Reactivity and Cross-Reactivity in

Redox Activation of the Uranyl Ion

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KEYWORDS: electrochemistry; redox; oxo-activation; tris(pentafluorophenyl)borane; titrations

Abstract

The properties of the uranyl dication (UO_2^{2+}) are governed in many respects by its redox chemistry, and functionalizing the strong U–O bonds often requires reduction from U(VI) to U(V) with solution-phase multicomponent reaction chemistry that involves both strong reductants and electrophiles. Here, we report the patterns of reactivity and cross-reactivity displayed by a model system in which oxo-activating conditions have been tested that involve either i) electrochemical or chemical reduction, or *ii*) coordinating or non-coordinating solvents. In acetonitrile (CH₃CN), a complex of the uranyl(V) monocation [UO₂⁺] can be formed reliably through treatment of the U(V) species with tris(pentafluorophenyl)borane (BCF), but it also results in a mixture of products arising in part due to direct electron transfer to BCF. In dichloromethane (CH₂Cl₂), attempts to chemically reduce and functionalize U(VI) revealed undesired cross-reactivity that precludes reduction of U(VI); Cp*₂Co can undergo cross-reactions with both CH₂Cl₂ and BCF, evidently by electron transfer from Co(II) followed by further reactions. Despite the cross reactivity in CH₂Cl₂, one uranium-containing product could be crystallized, and was characterized by solid-state X-ray diffraction analysis. This complex features a trinuclear, formally [U^V,U^{IV},U^V] core, but contains only four of the total of six oxo equivalents that were expected on the basis of the U(VI) starting material, confirming that electrophilic reactivity can proceed in this system upon reduction. Along this line, computational studies have been used to establish the baseline electronic properties of the U(V) and U(IV) centers in the trinuclear product, as well as gain insight to structural changes induced by the reduction of this compound. The documentation of the reactivity and crossreactivity patterns here are essential to guide design of improved multicomponent systems for actinide processing.

Introduction

Significant progress has been made in recent years towards the reduction of the uranyl dication $(UO_2^{2^+})$ in both aqueous and non-aqueous environments.^{1,2} While uranyl in the +VI oxidation state (O.S.) is water soluble and mobile in aqueous environments, reduction to U(IV) results in solid species that can be more easily isolated from the relevant media.^{3,4} Implicated in this pathway is the U(V) intermediate oxidation state, but isolation of U(V) species has proven to be challenging as the presence of the trans-dioxo ligands stabilize U(VI) and make this O.S. chemically inert to many reagents.¹ Indeed, uranyl is resistant to both reduction ($E^{\circ}(U^{VI/V}) = 0.16$ V vs the standard hydrogen electrode; SHE) and protonation in aqueous media, even by triflic acid.^{5,6} Additionally, U(V) species often engage in rapid self-disproportionation to yield U(IV) and U(VI) species, increasing the difficulties that can be encountered when attempting to gain control and insight into the reactivity pathways that govern uranium redox chemistry and speciation.^{7,8} Despite these challenges a few examples of complete oxo cleavage can be found,^{7,9,10} but reports aimed at documenting the many possible reactivity pathways behind uranyl reduction and functionalization have not appeared in the literature in great quantity,^{11,12} although many reports exist that present the products of such reactivity.

While the terminal oxo ligands in uranyl are only mildly basic when U is in the +VI oxidation state (O.S.), reduction to U(V) increases their basicity, motivating many oxo-functionalization strategies to involve association of an electrophile with the oxo(s) in tandem with reduction.¹ Dependent on the thermodynamic properties of the specific uranyl system of interest, one or several pathways to reduction and oxo-functionalization may be accessible. As shown in Scheme 1, a neutral uranyl(VI) complex could either engage directly with an electrophile (denoted as Z),

or may require reduction before binding of the electrophile; alternatively, electrophile coupled electron transfer (ECET) could occur in a manner mimicking proton coupled electron transfer (PCET).¹³ Further reduction and functionalization can occur in certain cases to access bisfunctionalized U(V) species or complexes of U(IV). In line with these idealized pathways, reports direct coordination to the oxo(s) of uranyl(VI) by the strongly electrophilic of tris(pentafluorophenyl)borane (BCF) are known, which result in a weakening of the U-O bond and allow for a more accessible U(VI/V) reduction (see the example product from Sarsfield & coworkers in Scheme 2).^{14,15} Some ligand systems preclude this possibility, however, necessitating reduction of uranyl(VI) to U(V) before electrophiles will engage in reactivity with the oxo moieties (see the work of Hayton & co-workers and one product shown in Scheme 2).^{15,16,17} Many systems have been reported to follow the pathways involving discrete electron transfer and electrophile coordination,¹ but few systems are documented to engage in ECET; both the examples that appear to involve this pathway employ a silane reagent and yield a doubly oxo-functionalized product. This pathway would be associated formally with gain of 1e⁻ and two equivalents of electrophile Z in Scheme 1.^{18,19} Finally, in a few systems, further controlled reduction to U(IV) is possible, giving rise to isolable bis-functionalized U(IV) species (see one example from Arnold, Love & coworkers in Scheme 2).^{16,17}



Scheme 1. Idealized pathways for electrophilic oxo-functionalization of a neutral uranyl(VI) compound (top left) promoted by reduction (Z = electrophile).



Scheme 2. Selected literature examples of BCF-functionalization products of uranyl in multiple oxidation states. BCF = tris(pentafluorophenyl)borane.

The outcome of reduction and oxo functionalization of uranyl varies widely depending on the equatorial coordination of U(VI), electrophile, reductant, and even solvent. Multidentate ligands are often chosen to house uranyl as they generally encourage the formation of molecular complexes whose reactivity can be more easily studied and allow for a greater degree of speciation control by limiting the available equatorial coordination sites. The monodentate atoms or small molecules, such as solvents, coordinated in this plane are typically labile and exchange of these can lead to multiple species in solution.^{20,21,22} Aside from the many ligands that have been reported to form complexes of uranyl, a large variety of electrophiles have been employed in oxo-functionalization strategies, including alkali metal cations,²³ p-block elements,²⁴ transition metals,^{12,18,25,26} and f-elements,²⁷ with **BCF** being one of the most common reagents.^{7,10,14,15,16,17,19} Similarly, many chemical reductants have been employed, each with very negative potentials (as necessitated by

the generally quite negative reduction potentials of the redox processes of uranyl complexes in non-aqueous media). As an alternative to chemical reductants, our group recently reported a unique system in which a complex of uranyl(VI) could be reduced electrochemically and functionalized sequentially with a much milder electrophile, triphenylborane.²⁸ Considering the virtually endless options of reagents and solvents to use in this work, however, we anticipated that a study in which both the desired *reactivity* of a uranyl(VI) complex with **BCF** and undesired *cross-reactivity* of the system would be useful for identifying patterns to inform future studies in the field. We hypothesized that use of parallelized methodology with both coordinating and non-coordinating solvents and both electrochemical and chemical reduction would enable the identification, in particular, of specific combinations of reagents that cause deviations from the desired reactivity, and we thus refer to these suboptimal reactions as *cross-reactivity pathways* in this study.

Here, we document the reactivity and cross-reactivity that can be operational when a strong Lewis acid is applied in the oxo-functionalization of uranyl across conditions involving coordinating and non-coordinating solvents and under electrochemically or chemically reducing environments. A reduced complex of the uranyl(V) monocation $[UO_2^+]$ could be formed consistently CH₃CN but a mixture of products resulted when **BCF** was introduced due to disproportionation, decomposition, and other reactivity observed here. In the non-coordinating solvent CH₂Cl₂, the same uranyl(V) complex can be generated electrochemically, but efforts to prepare it with a chemical reductant (Cp*₂Co) and induce reactivity with **BCF** revealed crossreactivity between Cp*₂Co and **BCF**, as well as resulted in decomposition of Cp*₂Co in the CH₂Cl₂, as recently reported in a preliminary communication.²⁹ The very Lewis acidic **BCF** electrophile can, however, interact directly with the weakly Lewis basic oxo moieties of uranyl(VI) in CH₂Cl₂ and reduction of this mixture gave rise to one crystalline product which was characterized by solid-state X-ray diffraction (XRD) analysis. Computational findings provide complementary insights into the experimentally observed differences in the electrophilicity of **BCF** in coordinating vs. non-coordinating solvents and provide evidence in support of the proposed oxidation states present in the structurally characterized product. On the basis of the comprehensive studies presented here, we conclude that the multicomponent requirements of oxo functionalization can lead to intrinsic limitations in selectivity and efficiency. However, our findings also suggest opportunities for future improvements, particularly in matching of Lewis acidity/electrophilicity and uranium redox chemistry in order to avoid cross reactivity driven by unproductive electron transfer.

Results

Reduction of $U^{VI}O_2$. We have reported the clean, highly reversible reduction reactivity of a model U(VI) complex, $U^{VI}O_2$, to U(V) under both electrochemical and chemical conditions (structure of $U^{VI}O_2$ shown in Scheme 3). Briefly, cyclic voltammetry data for $U^{VI}O_2$ displays a single accessible reduction at $E_{1/2} = -1.55$ V vs ferrocenium/ferrocene (denoted hereafter as Fc^{+/0}) in electrolyte based on acetonitrile (CH₃CN/TBAPF₆; see SI, Figures S59 & S60) and at $E_{1/2} = -1.59$ V (all potentials quoted vs. Fc^{+/0}) in electrolyte based on dichloromethane (CH₂Cl₂/TBAPF₆; see SI, Figures S64 & S65).^{28,29} The identity of this reduction product in CH₃CN is a structurally similar complex U^VO_2 that retains the uranyl moiety, albeit with the +V formal oxidation state. The pentadentate equatorial coordination environment is also maintained in this species, which features an overall charge of $-1.^{28,29,30}$ A similar compound is formed upon electrochemical reduction of $U^{VI}O_2$ in CH₂Cl₂ as implicated by the spectroscopic data. The electronic absorption profiles of $U^{VI}O_2$ are almost identical in CH₃CN and CH₂Cl₂, featuring ligand-based $\pi \rightarrow \pi^*$

transitions at 238 nm in CH₃CN or 248 nm in CH₂Cl₂ and LMCT transitions attributable to imine \rightarrow U, phenoxide \rightarrow U, and O_{yl} \rightarrow U between 342–483 nm in CH₃CN or 348–482 nm in CH₂Cl₂ (see SI, Figures S49 & S54).^{31,32} To generate U^VO₂ in both acetonitrile- and dichloromethanebased electrolytes, polarization at a negative potential can be applied to solutions of U^{VI}O₂, revealing the spectral profile of U^VO₂ as monitored by UV-visible detection.²⁹ This profile clearly resembles that of other similar U(V) complexes with strong ligand-based absorptions centered around 248 nm and a single other absorption at 355 nm.^{8,33}

However, while the $U^{v}O_{2}$ complex can also be cleanly isolated by the reduction of $U^{vI}O_{2}$ by Cp*₂Co in CH₃CN as reported in our prior study (see SI, Figure S51),²⁸ attempts to generate $U^{v}O_{2}$ with Cp*₂Co in CH₂Cl₂ ($E_{1/2} = -1.97$ V in CH₂Cl₂/TBAPF₆)²⁹ did not yield the anticipated clean reactivity when monitored by NMR and UV-visible spectroscopy (see SI, Figures S36 & S55). This alerted us to the possibility of undesirable side-reactivity in this non-coordinating solvent and led us to report the reactivity of Cp*₂Co with CH₂Cl₂ in a prior communication,²⁹ revealing its instability in CH₂Cl₂ (summarized in Scheme 3). Unfortunately, this decomposition pathway implies that electron transfer reactions induced by Cp*₂Co in CH₂Cl₂ are very unlikely to yield clean 1e⁻ reduction reactivity, an observation reflected in the consistent yields below 75% reported for reduction reactions carried out in related conditions.^{15,34}



Scheme 3. a) Structure of $U^{VI}O_2$. b) Reactivity of $Cp*_2Co$ with CH_2Cl_2 .

Speciation of tris(pentafluorophenyl)borane in coordinating and non-coordinating solvents. Adduct formation of BCF with coordinating solvents is well-documented in several cases; X-ray diffraction data is available for the CH₃CN adduct of BCF, underscoring the innate Lewis acidity of this reagent.^{35,36,37,38} To provide context for our studies of uranyl reactivity with BCF, we monitored the formation of this adduct under our chosen conditions in both a coordinating and also a non-coordination solvent via infrared (IR) spectroscopy, NMR spectroscopy, and investigated the species formed by computational analysis (vide infra). On the one hand, we measured a shift in the C=N stretching frequency of acetonitrile upon adduct formation with **BCF** from 2268 cm⁻¹ to higher wavenumbers (2368 cm⁻¹; $\Delta \tilde{\nu} = 100$ cm⁻¹), which is consistent with previously reported IR frequencies and contraction of the C=N bond observed by XRD analysis ($\Delta d_{C-N} = 0.033$ Å; see SI, Figure S42).³⁸ On the other hand, the IR spectrum of BCF in CH₂Cl₂, shows excellent agreement with the ATR spectrum of solid BCF, indicating that the effective electrophilicity of BCF in CH₂Cl₂ is similar to that of free BCF (see SI, Figures S41 & S45). The behavior of solid BCF and BCF dissolved in CH₂Cl₂ is anticipated to contrast starkly with the diminished effective electrophilicity in the coordinating solvent CH₃CN; this is indicated both by the change in the nitrile stretching frequency and the C-N bond length (vide supra).

Effects of CH₃CN coordination on the properties of **BCF** are also apparent in ¹⁹F NMR spectra, wherein the three distinct *ortho-*, *meta-*, and *para-*fluorine environments of the phenyl rings in **BCF** give rise to three signals that provide sensitive information about their electronic environment. For example, monitoring the ¹⁹F NMR of **BCF** in CD₂Cl₂ as it is titrated with CH₃CN revealed a decrease in intensity of the **BCF** features at the expense of ingrowth of three new, upfield resonances ($\Delta \delta = 5.24$, 11.73, and 3.33 ppm, respectively; see SI, Figure S28). This suggests that the coordination of CH₃CN to **BCF** yields a strongly bound **BCF**–acetonitrile adduct (**BA**) effectively increasing the electron density and steric crowding about the boron center in **BCF** and generally decreasing its electrophilic nature. Together, this evidence confirms the formation of **BA** under our chosen conditions and demonstrates that the electronic and structural properties of the solvated **BCF** electrophile vary widely depending on the coordinating or non-coordinating nature of its solvent environment.

Cross-reactivity between electrophile, electrolyte, and reductant. Informed by literature reports regarding the reactivity of **BCF** with polyatomic anions, the incompatibility of **BCF** with TBAPF₆ in CH₂Cl₂ could be anticipated in an electrochemical/electrolyte context. Indeed, we observed this under our conditions. NMR spectra of a **BCF**/TBAPF₆ mixture in CD₂Cl₂, show peaks associated with a **BCF**-containing species that are shifted drastically upfield and the absence of ³¹P resonance associated with TBAPF₆ (see SI, Figure S30 & S31). In the ³¹P spectrum of this mixture, a single set of resonances at $\delta = -34.9$ ppm ($J_{PF} = 1072$ Hz) can be seen corresponding to phosphoryl fluoride (OPF₃), a species which also gives rise to a doublet in the ¹⁹F spectrum of this mixture at $\delta = -88.5$ ppm ($J_{PF} = 1072$ Hz; literature reported shifts for OPF₃: ³¹P NMR (CDCl₃) $\delta = -33.9$ ppm, $J_{PF} = 1072$ Hz and ¹⁹F NMR (CDCl₃) $\delta = -88.6$ ppm, $J_{PF} = 1073$ Hz).^{39,40} Phosphoryl fluoride can form from the partial hydrolysis of PF₅ which was likely generated under our

conditions by **BCF**-induced halide abstraction from PF₆⁻ and subsequent reaction with adventitious water present in the NMR solvent (halide abstraction from PF₆⁻ by **BCF** has been reported).^{39,41} Consistent with this reaction sequence and the identity of the **BCF**-containing product are a set of resonances associated with $[(BCF)F]^-$ in the same ¹⁹F NMR spectrum at $\delta = -134.2, -158.0, -165.9, \text{ and } -190.0 \text{ ppm}$ (literature shifts of ["Bu₄N][B(C₆F₅)₃F]: ¹⁹F NMR (CDCl₃) $\delta = -133.9, -159.9, -164.6, \text{ and } -185.2 \text{ ppm}$; literature shifts of [Ph₃C][B(C₆F₅)₃F]: ¹⁹F NMR (CDCl₃) $\delta = -134.84, -161.90, -166.24, \text{ and } -186.99 \text{ ppm}).^{41,42}$ The upfield shift of the [(BCF)F]⁻ resonances compared to those of **BCF** is characteristic of an increase in electron density and coordination number at the boron center. All of these features notwithstanding, **BCF** appears stable in dichloromethane that is free of TBAPF₆. We conclude this on the basis of the satisfactory agreement between the ¹⁹F NMR resonances observed here and previously reported values for this compound in CD₂Cl₂.⁴³

With regards to its electrochemical properties, reductive characterization of **BCF** has been hindered in the past by reactivity with the anions of common supporting electrolytes (i.e., ClO_{4^-} , PF_{6^-} , and BF_{4^-}), with most previous attempts yielding ill-defined waves. The quasi-reversible reduction of **BCF** was measured, however, in 2011; the data from this study revealed a quasireversible couple ca. $E_{1/2} = -1.6$ V vs Fc^{+/0} in both non-coordinating solvent (CH₂Cl₂) and weakly interacting [*n*Bu₄N][B(3,5-(CF₃)₂C₆H₃)₄] as the supporting electrolyte. In the data, the re-oxidation of [B(C₆F₅)₃]⁻⁻ could only be observed at high scan rates, suggesting the radical could feature significant reactivity, a finding also consistent with our work here (*vide infra*).⁴⁴ We anticipate that the observation of reactivity of **BCF** with most electrolytes could be due to the important role that the Lewis basicity of the solvent may play in "protecting" **BCF** from decomposition in the presence of species (like PF_6^-) with which it may irreversibly react to form adducts, such as $[(BCF)F]^-$.

In light of all these findings, we hypothesized that formation of an alternative adduct via a pathway with a lower activation energy with coordinating solvent could kinetically preclude a reaction with a higher barrier, such as fluoride abstraction from PF6-. On the one hand, the coordinating solvent environment afforded by use of tetrahydrofuran (THF) does not appear to be sufficient to protect BCF from reactivity on the basis of literature studies.⁴⁵ On the other hand, in line with our theory, we have found that there is virtually no reactivity between **BA** and PF₆⁻ in the coordinating system of CH₃CN/TBAPF₆. Support for this finding was obtained through ¹⁹F and ³¹P NMR wherein no evidence for degradation of **BA** or TBAPF₆ could be measured when mixtures were combined in 1:1 or 1:5 ratios in CD₃CN (see SI, Figures S9-S12). These data indicate that coordination of CH₃CN to BCF, resulting in formation of the adduct (C₆F₅)₃B-NCCH₃ (**BA**) imparts sufficient stability to protect the boron center from reactivity with PF₆⁻. To capitalize on this finding, we next probed the cyclic voltammetry of **BA** in CH₃CN/TBAPF₆. The resulting voltammograms revealed an irreversible reduction event at -2.46 V and no corresponding re-oxidation in the scan rate-dependent data up to 300 mV/s (see SI, Figures S57 & S58). Across all scans, however, the current response remained measurable as a result of the increased stability of BA compared to BCF in a non-coordinating environment (see SI, Figure S63). Taken together, these findings imply that significant follow-up chemical reactivity occurs upon formation of the $[B(C_6F_5)_3]^-$ radical anion. This agrees well with the prior reactivity of the radical that was documented in CH₂Cl₂.^{44,46} Compared to the reported cathodic peak potential in the CH₂Cl₂/["Bu₄N][B(3,5-(CF₃)₂C₆H₃)₄] system, the reductive feature in CH₃CN/TBAPF₆ is shifted to significantly more negative potentials ($\Delta E_{p,c} = ca. 860 \text{ mV}$). This shift to a more negative

reduction potential may be attributed to the increase in electron density resident on **BA** arising from the bound CH₃CN in comparison to the bare **BCF** present in the CH₂Cl₂ electrolyte.

Turning to the question of direct chemical reduction of **BCF** by a chemical redox reagent, we mixed **BCF** and Cp*₂Co in CD₂Cl₂ and collected the ¹⁹F NMR spectrum for this mixture. We observed a single fluorine-containing product in the data, corresponding to formation of $[(BCF)Cl]^-$ (see SI, Figure S29; literature shifts of $[(BCF)Cl]^-$: ¹⁹F NMR (CD₂Cl₂) $\delta = -132.5$, -162.1, and -166.9 ppm).⁴⁷ This observation is consistent with our prior work on reactivity between dichloromethane and Cp*₂Co; as mixing these two reagents results in generation of chloride (see Scheme 3), the vast excess of dichloromethane in this experiment appears to promote solvent reactivity with the reducing agent, followed by chloride capture by **BCF**.

This proposed reaction sequence is in accord with the measured reduction potential of $Cp*_2Co$, which is more than 300 mV negative of the reduction potential for **BCF** in $CH_2Cl_2(E_{1/2} of [Cp*_2Co]^+/Cp*_2Co = -1.97 V vs Fc^{+/0}$ in CH_2Cl_2 electrolyte), although reduction of **BA** by $Cp*_2Co$ was not expected in CH_3CN as the reduction potential of $Cp*_2Co$ in CH_3CN media is more than 500 mV positive of the reduction potential for **BA** in $CH_3CN/TBAPF_6$ measured here $(E_{1/2} of [Cp*_2Co]^+/Cp*_2Co = -1.91 V vs Fc^{+/0}$ in CH_3CN electrolyte).^{29,44,48} Nevertheless, evidence for reduction of **BA** in CH_3CN media was encountered through multiple avenues. The ¹H NMR spectrum resulting from the mixture of **BA** with $Cp*_2Co$ shows a set of broad, shifted resonances between 8 and 14 ppm, rather than the characteristic broad resonance near 47 ppm for $Cp*_2Co$ or the intense singlet of $[Cp*_2Co]^+$ near 1.7 ppm that would be expected if electron transfer took place (see SI, Figures S7). With respect to the fluoride-containing species, two products can be detected from the mixture of **BA** with $Cp*_2Co$ in CH_3CN via ¹⁹F NMR and Mass Spectrometry in negative ion mode. The mass spectrum of this mixture diluted with methanol reveals two primary species

with m/z (M⁺) = 528.9901 and 543.0039 corresponding to the [B(C₆F₅)₃OH]⁻ and [B(C₆F₅)₃OCH₃]⁻ anions, respectively (see SI, Figures S46–S48).⁴⁹ These two species correspond to six total resonances in the ¹⁹F NMR spectrum between –135 and –169 ppm, which are in good agreement with the literature reported values for these compounds (see SI, Figure S8).^{50,51} The formation of these species is likely derived from reactivity of *in situ* generated $[B(C_6F_5)_3]^-$ with adventitious water in the absence of other oxygen sources. Finally, a time-based reactivity study of Cp*₂Co with **BA** monitored by UV-Visible spectroscopy reveals that BA can be reduced by $Cp*_2Co$ in CH₃CN on the order of minutes, with absorbance of the in-situ generated $[Cp*_2Co]^+$ levelling off after approximately 200 seconds after mixing (Figure 1). Therefore, the abundance of evidence from these reactivity and cross-reactivity studies suggests that use of very strongly Lewis acidic electrophiles places an inadvertent limitation on clean reductive oxo-activation strategies that can be explored for uranyl (reactivity summarized in Scheme 4). The combination of the potent reagents induces prolific cross-reactivity that could be avoided, as evident when compared to the beautifully clean electrochemical and chemical activation that takes place when a milder Lewis acid, triphenylborane, is employed.²⁸



Figure 1. Spectral changes resulting from the addition of BA to $Cp*_2Co$ in CH_3CN as monitored by UV-Visible spectroscopy.



Scheme 4. Summary of all species directly detected from the cross-reactivity between BCF and commonly used reagents including solvents, a chemical reductant (Cp*₂Co) and an electrolyte (TBAPF₆).

Reactivity of U^{VI}O₂ with BCF in coordinating and non-coordinating solvents. Consistent with the diminished Lewis acidity of the solvent adduct **BA** in comparison to **BCF**, no reaction was observed between $U^{VI}O_2$ and **BA** via NMR or UV-visible spectroscopies. On the NMR side, this was evident by the absence of any shifted or new peaks in the ¹H and ¹⁹F NMR spectra of these reaction mixtures. In the optical work, there was little change in absorption maxima when the reagents were mixed. (see SI, Figures S13–S16).

However, in line with the greater Lewis acidity of **BCF**, significant reactivity ensues between $U^{VI}O_2$ and **BCF** in CH₂Cl₂, conditions under which the **BCF** molecule is not bound by solvent or any other Lewis base prior to exposure to $U^{VI}O_2$. Multiple diamagnetic species were observed in ¹H NMR spectra of the reaction of $U^{VI}O_2$ with 1 and 2 equivalents of **BCF**, including $U^{VI}O_2$ as well as two other species that are shifted compared to the peaks of $U^{VI}O_2$ (see SI, Figures S32 & S34). The splitting patterns and number of peaks observed for these two new species are consistent

with the pseudo- C_{2v} symmetry of U^{VI}O₂, suggesting that interaction with BCF could be occurring through coordination of the terminal oxo ligands of the uranyl unit to the acidic boron center. Interaction of BCF with the phenoxide donors bound to uranium does not appear to be a significant contributor to the observed spectral changes, since we anticipate that engagement in this coordination mode would result in desymmetrization of the signals for the organic ligand backbone. Additionally, the downfield shift observed in the ¹H NMR spectrum coupled with the upfield shift seen in the ¹⁹F NMR spectra are in agreement with oxo-binding through one or more BCF molecules causing the uranyl unit to become more electron deficient and the BCF moiety to become more electron rich (see SI, Figure S33 & S35).

In accord with these findings from NMR spectroscopy, monitoring the reaction in CH_2Cl_2 by UV-Visible spectroscopy shows the evolution of the spectral profile of $U^{VI}O_2$ into new species with absorption maxima at 289 and 387 nm (see Figure 2). The reaction appears to produce more than one product, however, as isosbestic behavior was not observed. This finding is again consistent with the detection of multiple species by NMR. Although the synthesis and characterization of a few $U^{VI}O_2$ –BCF species supported by organic ligand frameworks have been reported,¹⁴ attempts at clean isolation of complexes of uranyl(VI) with BCF in this system were unsuccessful.



Figure 2. Spectral changes resulting from the addition of BCF to $U^{VI}O_2$ in CH₂Cl₂ as monitored by UV-Visible spectroscopy.

Reactivity of U^VO₂ with BA in CH₃CN. With the clean generation of U^VO₂ in CH₃CN under chemical/electrochemical conditions established on the basis of the spectroscopic results, as well as the baseline reactivity established for each of the individual components, we next investigated the electrochemical activation of U^{VI}O₂ with BCF by pursuing reduction of U(VI) to U(V) in the presence of BCF. Beginning with U^{VI}O₂ in CH₃CN/TBAPF₆, incremental additions of BA in CH₃CN/TBAPF₆ were made to the electrochemical cell. There were significant changes to the cyclic voltammetry profile, suggesting that reactivity does occur in this system (see Figure 3).

Beginning at ca. -0.5 V and scanning cathodically, cathodic current flow near -1.25 V was found to increase as increasing amounts of BA were added to the electrochemical cell. While current flow of this sort, positive of the main U^{VI}/U^V reduction wave, could be associated with a preequilibrium association step between $U^{VI}O_2$ and BCF, we anticipate that such an equilibrium is negligible in this system between $U^{VI}O_2$ and **BA** based on the spectroscopic evidence presented above. The more likely scenario for the increasing cathodic current at these potentials is a rapid reaction of the nascent U(V) form of the uranyl complex with the added BA. Support for this assignment comes from consideration of the classical characteristics of reactivity that is sufficiently fast to promote so-called kinetic potential shifts.⁵² In such a case, reaction of **BA** with $U^{V}O_{2}$ would be fast on the electrochemical timescale, resulting in perturbation of the Nernstian equilibrium associated with electron transfer to/from the unfunctionalized uranyl complex, resulting in turn to an apparent positive shift of that redox manifold in the presence of BA. As would be anticipated for such a case, the current flow at -1.25 V increases as a function of [BA] (see SI, Figure S61).^{53,54} In the reaction of the U(V) complex with BCF, we anticipate that the CH₃CN equivalent bound to BCF as in BA would be displaced by the more Lewis basic terminal oxo ligands of the $[UO_2^+]$ unit. On the anodic branch (return sweep of the CV), the oxidation of the electrogenerated $U^{V}O_{2}$ becomes progressively less reversible as the availability of BCF/BA is increased. This is consistent with follow-up reactivity between $U^{V}O_{2}$ and the added borane, as the electrogenerated $U^{V}O_{2}$ is depleted from the reaction-diffusion layer near the electrode surface when **BA** is present. Indeed, the return oxidation wave is completely absent when 1 equiv. of **BA** is present in the solution.



Figure 3. Electrochemical titration of $U^{VI}O_2$ with BA in CH₃CN/TBAPF₆ (scan rate: 100 mV/s, first scans shown).

As evident in the voltammetry data shown in Figure 3, there are no significant or well-defined oxidation waves that appear in the data at potentials positive of the couple associated with $U^{VI}O_2/U^VO_2$ redox cycling. This suggests that the reaction product(s) that result from reaction of U^VO_2 with **BA** may not have readily accessible oxidation processes under these conditions, may be associated with slow heterogeneous electron transfer kinetics, or may not be soluble/available at the electron surface for re-oxidation upon generation. However, we did observe broad waves with modest oxidizing currents at rather positive potentials (*E*_{onset} ca. -0.2 V and extending to 0.5 V) in

the data (see SI, Figure S62). We anticipate that these currents are associated with re-oxidation of reduced products formed at the electrode. As these currents appear in the data only when scanning to potentials associated with reduction of $U^{VI}O_2$ and in the presence of **BA**, we anticipate the species undergoing reoxidation likely arise from reactivity involving uranium. In accord with this proposal, the oxidizing currents associated with the processes between -0.2 and 0.5 V persisted in all relevant cycles of voltammetry interrogated in this system, and increased upon addition of up to 2 equiv. of **BCF** with respect to the initial $U^{VI}O_2$ concentration. Like all the other data presented, these observations support interaction of **BA** with U^VO_2 upon generation.

Considering all of the findings from the electrochemical work, we anticipate that reduced and borylated species are produced under the electrochemical conditions by rapid reaction of U^VO_2 with **BA**. This finding is similar to that in our group's related work with triphenyl(borane) as electrophile in an electrochemical reactivity scheme, although in the latter case the borylated species showed more well-behaved electrochemical properties upon formation.²⁸ We note here that substitution of **BCF** for triphenylborane appears to drive increased reactivity, but also induces irreversible behaviors that cloud identification of molecular reactivity pathways in the voltammetry data beyond the initial uranium reduction.

Spectrochemical titrations of $\mathbf{U}^{\mathbf{V}}\mathbf{O}_2$ with **BA** were carried out to better understand the reaction products that result from this system. To accomplish these titrations, $\mathbf{U}^{\mathbf{V}}\mathbf{O}_2$ was produced by stoichiometric reduction of $\mathbf{U}^{\mathbf{V}\mathbf{I}}\mathbf{O}_2$ with Cp^*_2Co , resulting in a solution of the reduced complex in the cuvette for our studies at a concentration of 100 μ M.^{28,29} Isosbestic behavior was observed upon the earliest additions of **BA** with (virtually) isosbestic points present in the data at $\lambda_{iso} = 346$ nm, 414 nm, and 533 nm and a uniform shift in the peak maximum of the major CT transition to a higher energy (3.32 eV in the profile of $\mathbf{U}^{\mathbf{V}}\mathbf{O}_2$ to 3.51 eV after the addition of 1 equivalent of **BA**; see SI, Figure S52). Similarly, when between 1 and 2 equivalents of **BA** were added in the spectrochemical titration, the spectral changes remain virtually isosbestic at 414 nm and 533 nm with the peak maximum for the major CT transition experiencing a minute shift to a higher energy from 3.51 eV to 3.55 eV (see SI, Figure S53). Thus, at a [U] = 0.0001 M, the reactivity of $U^{V}O_{2}$ with **BA** appears to be selective on the basis of spectroscopy.

However, NMR spectra collected on reactions conducted at bulk scale with [U] = 4-6 mM involving a 1:1 mixture of $U^{V}O_{2}$ and **BA** were consistent with unselective reactivity, in that they display multiple paramagnetically shifted peaks in addition to diamagnetic features corresponding to $U^{VI}O_2$. We anticipate that the portion of $U^{VI}O_2$ complex is likely generated by disproportionation reactions of reduced U-BCF species since U^VO₂ is stable on the time-scale of at least 24 hours in CH₃CN.²⁸ Similarly, the ¹H NMR spectrum of a reaction of U^VO₂ with 2 equivalents of **BA** conducted at [U] = 4-6 mM revealed paramagnetically shifted resonances in addition to the diamagnetic resonances of the $U^{VI}O_2$ complex (see SI, Figure S20). The ¹⁹F NMR spectrum of this reaction shows a veritable "forest" of resonances, including some corresponding to **BA** and some that resemble those measured in prior work⁵⁰ on oxygen-bound borane species on the basis of similar chemical shift values (see SI, Figure S21). Based on the use of necessarily higher concentrations in the synthetic work compared to the spectroscopic studies, we hypothesize that **BCF** does likely engages with the oxo moieties of $[UO_2^+]$ to form both 1:1 and 1:2 adducts. However, these species appear to be subject to significant disproportionation reactivity at elevated concentrations, and no diffraction-quality crystals of uranium-containing products were obtained over multiple attempts in this work.^{55,56} This observation is in accord with findings from our prior study on reactivity with triphenylborane.²⁸

Tying the electrochemical and chemical work conducted in acetonitrile together, we note that the observation of paramagnetically shifted resonances in ¹H NMR spectra of reactions of $U^{V}O_{2}$ with **BA** in CD₃CN in addition to the observation of very positive oxidative current in the electrochemical titration of $U^{VI}O_{2}$ with **BA** in CH₃CN/TBAPF₆ suggests that, upon reduction, inner-sphere reactivity likely occurs between **BCF** and the terminal oxo ligands of $U^{V}O_{2}$. The resulting reduced, functionalized species may engage in further reactivity, including disproportionation. In particular, the propensity toward disproportionation is supported by observation of selective reactivity (with isosbestic spectral changes) at [U] = 0.1 mM but complex mixtures of products at [U] = 4-6 mM.

Reactivity of U(VI), BCF, and Cp*₂Co in CH₂Cl₂. We also explored the reactivity of U^{VI}O₂ with BCF in a non-coordinating CH₂Cl₂ solvent, despite the known spurious reactivity of Cp*₂Co with CH₂Cl₂ and BCF. We did so because of the possibility that Cp*₂Co could display faster electron transfer kinetics to uranium complexes in light of the fast electron transfer behavior for U^{VI}O₂ in the cyclic voltammetry studies. Unfortunately, interrogation of the reaction of U^{VI}O₂ with BCF followed by additions of Cp*₂Co in CH₂Cl₂ through UV-visible detection showed non-isosbestic behavior implicating unselective reactivity (see SI, Figure S56). This is in accord with the previously identified cross-reactivity pathways that can operate between Cp*₂Co and CH₂Cl₂ and Cp*₂Co and BCF. The high concentration of solvent present under our accessible conditions could give the solvent reactivity an outside role here, as shown in our prior work.²⁹

Synthetic-scale work at higher concentrations (4-6 mM) resulted the apparent formation of multiple species as judged by ¹H NMR spectroscopy. Fewer paramagnetically shifted peaks were observed in the ¹H NMR spectrum of the reaction sequence { $U^{VI}O_2 + 1$ equiv. BCF, followed by 1 equiv. of Cp*₂Co in CD₂Cl₂} compared to the analogous reaction sequence in CH₃CN { $U^{VI}O_2$

+ 1 equiv. $Cp^{*}_{2}Co$, followed by 1 equiv. of **BA**). In both cases, however, the distinctive resonances associated with diamagnetic $U^{VI}O_{2}$ were detectable, implicating possible roles for disproportionation, as well as incomplete reduction in the case of work in $CD_{2}Cl_{2}$ (see SI, Figure S37). The ¹⁹F NMR spectrum of the reaction sequence in $CD_{2}Cl_{2}$ indicates that the **BCF**-containing specie(s) present in the mixture are more shielded, and thus more electron rich, than the **BCF** starting material. This is supported by the measured upfield shift of key resonances and the agreement of the chemical shift values to those associated with similar oxygen-bound **BCF** adducts (see SI, Figure S38).⁵⁰ Similarly, the ¹H NMR spectrum of the reaction of $U^{VI}O_{2}$ with 2 equivalents of **BCF** followed by the addition of $Cp^{*}_{2}Co$ reveals the presence of $U^{VI}O_{2}$ as well as nine paramagnetically shifted peaks; the ¹⁹F NMR spectrum shows shielded (electron rich) **BCF**-containing species as well (see SI, Figures S39 & S40). Taking all of this into account, the reactivity observed here for $U^{VI}O_{2}$ with **BCF** and $Cp^{*}_{2}Co$ in both coordinating and non-coordinating solvent is outlined in Scheme 5.



Scheme 5. Summary of reactivity and disproportionation behaviors between $U^{VI}O_2$ and the reagents employed here in CH₂Cl₂ (left) and CH₃CN (right) as supported by data from spectroscopic, chemical and electrochemical studies.

Structural Characterization of an Oxo-deficient Uranium Species Obtained by Reduction of a Uranyl(VI) Precursor. On one occasion, single crystals of a species denoted [U₃O₄], suitable for XRD analysis, were grown by vapor diffusion of diethyl ether into a concentrated reaction mixture in CH₂Cl₂. The reaction mixture was prepared according to the following sequence: $U^{VI}O_2$ was mixed with 2 equiv. BCF in CH₂Cl₂, followed by the addition of 1 equiv. of Cp*₂Co in CH₂Cl₂. The demonstrated ability of BCF to associate with $U^{VI}O_2$ in CH₂Cl₂ led us to conjecture that this sequence might enable BCF-bound uranium-containing species to undergo reduction by Cp*₂Co or cobalt-containing products of reactivity of Cp*₂Co with CH₂Cl₂.²⁹ Indeed, we were able to crystallize such a product (denoted [U₃O₄]), although we emphasize that a crystal of this product was obtained only on one occasion; we anticipate this was the case because of the sensitive and highly activated nature of [U₃O₄]. Further, in line with the view of the chemistry of this system demonstrated by the chemical and electrochemical experiments described in this report, the reactions leading to generation of [U₃O₄] cannot be concluded to be selective. $[U_3O_4]$ may not represent the major product of the reactivity obtained with the sequence that was utilized. Under routine circumstances, (inorganic) chemists with an eye toward balanced reactions and clean reactivity would perhaps not report the structure of a species obtained on only one occasion and lacking further characterization, as such activities could be construed as "crystal picking." However, in this case, the species that could be characterized by diffraction studies, [U₃O₄], represents a species of uncommon scholarly interest. Along this line, one unique feature of this species is that it was formed by reduction-induced uranyl activation and U–O bond cleavage. As demonstrated by the chemical and electrochemical studies reported here, this sort of reactivity remains challenging to control and few examples are available of products produced in this way. As the diffraction data and refined structural model (see Figure 4) were found to be unambiguous, and indeed, of a rather high quality, the structure of $[U_3O_4]$ has been included in this work for discussion and computational modelling has been carried out on a limited scale to better understand the properties of this species.



Figure 4. Solid-state structure (XRD) of $[U_3O_4]$. All hydrogen atoms, co-crystallized outersphere solvent molecules, and disordered atoms associated with the chelating ligands are omitted for clarity. Displacement ellipsoids are shown at the 20% probability level.

Experimental details regarding the crystallography can be found in the Supporting Information (pp. S48–S56 and Table S5). The structure of the crystalline product revealed an oxodeficient and linear trinuclear uranium core. This core features an uncommon U:O_{oxo} ratio of 3:4, rather than the ratio of 3:6 expected for conventional species with stoichiometry based on multiples of the uranyl motif (U:O_{oxo}, 1:2). Each uranium center is supported by a complete, pentadentate chelating ligand, as well. The asymmetric unit of the structure corresponds to exactly half of the molecular product, and features one **BCF** (B1) bound to one intact uranyl(VI)-derived moiety (U1A) as well as a half-occupied U atom at the center of the linear core motif (U1B). The noted central atom (U1B) is located along a two-fold rotation axis (approximately perpendicular to the axis along which the trinuclear core of the complex lies), with the result that the full trinuclear species can by visualized by rotation about the two-fold axis. Generally speaking, the uranium atoms are in close proximity to each other with interatomic U1A•••U1B distances of 4.179(1) Å (see Table 1). However, these U–O–U contacts cannot be considered as conventional "cation-cation" interactions between intact actinyl cations (of the Sullivan type⁵⁷) because of the deviation from U:O_{oxo} stoichiometry which was already noted.^{1,58,59} We note that, at this range, magnetic interactions could occur between unpaired spins on the individual U centers^{60,61,62} and these were investigated with quantum chemical calculations. A series of calculations were performed with different spin multiplicities (*vide infra*); the quintet multiplicity yielded the lowest energy and it was used for our subsequent analysis.

With regard to the organic ligand backbone structures, those which chelate the outer uranium centers appear more distorted compared to that chelating the inner uranium center as quantified by the organic ligand fold angles (denoted χ) of 138.7(2)° about U1A and 173.1(4)° about U1B.^{63,64} (χ is the angle between the centroid of the mean plane of the carbon atoms composing each aromatic ring of a ligand backbone, two per U-ligand moiety, with the center point of the angle being a point on a plane normal to and centered on a line connecting the centroids of the two previously defined planes.) The extent of folding for the outer ligand appears to be driven by a series of noncovalent π interactions wherein the imine carbon interacts with a phenyl ring (see SI, Figure S82). Two such interactions bend the outer ligand motif towards the inner ligand through interactions between C14A and the phenyl ring composed of C2B-C7B and between C1B and the ring composed of C8A-C13A, with an inter-ring angle of 20.0(3)°. A third interaction between the imine carbon of the outer ligand (C14A) and a ring on the BCF moiety (containing C1-C6) causes the rings to be nearly parallel with an inter-ring angle of 7.9(1)°. Finally, weak electrostatic interactions between the fluorine atoms of the BCF moiety and the outer organic ligand influence the orientation of the phenyl rings about B1 as well (see SI, Figure S79–S81).

	[U3O4]			[U3O4] ⁻	
	XRD	DFT	$\Delta \boldsymbol{R}$	DFT	$\Delta \boldsymbol{R}$
U1A••••U1B (Å)	4.179(1)	4.182	0.003	4.183	0.004
BVS U1A	4.9	-	-	-	-
BVS U1B	3.8	-	-	-	-
U1A–O1A _{phenoxide} (Å)	2.179(4)	2.181	0.002	2.190	0.011
U1A-O2Aphenoxide (Å)	2.163(4)	2.172	0.009	2.139	-0.024
U1A-O _{phenoxide} (avg) (Å)	2.171(4)	2.177	0.006	2.165	-0.006
U1A–O1 _{outer oxo} (Å)	1.994(4)	1.982	-0.012	2.012	0.018
U1A–O2 _{inner oxo} (Å)	1.976(4)	1.981	0.005	1.995	0.019
U1A-O _{oxo} (avg) (Å)	1.985(4)	1.981	-0.004	1.984	-0.001
O1 _{outer} –U1A–O2 _{inner} (deg)	170.9(2)	173.4	2.5	169.7	-1.2
U1B–O1B _{phenoxide} (Å)	2.192(4)	2.177	-0.015	2.204	0.012
U1B–O2 _{inner oxo} (Å)	2.220(4)	2.206	-0.014	2.230	0.010
O2 _{inner} –U1B–O2 _{inner} (deg)	172.2(2)	176.9	4.7	174.1	1.9
N1A–C1A (Å)	1.288(9)	1.315	0.027	1.428	0.140
N2A–C14A (Å)	1.272(9)	1.286	0.014	1.278	0.006
N1B–C1B (Å)	1.297(8)	1.284	-0.013	1.447	0.150
B1–O1 _{outer} (Å)	1.499(7)	1.538	0.039	1.575	0.076

Table 1. Comparison of selected structural parameters of $[U_3O_4]$ from X-ray diffraction analysis and DFT calculations for the quintet spin state. Additionally, computed $[U_3O_4]^-$ at sextet spin state are also presented. ΔR denotes the difference between calculated and observed values.

The U1A–O_{oxo} bond distances and O_{oxo}–U1A–O_{oxo} angles are 1.994(4)/1.976(4) Å and 170.9(2)° for the outer uranium centers, while the inner U1B–O_{oxo} distances are longer at 2.220(4) Å with an O_{oxo}–U1B–O_{oxo} angle (spanning the two-fold rotation axis for the central uranium atom U1B) of 172.2(2)°. The bond metrics for the outer uranium centers are in good agreement with those from literature reports of $[U^VO_2]$ species supported by boranes.^{17,28} The uranium atom U1A and its symmetry-generated analogue U1A' have computed bond valence sum (BVS) values of 4.9, in line with assignment of the formal U(V) oxidation state for the outer U atoms (see Table 1).^{17,28,65} The structural data for the inner uranium center (U1B) result in a computed BVS of 3.8,

in line with assignment of the formal U(IV) oxidation state for this atom. These formal oxidation state assignements are supported by the results of computational studies as well (*vide infra*). The U1B–O_{oxo} distances are also consistent with a formal U(IV) O. S. based on the reasonable agreement to literature examples of U(IV) complexes ligated by anionic oxygens.^{17,65,66} The metrical data obtained from the structure of $[U_3O_4]$ are thus in accord with assignment of this compound as featuring a linear $[O-U^V-O-U^{IV}-O-U^V-O]$ core motif.

Both $[U^{V}O_{2}]$ equivalents in $[U_{3}O_{4}]$ are capped by BCF molecules that are engaged in Lewis acid-base interactions with the outer oxo moieties of the linear trinuclear core motif. These boranes show a virtually tetrahedral geometry about boron (B1) on the basis of the calculated τ_{4} geometry index of 0.93.⁶⁷ The net loss of two oxo moieties from the three total uranium atoms contained within $[U_{3}O_{4}]$ likely occurs via oxo abstraction from reduced uranyl species by BCF. This conclusion is based on the observation that the U–O bonds of $U^{VI}O_{2}$ remained intact according to all chemical and electrochemical tests, except the one case where the powerful combination of CH₂Cl₂ as solvent, Cp*₂Co as reductant, and BCF as electrophile were utilized. The observation of the uniquely effectiveness of this combination of reagents is reminiscent of the finding of generation of [OBPh₃]⁻ by oxo abstraction from uranyl species by BPh₃ in a portion of our prior work.^{28,68} An alternative hypothesis for the chemical mechanism underlying U–O bond cleavage in this system could involve adventitious water present under the reaction conditions; this possibility is worthy of further exploration as well.

Considering the noted oxo-deficient nature of $[U_3O_4]$ that must result in this system from oxo abstraction, we emphasize here that conventional "cation-cation" interactions (CCIs) of the Sullivan type⁵⁷ are not present in this structure. CCIs are customarily considered to form between intact actingl species with 2:1 O_{oxo}:An stoichiometry. However, the structure of $[U_3O_4]$ does enable observation of a unique interaction between U(V) and U(IV) via oxo bridges. While T-shaped CCIs of the type $[U^{V}O_{2}^{+}]$ ••• $[U^{V}O_{2}^{+}]$ and interactions involving formation of diamond cores are often observed in complexes containing reduced uranium, bridging oxo interactions between U(V) with U(IV) are much more uncommon.^{17,57,58,59} In one example from Mazzanti and co-workers, a tetranuclear complex of mixed valent U(V) and U(IV) denoted here as $[(U^{V}O_{2}L)_{2}(U^{IV}L)_{2}]$ was reportedly synthesized in a targeted fashion from the reaction of a U(V) precursor complex with UI₄(Et₂O)₂ and the potassium salt of an organic chelating ligand.⁶⁶ However, unlike the noted prior work that yielded the tetrameric complex, the conditions utilized here were found to be effective for generation of the multimetallic mixed-valent U(V/IV) species denoted [U₃O₄] solely from a uranyl(VI) starting material using multicomponent reactivity. This route utilized delivery of reducing equivalents and exogeneous electrophiles to uranyl(VI) for oxo activation and abstraction. Thus, the structure of [U₃O₄] highlights the potency of the reagents employed in the noted test conditions and provides confirmation that multicomponent reactivity can be productive, even if selectivity remains an unmet challenge.

Computational Studies. To gain additional insight into the properties of $[U_3O_4]$, the structure obtained from single-crystal XRD was optimized. Using density functional theory (DFT), we analyzed the neutral species $[U_3O_4]$ and also explored of a hypothetical form of the complex resulting from one-electron reduction, $[U_3O_4]^-$ (see Computational Details). Based on the coordination of $[U_3O_4]$ discussed above, each of the outer uranium (V) ions have one unpaired electron, while the central uranium (IV) possesses two unpaired electrons on their 5f orbitals. Therefore, highest possible spin state was assumed to be S = 2 for the neutral and S = 5/2 for the anionic structure. The calculated geometric parameters for $[U_3O_4]$ are compared to those from XRD in Table 1, indicating an excellent agreement with an average difference of approximately

0.011 Å for a neutral complex. This confirms that the chosen theoretical approach is suitable for reproducing the properties of the complexes.

The geometry optimization of neutral $[U_3O_4]$ structure reveals that the U1A–O_{oxo} bond lengths are on average 1.981 Å, while the U1B–O2_{oxo} distance is found to be 2.220 Å. Overall, these are consistent with the oxidation state of U1A (formally U^V) and the U1B (formally U^{IV}). ^{1,17,28} Upon reduction by 1e⁻, only minimal changes in the geometry parameters are observed. For instance, $[U_3O_4]^-$ features U–O_{oxo} bonds that are shortened by approximately 0.01–0.04 Å, leading to slightly smaller O_{oxo}–U1A–O_{oxo} angle compared to neutral complex (173.4° vs. 169.7°). This suggests little involvement of metal-centered reduction.

The highest occupied molecular orbitals (HOMO) of $[U_3O_4]$ are composed of hybridized 5f orbitals surrounding mainly U1B, while the lowest unoccupied molecular orbitals (LUMOs) surround all uranium atoms, also featuring orbitals resembling mixture of 5f (Figure 5). In $[U_3O_4]^-$, the HOMO is shifted towards U1A', while the LUMO is shifted towards U1A. Furthermore, the appearance of HOMO-1 and HOMO-2 suggest electron gain in the ligand (see Figures S67-S68). The reduction process further inpacts the HOMO and LUMO energy levels. As calculated the HOMO-LUMO energy gap in the neutral structure is 2.9 eV, while in the reduced species, the gap decreases to 2.1 eV. This change in energy gap levels indicates a decrease the stability of the system, which is in line with the observed non-selective reduction chemistry that resulted from mixing of $U^{VI}O_2$ and reductants.^{14,15,16,17,18,19}



Figure 5. HOMO and LUMO of (a) [U₃O₄] (left) and (b) [U₃O₄]⁻ (right). All hydrogen atoms omitted for clarity. Isosurface value of 0.005.

For a deeper understanding of the bonding, natural bond orbital (NBO) analysis was employed as a tool for interpreting chemical bonding and electron density transfer between atoms.⁶⁹ This analysis involves examining charge transfer using second-order perturbation analysis of the Fock matrix between filled orbitals of one subsystem and vacant orbitals of another to determine the strength of the interaction energies.⁷⁰ As shown in Figure 6 (left structure), the localized orbitals of U1A in [U₃O₄] exhibit $5f_{xz^2}$ character, which contribute to the σ -bonding with O1_{oxo} and O2_{oxo}. Specifically, there is a significant donation from U1A–O1 to the anti-bonding of U1A–O2, with interaction energies of 0.4 eV. According to natural charges derived from NBO analysis (Table 2), the U1B has a higher charge than U1A (+2.282 vs. +2.140 |e|). Additionally, the O2_{oxo} atom carries more negative charge compared to O1_{oxo}, suggesting that the interaction with a highly electrophilic U1B results in weaker bonds between U1B and O2_{oxo} than are often observed in other actinyl compounds.^{15,16,17,18,19} This aligns with the observation that the 5*f*_{yz²} orbitals of U1B show less involvement in the U1B–O2_{oxo} bond, as indicated by the more modest interaction energy of 0.2 eV (see Table S3).



Figure 5. Cut-away views of selected NBOs of $[U_3O_4]$ (left, NBO 683 α) and $[U_3O_4]^-$ (right,

NBO 684 α) associated with U–O bonding in the trinuclear core of the structure. All hydrogen

atoms omitted for clarity. Isosurface value of 0.025.

Atom	[U ₃ O ₄]	[U ₃ O ₄] ⁻	Δ
B1	0.721	0.724	-0.003
Olouter oxo	-0.894	-0.912	0.018
U1A	2.140	2.107	0.033
O2 _{inner oxo}	-0.981	-0.978	-0.003
O1A phenoxide	-0.751	-0.753	0.002
O2A phenoxide	-0.749	-0.753	0.004
N1A	-0.428	-0.646	0.218
U1B	2.282	2.291	-0.009
O1B _{phenoxide}	-0.776	-0.774	-0.002

Table 2. Comparison of selected natural charges for the neutral and anionic forms of [U₃O₄].

Upon the reduction to the $[U_3O_4]^-$ species, the U1A exhibits $5f_{xyz}$ character, with the electron density shifting towards U1A–O1_{oxo} bond (see Figure 6, right structure) making this bond slightly elongated in comparison to in $[U_3O_4]$. Additionally, this bond displays a higher interaction energy of 0.5 eV, contrasting with the 0.3 eV observed in the inner U1A– O2_{oxo} bond. This aligns with an increase in spin density at the U1A atom and decrease at the N1A atoms. Consequently, the N1A atom decreases its natural charges and elongate of the N1A-C1A bond, indicating electron gain in that region (see Table S1-S2). Overall, the computational results suggest that the reactivity of $[U_3O_4]$ can be promoted by ligand-centered reduction, reminiscent of prior findings from Bart and co-workers.⁷¹

Discussion

Uranyl has long been the focus of investigations targeted at reduction and functionalization of its robust actinyl bonds in an effort to accomplish changes in its oxidation state to thereby control its speciation. Studies of this type have employed a wide range of reductants, Lewis acids, and solvents to induce reactivity and have resulted in the characterization of a variety of molecular complexes of functionalized uranyl in oxidation states below +VI. Despite the many examples of molecular products derived from such conditions, disproportionation remains a mode of reactivity that strongly impacts actinide systems and thus plagues analyses of reaction outcomes. In this work, we have evaluated the effectiveness of applying harsh, but commonly used, reagents in the reductive activation of uranyl(VI) housed in an organic ligand under coordinating and non-coordinating solvation environments. (To the best of our knowledge, no other studies have directly compared such conditions on a level playing field as was done here.)

On the one hand, in acetonitrile (a solvent suitable for electrochemical activation strategies), we found that reaction with BCF could be achieved upon reduction of uranium, an outcome bolstered by the redox immunity offered to BCF by formation of its adduct with acetonitrile. Following activation, disproportionation reactivity ensued and thus appears to preclude the isolation of any reduced products. On the other hand, the unattenuated Lewis acidity of BCF in a non-coordinating environment (CH₂Cl₂) enabled reactivity with the very weakly basic oxos of uranyl(VI), providing an electron-deficient species for reduction; these conditions gave rise to a crystalline product of disproportionation intermediate on one occasion. As reactivity of BCF with common electrolyte anions (especially PF_6^-) impedes the use of **BCF** in electrochemical reductive activation pathways in non-specialty electrolytes, we abstained from investigating electrochemical activation under these conditions. However, work with a chemical reductant in the absence of electrolyte could be more confidently carried out; these efforts enabled investigation of the possible modes of spurious cross- and side-reactivity. Lurking in the background of a functionalization scheme employing U(VI), Cp*₂Co, BCF, and acetonitrile or dichloromethane, we found spurious cross-reactivity of between multiple of the components which is undoubtedly at play in related systems. Insights into cross-reactivity highlights the many accessible reactivity pathways across ubiquitous reagents and emphasizes the need to proceed carefully in choices of reagents for these strategies.

The results here, at first glance, may not strike the reader as being associated with an especially promising line of research. Indeed, the concept of developing chemical reactivity schemes that involve simultaneous (or sequential) use of reductants and electrophiles is challenging. However, such chemistry is needed for processing of the actinide elements between oxidation states, especially the important early actinides U, Np, and Pu that display a pronounced bonding preference that favors the actinyl ions. In this context, our observations represent a compendium of insights regarding the possible outcomes from, and strategies for, implementing the state-of-the-art approach to U–O bond functionalization chemistry. Clearly, improvements are needed and this work highlights several of them: electrophiles are needed that are resistant to reduction; solvents are needed that are resistant to redox degradation; reductants are needed that are inexpensive and recyclable; tunable reduction potentials could avoid use of harsh reagents. Approaches to several of these challenges are currently under investigation in our laboratories, including implementation of the concept that ligand design for stabilizing reduced intermediates could afford chemistries that avoid the need for harsh stoichiometric reagents.

Conclusions

This report has described desirable reactivity and undesirable cross-reactivity that can be at play in a system targeted at oxo-functionalization of the uranyl ion, as well as insights into the processes possible when employing common reagents. Significant cross reactivity has been outlined here, highlighting that care should be taken in the design of strategies for actinyl ion processing. On one occasion, the structure of a product of disproportionation reactivity was identified giving insight into the uranium-based reactivity that can be operational under strongly reducing conditions and in the presence of strong Lewis acids. Computational studies predict that the $[U_3O_4]$ species could undergo ligand-centered reduction to a more reactive form, giving insights into the electronic structure of both the observed neutral species and the predicted reduced form. Taken together, this work emphasizes the need for mechanistic insight into oxo-activation strategies of the uranyl ion.

Experimental Section

General Considerations. All manipulations were carried out in dry N₂-filled gloveboxes (Vacuum Atmospheres Co., Hawthorne, CA, USA) unless otherwise noted. All solvents were of commercial grade and dried over activated alumina using a PPT Glass Contour (Nashua, NH) solvent purification system prior to use, and were stored over molecular sieves. All chemicals were obtained from major commercial suppliers and used as received or after extensive drying. CD₃CN and CD₂Cl₂ for NMR studies were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA) and dried over 3 Å molecular sieves or CaH₂, respectively. U^{VI}O₂ was prepared according to literature procedure.²⁸ ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were collected on 400 or 500 MHz Bruker spectrometers at room temperature and referenced to the residual protio-solvent signal in the case of ¹H and ¹³C. ¹⁹F and ³¹P NMR spectra were referenced and reported relative to CCl₃F and H₃PO₄, respectively, as external standards following the recommended scale based on ratios of absolute frequencies (Ξ). Chemical shifts (δ) are reported in units of ppm and coupling constants (J) are reported in Hz. Electronic absorption spectra were collected with an Ocean Optics Flame spectrometer equipped with DH-Mini light source, in a 1 cm path length quartz cuvette. IR spectra were collected under an inert atmosphere in a dry N2-filled gloveboxes (Vacuum Atmospheres Co., Hawthorne, CA, USA). Spectra were collected using a Shimadzu IRSpirit Fourier transform infrared spectrometer equipped with a QATR-S single-reflection attenuated total reflectance ATR accessory and diamond prism plate, as well as accessories for conventional transmission measurements in a cell with KBr windows.

Regarding special safety precautions needed for this work, depleted uranium is a weak alphaparticle emitter; all manipulations of U-containing materials should be carried out in a laboratory equipped with appropriate radiation safety protocols.

X-Ray Crystallography

Crystals were mounted using Paratone oil with MiTeGen loops and placed under a nitrogen stream for data collection. Low temperature data (100 K) X-ray data were collected using 0.5° -wide ω - or φ -scans on a Bruker D8 Venture diffractometer with a Photon III CPAD detector equipped with Helios high-brilliance multilayer mirror optics. X-rays were provided by a IµS 3.0 Microfocus Mo sealed tube running at 1.4 mA and 50 kV (Mo K α = 0.71073 Å). All data manipulations were carried out using the Bruker Apex4 Software Suite.^{72,73} The data set was corrected for absorption using multi-scan method by SADABS.⁷⁴ The Bruker software package SHELXTT was used to solve each structure using intrinsic direct methods phasing.⁷⁵ Final stages of weighted full-matrix least-squares refinement were conducted using F₀² data with SHELXTL in SHELXIe and/or Olex2.^{76,77,78}

Computational Details

Geometry parameters and energies of uranium complexs [U₃O₄] and [U₃O₄]⁻ were carried out in a gas phase by employing the Perdew-Burke-Ernzerhof (PBE)⁷⁹ corrected with D3 semiempirical van der Waals corrections⁸⁰ within a Gaussian plane wave hybrid basis set scheme.⁸¹ The double zeta basis set was used to describe the valence electron with the cutoff of 400 Ry, where the Goedecker–Teter–Hutter (GTH) type pseudopotential⁸² was applied to describe the effect of core electrons. Geometry parameters were done using the CP2K package.⁸³ The optimized coordinates were then used to perform the single point calculations with PBE0⁸⁴ along with segmented all-electron relativisticaly contracted basis sets and the zeroth-order regular approximation with triple zeta quality (SARC-ZORA-TZVP)⁸⁵ for the uranium atoms and ZORAdef2-TZVP⁸⁶ for rest of the atoms together with the SARC/J auxiliary basis set using ORCA ver. 4.1.1.⁸⁷ Finally, the Natural Bond Orbital (NBO) analysis with the NBO7 code⁸⁸ was also carried out. The visualization of molecular orbitals, the NBOs and spin densities are visualized with Chemcraft.⁸⁹

Electrochemistry

Electrochemical experiments were carried out in a nitrogen-filled glove box. Tetra(nbutylammonium) hexafluorophosphate (Sigma-Aldrich; electrochemical grade) (0.1 M in MeCN or DCM) served as the supporting electrolyte for all experiments. Measurements were made with a Gamry Reference 600 Plus Potentiostat/Galvanostat using a standard three-electrode configuration. The working electrode was the basal plane of highly oriented pyrolytic graphite (HOPG) (GraphiteStore.com, Buffalo Grove, IL; surface area: 0.09 cm2), the counter electrode was a platinum wire (Kurt J. Lesker, Jefferson Hills, PA; 99.99%, 0.5 mm diameter), and a silver wire immersed in electrolyte served as a pseudo-reference electrode (CH Instruments). The reference was separated from the working solution by a Vycor frit (Bioanalytical Systems, Inc.). Ferrocene (Sigma Aldrich; twice-sublimed) was added to the electrolyte solution at the conclusion of each experiment (~1 mM) and the midpoint potential of the ferrocenium/ferrocene couple (denoted as Fc^{+/0}) served as an external standard for comparison of the recorded potentials.

Associated Content

Supporting Information. The following files are available free of charge:

NMR spectra, characterization data for the complexes reported here, and detailed information regarding the single-crystal X-ray diffraction analysis (PDF) Cartesian coordinates for the structures from XRD (CIF, XYZ)

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences through the Early Career Research Program (DE-SC0019169). E.R.M. was supported by a U.S. National Science Foundation Research Traineeship (NRT) at the University of Kansas (DGE-1922649). MZM and VAG were supported by ORNL's Laboratory Directed Research and Development (LDRD) program. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DEAC02-05CH11231, as well as resources of the Compute and Data Environment for Science (CADES) at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-000R22725.

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TOC Graphic



TOC Synopsis

A multicomponent model system for reductive activation and functionalization of the uranyl ion, UO_2^{n+} , has been studied. Reactivity and cross-reactivity pathways have been mapped for the system in two solvents (acetonitrile and dichloromethane) and under both chemical and electrochemical conditions. One crystalline and oxo-deficient product featuring a trimetallic uranium core was characterized, highlighting the usefulness of the reductive activation scheme.