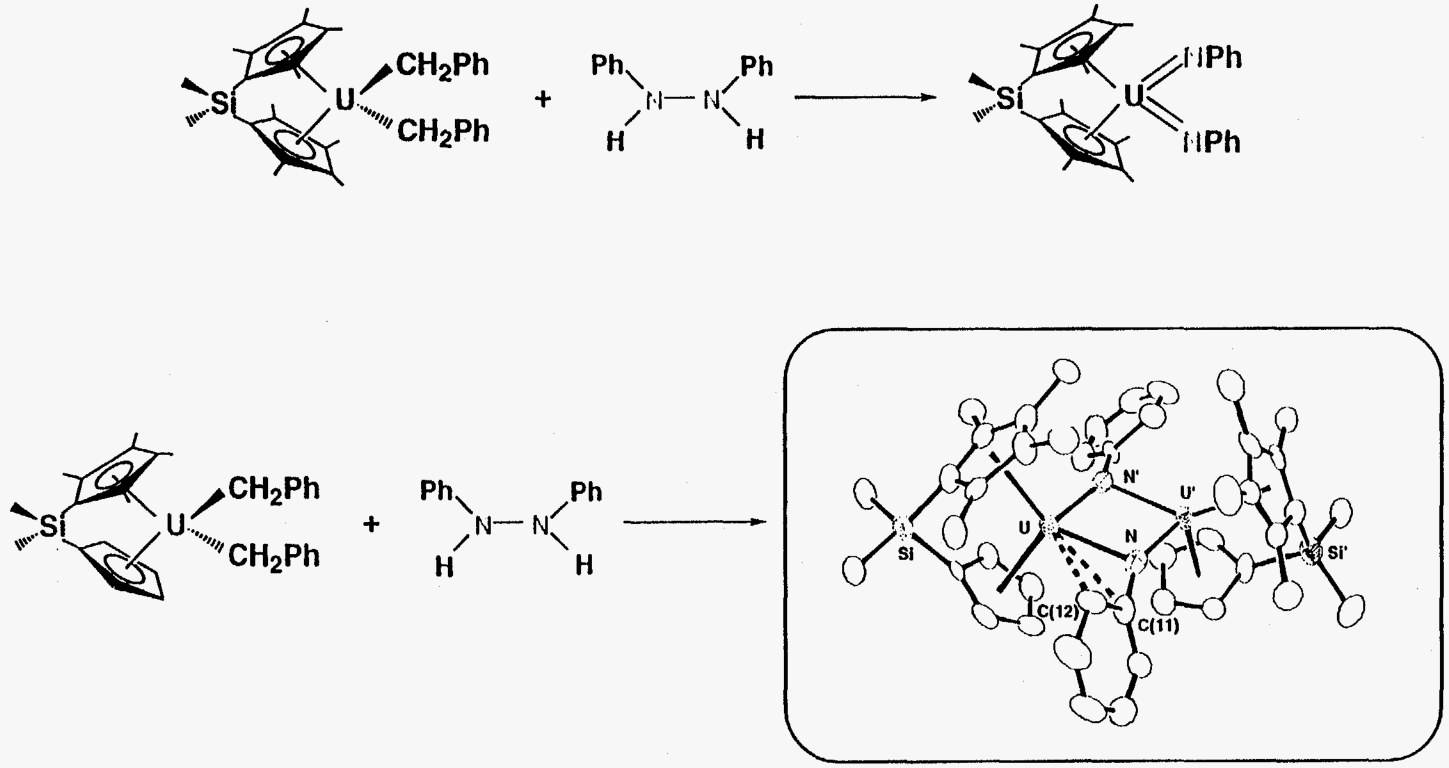
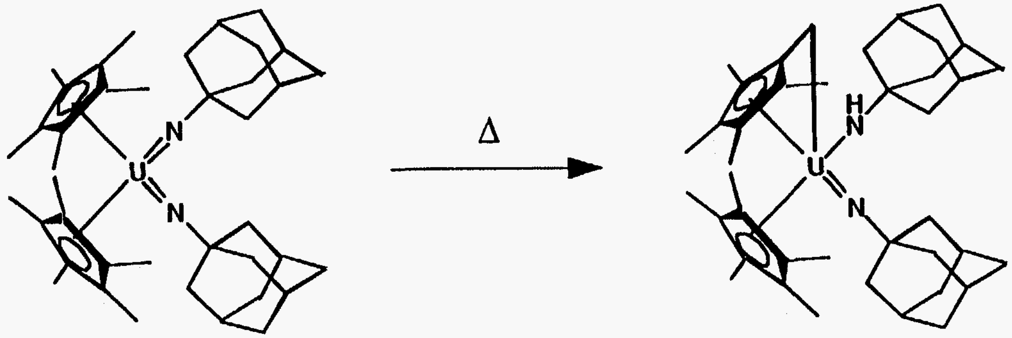
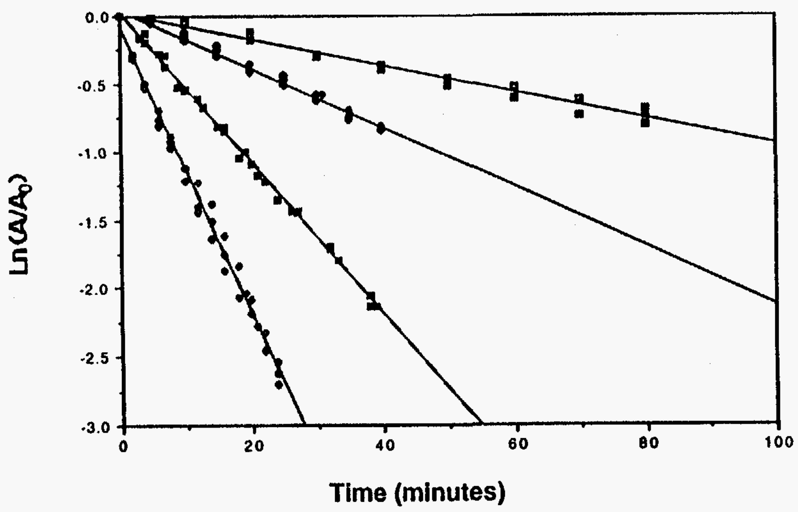


Figure 2. Thermolysis of U(VI) alkylimido complexes yields unprecedented ring activation.

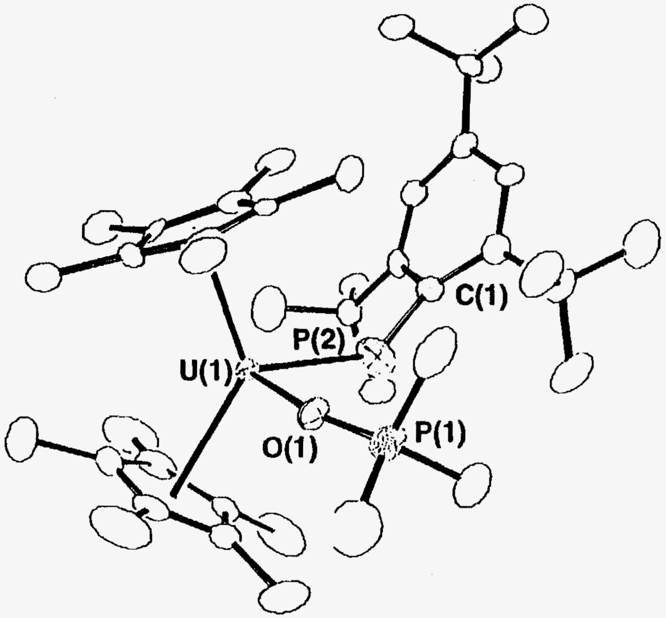




at 70 °C:

ΔH‡ = 21.2 kcal/mol
ΔS‡ = 2 eu

Figure 3. Varying the reduction potential of the metal center affects the stability of hexavalent uranium.



U(1)-P(2) = 2.562(3) Å
U(1)-O(1) = 2.370(5) Å
P(1)-O(1) = 1.500(6) Å
P(2)-C(1) = 1.851(9) Å

O(1)-U(1)-P(2) = 95.1(2)°
U(1)-O(1)-P(1) = 157.5(4)°
U(1)-P(2)-C(1) = 143.7(3)°

Figure 4. Molecular structure of $(\eta^5\text{-Me}_5C_5)_2U(=PAr)(O=PPh_3)$ [Ar = 2,4,6-t-$Bu_3C_6H_2$].

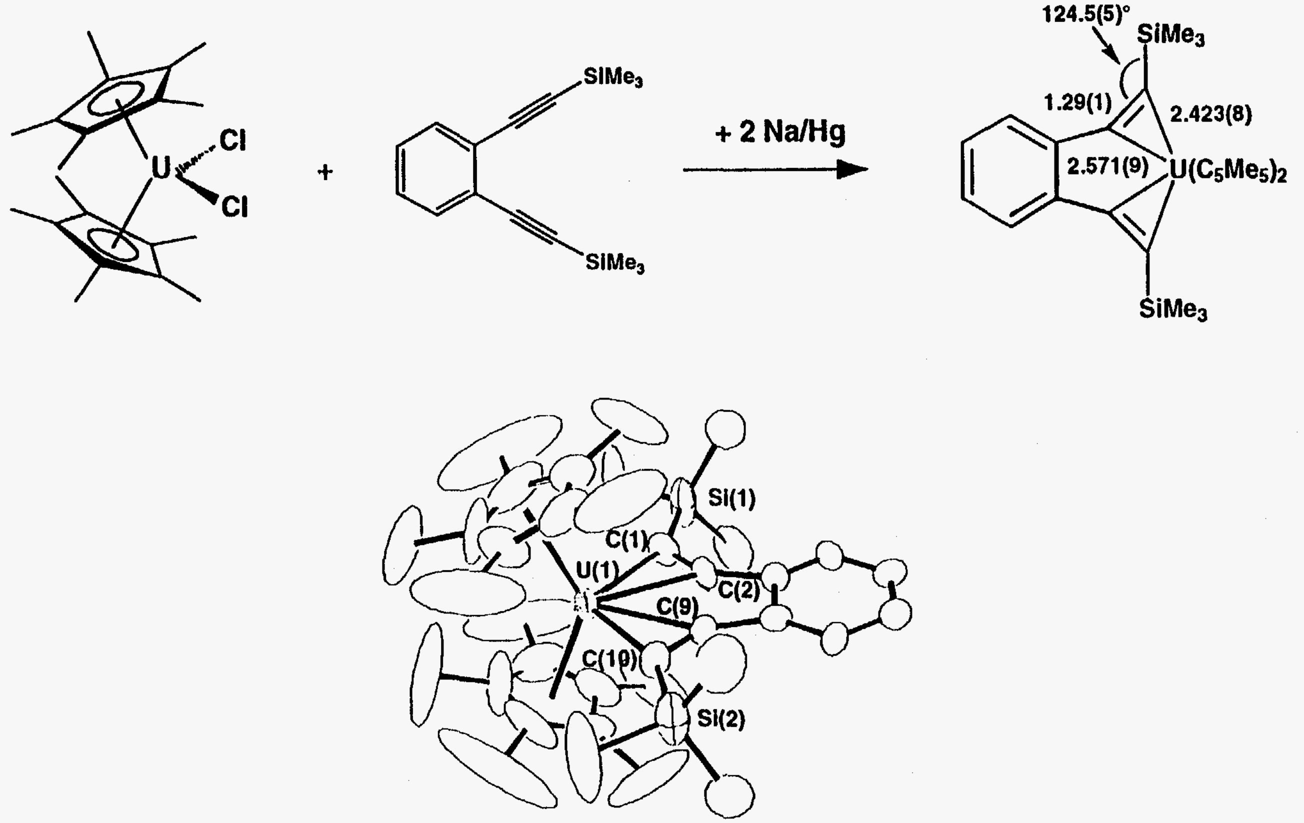


Figure 5. Uranium-mediated coupling of alkynes can be sterically arrested by linking the two alkyne units.