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ARTICLE

The Synthesis and Versatile Reducing Power of Low-Valent Uranium Complexes

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This Perspective provides a detailed overview of the chemistry of low-valent (di- and trivalent) uranium. The reactivity of uranium(II) and uranium(III) complexes is discussed both to illustrate the general types of reactions that might be expected and to highlight the many unusual modes of reactivity observed with this element. A particular emphasis is given to redox reactions with uranium(III) species, including reduction of small molecules, multi-electron reductions involving redox-active ligands, and formation of uranium–ligand multiple bonds. In addition, redox-neutral adduct formation with uranium(III) complexes as well as the current state of the young field of uranium(II) redox chemistry are also covered. Synthetic protocols to prepare a wide range of low-valent compounds are presented.

1. Introduction

While the nuclear properties of uranium have brought this element global importance, its unique and diverse chemical reactivity has also fascinated inorganic chemists for many years. The chemistry of uranium continues to develop rapidly as its relatively high natural abundance and long half-life facilitate the safe study of uranium on convenient scales (e.g., multiple grams) in the laboratory with appropriate training, protective equipment, and handling procedures. In fact, uranium is more common than tin in the earth's crust and is present in ppb concentrations (and, therefore, enormous quantities) in the world's oceans.^{1–3} Furthermore, depleted uranium is most commonly used in chemical laboratories, and it consists almost entirely of the isotope ²³⁸U, which is an alpha-emitter with a half-life of 4.47 billion years.⁴

Regarding its chemistry, a combination of properties sets uranium apart from the rest of the periodic table. Compared to transition metals, uranium ions are, generally, quite large.⁵ In terms of its high electrophilicity and oxophilicity, uranium resembles early transition metals and lanthanides, yet the significant involvement of the f-orbitals in bonds with uranium sets it apart from these other elements and leads to different chemical behavior. Furthermore, unlike the lanthanides and most of the heavier actinides, uranium displays extensive redox chemistry with features distinct from that of the other early actinides.

In aqueous solution, the chemistry of uranium is dominated by uranium(VI) in the form of the uranyl ion (UO₂²⁺), though uranium(IV) is also commonly observed.⁶ Aqueous uranium(V)

typically disproportionates into uranium(VI) and uranium(IV), while aqueous uranium(III) is unstable toward oxidation.⁶ In non-aqueous media, a wide range of stable uranium(III) and uranium(V) complexes have been isolated, however, ligands can be incompatible with these oxidation states, as both uranium(III) and uranium(V) may lie outside of accessible redox potentials, may directly oxidize or reduce ligands, or may be susceptible to disproportionation;^{7–15} oxidation of uranium(III) starting materials to uranium(IV) products may therefore occur during a reaction without clear identification of an oxidant.^{16–21}

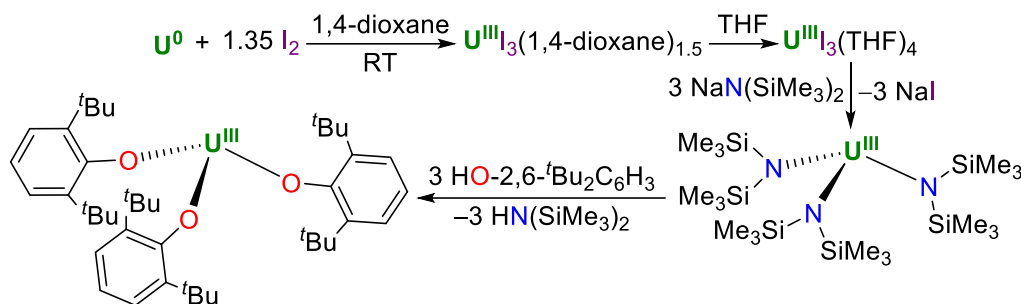
Recently, the redox chemistry of uranium was extended to the formal uranium(II) state with the isolation of [K(2.2.2-cryptand)][C₅H₄SiMe₃]₃U,²² although this oxidation state still remains quite rare for uranium. Molecular solution-phase or solid-state uranium(I) or uranium(0) species have not been reported, but a computational study suggested that a monovalent uranium complex may be synthetically accessible.²³ Additionally, the UFe(CO)₃[–] anion was observed in the gas-phase and assigned as containing uranium(I).²⁴

This short review article is intended to provide a general but non-comprehensive overview of the synthetic routes to and reactivity of molecular low-valent (di- and trivalent) uranium complexes. Some of the topics discussed here have been addressed to various extents in other review and perspective articles.^{25–47}

2. Low-Valent Starting Materials

The development of convenient syntheses of low-valent uranium starting materials, particularly uranium(III) halides, has contributed greatly to the rapid progress in the chemistry of this element.⁴⁶ In many cases, these uranium(III) precursors have provided more direct synthetic access to target complexes by avoiding routes involving preparation and subsequent reduction of uranium(IV) precursors. Additionally, highly reducing ligand classes may spontaneously reduce uranium(IV)

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Scheme 1 Synthetic route to uranium(III) aryloxy species starting from uranium metal turnings.^{48–50}

species and lead to undesired byproducts, necessitating the installment of these ligands using uranium(III) starting materials.^{9,51} Among uranium(III) halides, the iodide and its Lewis base adducts have seen the most widespread use and can be prepared directly from uranium metal turnings.

A crucial advance was the synthesis of $U_3(THF)_4$ from amalgamated uranium and iodine.^{48,52} More recently, the room temperature, mercury-free reaction of U^0 with I_2 in 1,4-dioxane to form $U_3(1,4\text{-dioxane})_{1.5}$ in nearly quantitative yield represented further progress, as $U_3(1,4\text{-dioxane})_{1.5}$ is more thermally stable than $U_3(THF)_4$, can often replace $U_3(THF)_4$ in syntheses, and can be converted easily to $U_3(THF)_4$ by dissolution in THF.⁴⁹ Additionally, it is possible to prepare solvent-free U_3 on large scales by reaction of U^0 and I_2 in diethyl ether at room temperature with sonication,⁵³ a method that eliminated the need for the use of mercury or very high temperatures.^{54–56}

In many cases, use of U_3 and its solvates has replaced earlier protocols involving UCl_3 .⁴⁸ However, a variety of reactions have used UCl_3 generated *in situ*, for example by reduction of UCl_4 by sodium naphthalenide in THF.⁵⁷ Early attempts to isolate UCl_3 solvates (e.g. $UCl_3(THF)_x$) gave ambiguous products or potential impurities,⁵⁸ although well-defined uranium(III) chlorides were recently reported.⁵⁹ The uranium(III) starting materials UH_3 ,^{60,61} $UBr_3(\text{solvent})_x$,^{48,61} $U(OTf)_3(\text{solvent})_x$,^{62,63} and $U(BH_4)_3(\text{solvent})_x$ ^{64,65} have also been employed in a range of transformations.

Halide starting materials provide access to low-valent complexes principally via salt metathesis reactions, so another critical step forward was the synthesis of the trivalent uranium amide $U[N(\text{SiMe}_3)_2]_3$,⁵⁷ which can be isolated by reaction of three equiv of $\text{NaN}(\text{SiMe}_3)_2$ with either $U_3(THF)_4$ or $UCl_3(THF)_x$.⁴⁸ While the properties and reactivity of $U[N(\text{SiMe}_3)_2]_3$ have been studied extensively, its application in protonolysis reactions is particularly important for providing access to new ligand systems for uranium(III) such as aryloxides (Scheme 1),^{45,50,66} thiolates,⁶⁷ and macrocycles.^{68,69} Other homoleptic uranium(III) amide,⁷⁰ alkyl,⁷¹ and aryl⁷² complexes have been prepared directly by salt metathesis from uranium(III) iodide or aryloxy starting materials, but the protonolysis chemistry of these species has not been studied in as much detail as for $U[N(\text{SiMe}_3)_2]_3$.

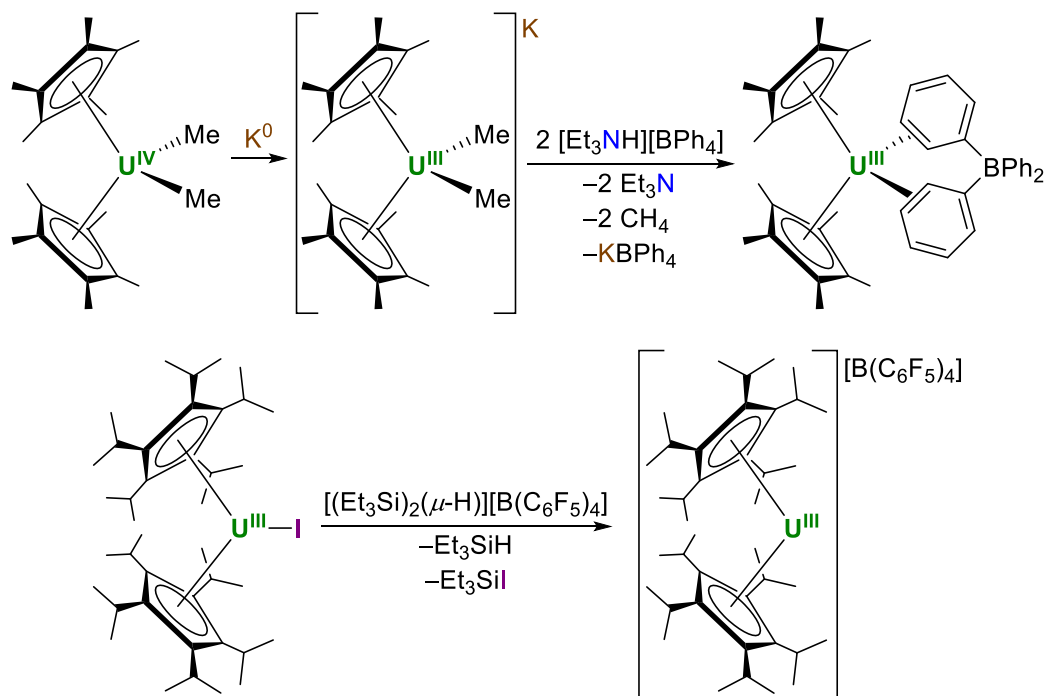
Carbocyclic ligands, particularly cyclopentadienyl ligands and their substituents, have played a central role in advancing

the chemistry of uranium,^{41,47,73,74} and such is especially the case for trivalent uranium. Tris(Cp^R) (Cp^R = substituted cyclopentadienyl) uranium(III) complexes and their solvates can often be prepared by salt metathesis directly from uranium(III) halides,^{51,54,75–79} although one-electron reduction with loss of halide from corresponding (Cp^R)₃ UX species (X = halide) is another common approach.^{19,80–83} Protonolysis,⁸⁴ hydride insertion into tetramethylfulvene,⁸⁵ salt metathesis using uranium(III) bis(Cp^R) species^{86,87} and photolysis of (Cp^R)₃ $U(\text{alkyl})$ and (Cp^R)₃ $U(\text{H})$ compounds^{81,88} have provided additional routes to (Cp^R)₃ U complexes.

Bis(Cp^R) uranium(III) species (bent metallocenes)[†] have proven particularly useful for synthetic applications due to the presence of multiple open coordination sites. Complexes of the form (Cp^R)₂ UX (X = halide) are most commonly isolated via one-electron reduction of (Cp^R)₂ UX_2 species^{89,90} or by reaction of two equiv of $M(\text{Cp}^R)$ (M = alkali metal) with a uranium(III) halide.^{9,49,91–95} Dimerization^{89,90} or ate complex formation^{9,96,97} are often observed in these species with varying effects on resultant reactivity.

Several uranium(III) metallocenium complexes have been isolated, including $[\text{Cp}^*_2\text{U}(\text{THF})_2][\text{BPh}_4]$, which was prepared by reaction of $\text{Cp}^*_2\text{U}[\text{N}(\text{SiMe}_3)_2]$ with $[\text{NH}_4][\text{BPh}_4]$ in THF.⁹⁸ Related salts without coordinated solvent, $[(\text{C}_5\text{Me}_4\text{R})_2\text{U}][(\mu\text{-Ph})_2\text{BPh}_2]$ (R = H,⁹⁹ Me,⁸⁷ SiMe_3 ⁸⁶), can be isolated by combined salt metathesis and protonolysis reactions between $(\text{C}_5\text{Me}_4\text{R})_2\text{UMe}_2\text{K}$ and two equiv of $[\text{Et}_3\text{NH}][\text{BPh}_4]$ (Scheme 2, top). Quite recently, base-free uranium(III) metallocenium salts $[(\text{C}_5(\text{Pr})_4\text{R})_2\text{U}][\text{B}(\text{C}_6\text{F}_5)_4]$ (R = H,⁹ ^{*i*}Pr⁹³) were isolated via halide abstraction with the silylium species $[(\text{Et}_3\text{Si})_2(\mu\text{-H})][\text{B}(\text{C}_6\text{F}_5)_4]$ ¹⁰⁰ (Scheme 2, bottom).

Due to the unstable nature typical of divalent uranium complexes, as well as a lack of simple uranium(II) precursors, isolation of uranium(II) complexes has been reported exclusively via reduction of uranium(III) species already incorporating supporting ligands. Anions of the form $[(\text{Cp}^R)_3\text{U}]^-$ (for Cp^R = $\text{Me}_3\text{SiC}_5\text{H}_4$, 1,3-(Me_3Si)₂ C_5H_3 , or $\text{C}_5\text{Me}_4\text{H}$), $[(\text{Ad},\text{MeArO})_3\text{MesU}]^-$ ($(\text{R},\text{R}'\text{ArOH})_3\text{Mes}$ = 1,3,5-trimethyl-2,4,6-tris((2-hydroxy-3-R-5-R'-phenyl)methyl)benzene, Ad = 1-adamantyl), and $[U\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ were prepared by reduction of the corresponding (Cp^R)₃ U species, $(\text{Ad},\text{MeArO})_3\text{MesU}$, or $U[\text{N}(\text{SiMe}_3)_2]_3$, respectively, with alkali metals, often (but not always)¹⁰⁷ in the presence of an appropriate chelating agent for the alkali metal cation.^{22,108–110} Neutral uranium(II) complexes



Scheme 2 Synthetic routes to uranium(III) metallocenium species with a weakly-coordinating $[\text{BPh}_4]^-$ anion (top) or an outer-sphere $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion (bottom).^{87,93}

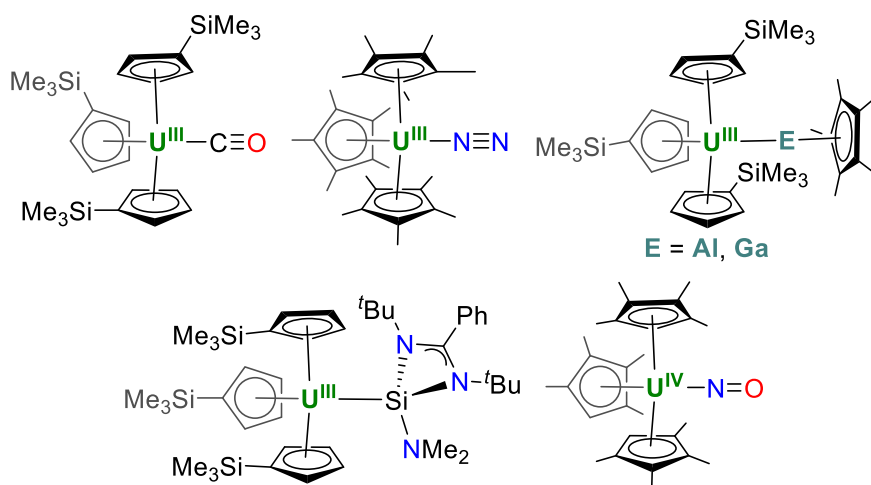


Chart 1 Selected examples of adducts formed with $(\text{Cp}^*)_3\text{U}$ fragments.^{101–106}

$\text{U}(\text{NHA}r^{\text{iPr}_6})_2$ ($\text{Ar}^{\text{iPr}_6} = 2,6\text{-}(2,4,6\text{-iPr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$) and $(\text{C}_5(\text{iPr})_5)_2\text{U}$ were also isolated via reduction of uranium(III) iodide precursors $\text{IU}(\text{NHA}r^{\text{iPr}_6})_2$ and $(\text{C}_5(\text{iPr})_5)_2\text{UI}$ with KC_8 .^{111,112}

3. Reactivity of Low-Valent Uranium

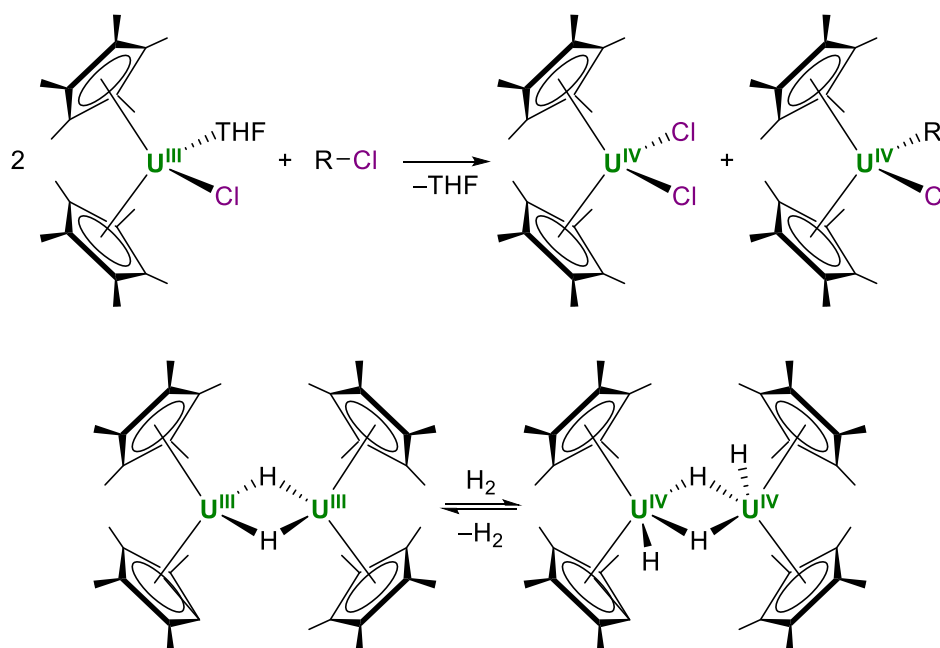
3.1. Redox-Neutral Adduct Formation

Coordinationally unsaturated complexes of uranium(III) have been observed to form adducts with a range of neutral molecules, some rarely or never observed for any other f-block element. These studies have provided important insight into the nature of bonding in uranium. Adducts of carbon monoxide and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$,¹⁰¹ $(\text{C}_5\text{Me}_4\text{H})_3\text{U}$,¹¹³ $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$,⁸³ $(1,3\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3)_3\text{U}$,⁸³ and Cp^*_3U ¹¹⁴ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) were observed,

with ν_{CO} values of 1969, 1880, 1960, 1988, and 1922 cm^{-1} , respectively, in the solid-state or hydrocarbon solution. Computational studies suggest the decrease in ν_{CO} relative to free CO (2143 cm^{-1}) is due to back-donation from $\text{Cp}^{\text{R}}\text{-U}$ bonding orbitals to the π^* orbitals of CO.¹¹⁵ Back-bonding from uranium 5f to isocyanide π^* orbitals has also been studied in adducts of $(\text{Cp}^{\text{R}})_3\text{U}$ species.^{83,84}

Tris(Cp^{R}) uranium(III) fragments have proven capable of forming other uncommon motifs, including an end-on dinitrogen adduct,¹⁰² unsupported U–Al and U–Ga bonds^{103,104} and uranium-silylenes (Chart 1).¹⁰⁵ Side-on dinitrogen binding has also been observed in the diuranium(III) species $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^t\text{BuMe}_2)_3\}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$.¹¹⁹

Since the first report in 1971,¹²⁰ several unsupported η^6 -



Scheme 3 Selected examples of bimetallic oxidative addition with uranium(III) complexes. *Top*: reaction of Cp*₂U(III)(Cl)(THF) yields uranium(IV) products Cp*₂UCl₂ and Cp*U(R)(Cl) (R = alkyl); *bottom*: reversible addition of H₂ to [Cp*₂U(III)(μ-H)]₂ to form [Cp*₂U(IV)(μ-H)]₂.^{116–118}

arene complexes of uranium(III) have been characterized.^{121–124} Bridging η^6 -arene interactions were also observed in the dimeric solid-state structure of [U(O-2,6-Pr₂C₆H₃)₂].⁵⁰ More recently, the chemistry of tris(aryloxo) ligands with tethered arene moieties has been developed;^{109,125–129} δ symmetry back-bonding from uranium 5f orbitals to arene π^* orbitals were calculated in the case of trivalent uranium and furthermore are implicated as a key factor in stabilizing a divalent uranium center^{109,125} and in electrocatalytic water reduction.¹²⁸ Another tethered arene ligand was used with uranium(III) to isolate an unsupported U–Fe bond, but significant δ back-bonding was not found in computational studies of this system.¹³⁰

Finally, crystallographic evidence for η^2 -C,H coordination of an alkane to the uranium(III) tris(aryloxo) complex ((^tBu,^tBuArO)₃tacn)U ((^{R,R'}ArOH)₃tacn = 1,4,7-tris((2-hydroxy-3-R-5-R'-phenyl)methyl)-1,4,7-triazacyclononane) was reported in 2003;¹³¹ a more recent study attributed alkane binding to London dispersion interactions with the ((^tBu,^tBuArO)₃tacn)³⁻ ligand.¹³²

3.2. Redox Reactions

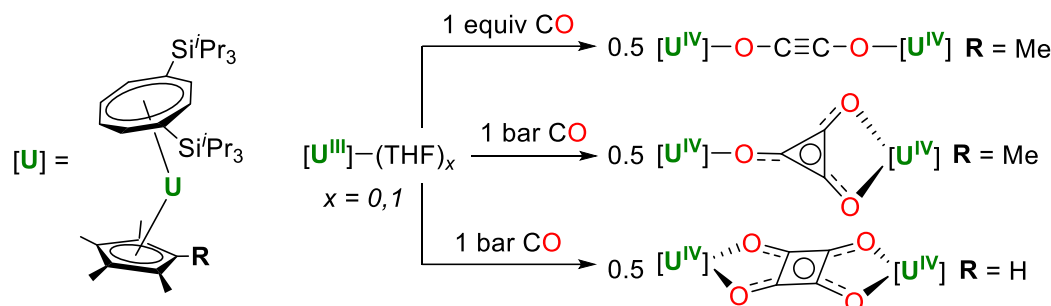
3.2.1. General Comments. The redox chemistry of uranium is characterized by a propensity to undergo one-electron steps.^{26,43} Despite this general reactivity pattern, various strategies—including application of redox-active ligands, use of multinuclear complexes, and careful choice of multi-electron oxidants—have been devised to engender multi-electron reactivity with uranium.

An illustrative example of one-electron steps in uranium chemistry is the reaction between the uranium(III) complex Cp*₂U(III)(Cl)(THF) and alkyl halides (RCl), which leads to uranium(IV) products Cp*₂UCl₂ and Cp*U(IV)(R)(Cl) (Scheme 3, top).^{116,117} In this type of reaction, the overall two-electron

process—a bimetallic oxidative addition—occurs with one-electron oxidation and one new bond formed at two metal centers (per alkyl halide molecule) instead of the type of oxidative addition in which one metal center is oxidized by two electrons and forms two new bonds.⁴³ Similarly, the solution-state equilibrium between diuranium(IV) species [Cp*₂U(IV)(μ-H)]₂ and diuranium(III) complex [Cp*₂U(III)(μ-H)]₂ occurs via bimetallic reductive elimination and oxidative addition reactions (Scheme 3, bottom).¹¹⁸

Recently, and in contrast to the one-electron step paradigm for uranium(III) reactivity, single-metal two-electron oxidative addition across the uranium(III/IV) redox couple was reported as a step in the mechanism of two different reactions. Oxidative addition of PhNNPh to U(Ts^{Xy}) (Ts^{Xy} = HC(SiMe₂NAr)₃, Ar = 3,5-Me₂C₆H₃) was proposed as a step in the overall bimetallic four-electron reduction of azobenzene to yield {U(Ts^{Xy})(μ-NPh)}₂,¹³³ and oxidative addition of H₂O to ((^{Ad,Me}ArO)₃Mes)U was reported as a step in the mechanism for water reduction.¹²⁸

While the potential of the uranium(III/IV) redox couple can shift considerably based on the ligands coordinated to the uranium center,^{9,13} uranium(III) species are generally quite reducing and can therefore be oxidized to uranium(IV) even with mild oxidants. Through one-electron oxidation reactions, uranium(III) species have found use as precursors for uranium(IV) complexes with a wide range of ligand types.^{19,134} Some uranium(III) species have even been observed to cleave aryl C–F bonds to form uranium(IV) fluorides;^{135–137} oxidation of uranium(III) species to uranium(IV) fluorides has been performed using other reagents, including AgF,¹³⁸ CuF₂,^{139–141} HgF₂,¹⁴² PF₃,¹⁴³ and (Ph₃P)AuCF₃.¹⁴¹ Furthermore, the risk of over-oxidation to uranium(V) is usually low, since the uranium(IV/V) redox couple tends to lie at much higher potentials.^{13,139} However, uranium(V) dihalides of the form



Scheme 4 Synthesis of diuranium(IV) ynediolate (top), deltate (middle), and squarate (bottom) complexes from uranium(III) mixed sandwich compounds.^{144–146}

$Ux_2[N(SiMe_3)_2]_3$ were prepared directly from $U[N(SiMe_3)_2]_3$ using AgF , $[Ph_3C][PF_6]$, or $[TEMPO][BF_4]$ (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) for $X = F$; $CuCl_2$ or WCl_6 for $X = Cl$; or $CuBr_2$ for $X = Br$.¹⁴⁷

3.2.2. Small Molecules. The potent reducing ability of uranium(III) species has been exploited extensively for the reductive binding of small molecules. The uranium(III) pentalene complex $Cp^*U(\eta^8-1,4-(Si^iPr_3)_2C_8H_6)U$ as well as the uranium(III) tris(aryloxides) $U(O-2,6-tBu_2C_6H_3)_3$ and $U(O-2,4,6-tBu_3C_6H_3)_3$ reversibly bound dinitrogen to form species assigned as diuranium(IV) bridged by a side-on N_2^{2-} unit.^{55,66} Interestingly, heating was necessary to eliminate N_2 from the latter aryloxide, but the other two systems favored the non-adduct species at ambient conditions under 1 atm of N_2 .^{55,66} Stirring the trivalent complexes $U[N(tBu)(3,5-Me_2C_6H_3)]_3(THF)$ and $Mo[N(tBu)(Ph)]_3$ in a nitrogen atmosphere led to formation of $[(tBu)(3,5-Me_2C_6H_3)N]_3U(\mu-\eta^1:\eta^1-N_2)Mo[N(tBu)(Ph)]_3$ in which both metal centers were assigned as tetravalent with a bridging linear N_2^{2-} ligand.¹⁸ As no reactivity was observed between the uranium(III) starting material and dinitrogen, this reaction likely occurred via reaction of the uranium(III) complex with the intermediate $(\eta^1-N_2)Mo[N(tBu)(Ph)]_3$.¹⁸ Recently, nitride-bridged diuranium(III) siloxide species were found to bind and reduce N_2 to form diuranium(V) complexes with N_2^{4-} fragments that could subsequently be functionalized by several means.^{148,149} Direct cleavage of dinitrogen was achieved by reduction of the uranium(III) complex $[K(DME)][(Et_8-calix[4]tetrapyrrole)U(DME)]$ with potassium naphthalenide under an N_2 atmosphere, resulting in a mixed-valent bis(μ -nitrido) diuranium(IV/V) complex.¹⁵⁰

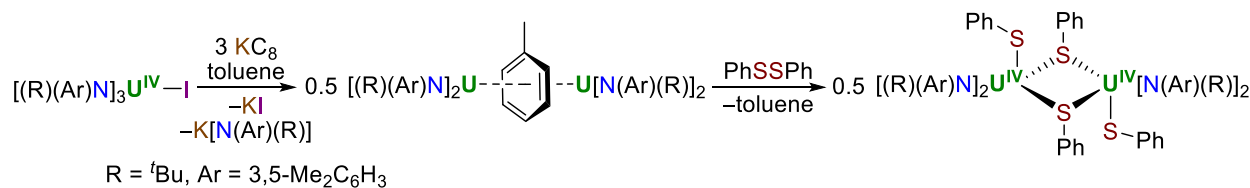
As observed with N_2 , uranium(III) complexes with minor differences in supporting ligands have exhibited large differences in reactivity toward CO_2 . Reductive binding of CO_2 by $((^{Ad,tBu}ArO)_3tacn)U$ was reported to form a complex assigned as containing a uranium(IV) center exhibiting η^1-O coordination to the $CO_2^{\cdot-}$ radical anion.¹⁵¹ In contrast, reaction of $((^{tBu,tBu}ArO)_3tacn)U$ with CO_2 led to two-electron reduction of CO_2 with C–O bond cleavage to form the μ -oxo diuranium(IV) complex with accompanying evolution of CO. Similarly, reactions of $(Me_3SiC_5H_4)_3U$ with CO_2 or N_2O were both found to yield the corresponding μ -oxo diuranium(IV) species.¹⁵² Reductive disproportionation of CO_2 to form CO_3^{2-} and CO has been observed with more than one uranium(III) system,^{153,154} although multiple different product outcomes are possible

between uranium(III) species and CO_2 .^{44,155} Similarly, a variety of reactivity modes have been observed between CS_2 and uranium(III) species, including reduction to form bridging CS_2^{2-} species, reductive dimerization, and reductive disproportionation.^{75,154,156–158}

A diverse range of reduction products have also been observed between uranium(III) complexes and CO.²⁷ The complex $((^{tBu,tBu}ArO)_3tacn)U$ reacted with CO to form a species assigned as mixed-valent diuranium(III/IV) with a bridging singly reduced $\mu-\eta^1:\eta^1-CO^{\cdot-}$ ligand.¹⁵⁹ Reductive coupling to form C–C bonds has been observed with multiple systems. Exposure of $U[N(SiMe_3)_2]_3$, $U(O-2,6-tBu_2C_6H_3)_3$, $U(O-2,4,6-tBu_3C_6H_3)_3$, or $U[N(CH_2CH_2NSiMe_2^tBu)_3]$ to CO led to formation of diuranium(IV) species bridged by the linear ynediolate dianion, $[OCCO]^{2-}$.^{66,160,161} The stoichiometric reaction of CO with mixed sandwich complex $Cp^*U(\eta^8-1,4-(Si^iPr_3)_2C_8H_6)(THF)$ yielded the ynediolate-bridged diuranium(IV) species (Scheme 4, top),¹⁴⁴ while use of excess CO yielded a diuranium(IV) species bridged by the deltate dianion, $C_3O_3^{2-}$ (Scheme 4, middle).¹⁴⁵ Remarkably, reaction of the extremely similar starting material $(C_5Me_4H)U(\eta^8-1,4-(Si^iPr_3)_2C_8H_6)(THF)$ with excess CO led to a diuranium(IV) complex bridged by the squarate dianion, $C_4O_4^{2-}$ (Scheme 4, bottom).¹⁴⁶ Further work has been carried out to correlate steric properties of related uranium(III) mixed sandwich complexes with reactivity outcomes toward CO and CO_2 .^{162,163}

The chemistry of this uranium(III) mixed sandwich system with CO has been extended by using combinations of gases to synthesize other fragments. Treatment of $Cp^*U(\eta^8-1,4-(Si^iPr_3)_2C_8H_6)$ with one equiv of CO followed by two equiv of H_2 led to isolation of a uranium(IV) methoxide complex.¹⁶⁴ Notably, addition of one equiv of CO to diuranium(IV) dihydride $K_2\{[U(OSi(O^tBu)_3)_2(\mu-O)(\mu-H)]_2\}$, formed by addition of H_2 to the corresponding diuranium(III) precursor, produced a complex with a bridging oxomethylene dianion $[CH_2O^{2-}]$ that yielded methoxide upon further reaction with H_2 .¹⁶⁵ Furthermore, treatment of $Cp^*U(\eta^8-1,4-(Si^iPr_3)_2C_8H_6)$ with mixtures of NO and CO has been found to lead to concurrent formation of bridging cyanate and oxo complexes in a process proposed to occur via CO attack on a bridging, side-on, doubly reduced NO molecule.^{166,167}

Beyond this reactivity, reports of reactions of NO with trivalent uranium are limited. The nature of the bonding in the NO adduct of Cp_3U was predicted in 1989.¹⁶⁹ Reaction of



Scheme 5 Formation of a diuranium inverse sandwich complex by reduction of a uranium(IV) precursor in the presence of arene solvent and subsequent reactivity as a four-electron reductant.¹⁶⁸

(C₅Me₄H)₃U with one equiv of NO led to isolation of (C₅Me₄H)₃UNO (Chart 1), formally containing singly reduced NO⁻ coordinated in a linear fashion to a uranium(IV) center, as was predicted for Cp₃UNO.^{106,169} Finally, reaction of uranium tris(aryloxide) U(O-2,6-Ad₂-4-MeC₆H₂)₃ with excess NO led to formation of the uranium(V) oxo complex U(O)(O-2,6-Ad₂-4-MeC₆H₂)₃ and N₂O; this reductive disproportionation process was proposed to occur via a uranium(IV) η^1 -ONNO⁻ intermediate.¹⁷⁰ The same oxo complex was isolated by reaction of U(O-2,6-Ad₂-4-MeC₆H₂)₃ with N₂O.¹⁷⁰

3.2.3. Redox-Active Ligands. A variety of low-valent uranium precursors, often generated *in situ*, have been found to bind and reduce arenes to form diuranium inverse sandwich complexes.^{14–16,28,154,168,171–177} Reaction of [(^tBu)(3,5-Me₂C₆H₃)N]₃UI with three equiv of KC₈ in toluene yielded the toluene-bridged species {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}₂(μ - η^6 : η^6 -C₆H₅Me) (Scheme 5).¹⁶⁸ While the formal oxidation state of uranium in this complex was initially ambiguous, calculations indicated four uranium-centered electrons of 6d and 5f character involved in δ back-bonding,¹⁶⁸ in fact, δ -bonding is a common and important stabilizing feature of this class of complexes.²⁸ Furthermore, reaction of {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}₂(μ - η^6 : η^6 -C₆H₅Me) with two equiv of PhSSPh or one equiv of PhNNPh yielded uranium(IV) species {[(^tBu)(3,5-Me₂C₆H₃)N]₂U(SPh)}₂(μ -SPh)₂ and {[(^tBu)(3,5-Me₂C₆H₃)N]₂U(μ -NPh)}₂, demonstrating that the inverse sandwich complex could act as a four-electron reductant.¹⁶⁸

While this four-electron reactivity might formally be described as {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}₂(μ - η^6 : η^6 -C₆H₅Me) acting as a divalent uranium synthon, all of the electrons for such transformations need not be localized on uranium. Studies on a structurally similar species (Cp*₂U)₂(μ - η^6 : η^6 -C₆H₆), prepared either by reduction of Cp*₃U or [Cp*₂U][(μ -Ph)₂BPh₂] with potassium in benzene, suggested that these complexes were best described as diuranium(III) with arene dianions based on evidence from structure, reactivity, and quantum chemical calculations.¹⁷⁴ Multiple other examples of arene-bridged diuranium complexes have been assigned as diuranium(III) with a dianionic arene,^{14,16,172,173,178} but exceptions include mixed-valent species^{15,177} and uranium(IV) or uranium(V) species with tetraanionic toluene bridges.^{154,171,175,179}

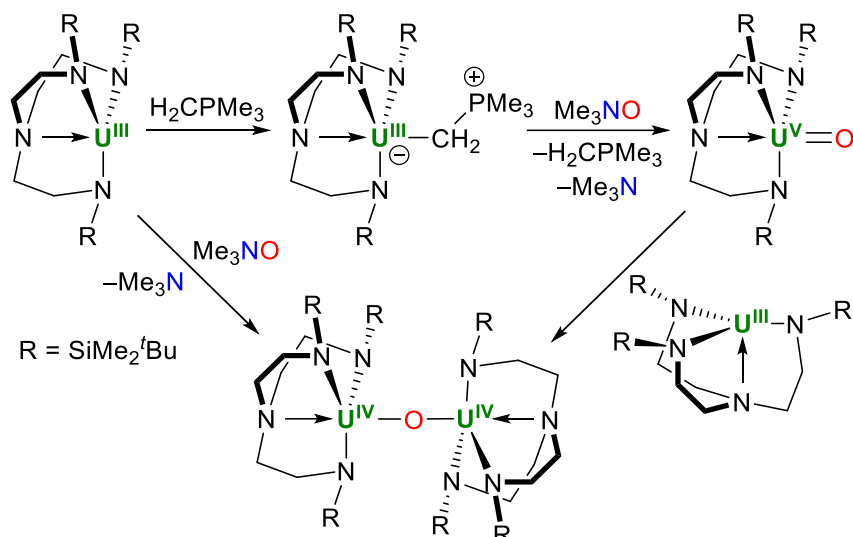
Reaction of (Cp*₂U)₂(μ - η^6 : η^6 -C₆H₆) with three equiv of C₈H₈ revealed its ability to act as a six-electron reductant, forming the uranium(IV) complex [(Cp*)(C₈H₈)U]₂(μ - η^3 : η^3 -C₈H₈) (containing three C₈H₈²⁻ ligands) along with neutral (C₅Me₅)₂ and free benzene.¹⁷⁴ Here, four of the reducing electrons are derived from the uranium(III/IV) and C₆H₆²⁻/C₆H₆ processes, while the other two electrons come from the C₅Me₅⁻/C₅Me₅ process.¹⁷⁴

This use of electrons derived from the C₅Me₅⁻/C₅Me₅ process for reductive reactivity at the uranium center is an example of a sterically induced reduction, which has been studied extensively in both lanthanides and actinides.^{25,29,30,142,174,180–183}

Beyond reduced arenes and C₅Me₅⁻, numerous other redox-active ligands have been used with uranium(III) to prepare complexes that can function as multi-electron reductants. Binding and reduction of 2,2'-bipyridine (bipy), 2,2':6'2''-terpyridine (terpy), or benzophenone has yielded complexes containing the bipy^{•-},^{94,184–187} terpy^{•-},^{92,187} or ketyl (OCPh₂^{•-})¹⁸⁸ radical anions coordinated to uranium(III). By concurrent oxidation to uranium(IV) and formation of the corresponding neutral molecule (i.e. bipy or benzophenone), these species have been observed to act as two-electron reductants,^{184,189,190} sometimes with accompanying radical coupling to the bipy ligand.^{94,186} Similar multi-electron reductive behavior has been observed in uranium(III) benzyl,^{189,191–195} hydride,^{196,197} and tetraphenylborate species.^{198,199} In benzyl and hydride complexes, one reducing equivalent may be provided by oxidative coupling to form half an equivalent (per benzyl or hydride ligand) of bibenzyl or dihydrogen, respectively. In the case of tetraphenylborate ligands, one reducing equivalent is afforded by its conversion to triphenylborane and a phenyl radical.²⁰⁰

3.2.4. Formation of Uranium–Ligand Multiple Bonds. Trivalent uranium complexes have played a major role in the synthesis of species containing uranium–ligand multiple bonds, commonly by acting as two-electron reductants toward group transfer reagents that directly form the corresponding uranium(V) multiply-bonded product.^{31–34} Uranium(V) terminal oxo,^{201–209} terminal imido,^{201,210–215} and alkali metal-capped terminal nitride^{202,215–217} complexes have all been isolated via reactions of uranium(III) precursors with oxo-transfer reagents, organic azides, and alkali metal azide salts, respectively. Uranium(V) nitridoborates have been formed both by reaction of an azidoborate salt with a uranium(III) precursor and by reaction of a borane with a uranium(III) azide species.^{218,219}

The two electrons for these transformations may derive from the uranium(III/IV) couple, obviating the need for redox-active ligands to perform such two-electron processes. Nevertheless, careful choice of supporting ligand is critical to synthetic efforts in this area. One of the main challenges in attempting to isolate uranium(V) complexes with terminal multiply-bonded groups is avoiding the formation of uranium(IV) species, which commonly contain a bridging ligand between two or more uranium centers. Multinuclear uranium(IV) complexes with bridging oxo,^{159,201,203} sulfide,^{220–223} selenide,^{220–223} telluride,^{220,223} imido,^{168,224} and nitride^{225–229}



Scheme 6 Reaction of a uranium(III) ylide adduct with trimethylamine *N*-oxide yielded the corresponding uranium(V) oxo complex (top); use of the uranium(III) adduct-free complex in similar conditions produced the diuranium(IV) μ -oxo species (bottom left), which was also formed by the comproportionation reaction between the uranium(V) oxo and uranium(III) adduct-free complexes (bottom right).²⁰¹

ligands have all been isolated from reactions of uranium(III) complexes with chalcogen atom transfer reagents, organic azides or azobenzene, or inorganic azides, respectively.

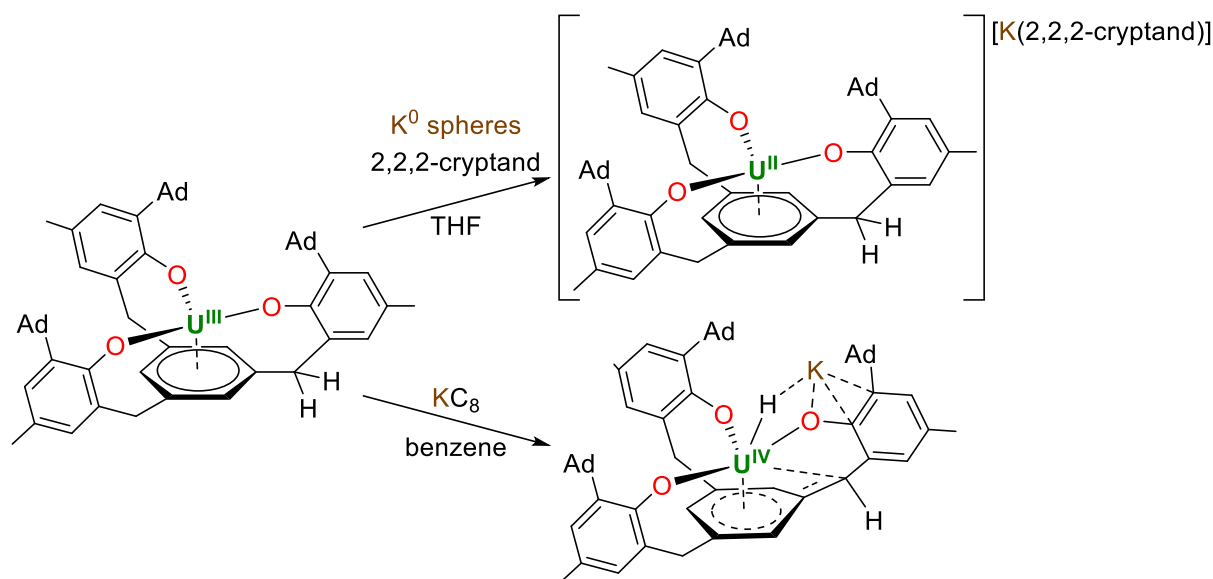
In general, the formation of mono- or multinuclear uranium(IV) products from reactions of group transfer reagents with uranium(III) precursors may occur via comproportionation reactions in which a uranium(V) complex with a terminal ligand reacts with the corresponding uranium(III) starting material to form uranium(IV) species,^{201,230–232} although mechanisms involving only single-electron steps may also be possible in certain cases.^{220,233} Therefore, the isolation of uranium(V) complexes directly from uranium(III) precursors requires not only that the ligand system be stable to both oxidation states, but also that reaction of the uranium(III) starting material be faster with the group transfer reagent than with the uranium(V) product. To address the latter point, strategies include using bulky ligands such as Tren-derivatives (Tren = triamidoamine), which contain well-defined, sterically protected binding pockets when coordinated to uranium.⁴⁰ An additional strategy is to use a ligand such as an ylide to block the open coordination site on the uranium(III) material, slowing reaction with the uranium(V) product while allowing for reaction with the group transfer reagent (Scheme 6).^{201,230}

A variety of strategies have been developed to prepare uranium(IV) species with terminal metal–ligand multiple bonds from uranium(III) starting materials. Addition of $\text{K}(\text{E})\text{PPh}_3$ ($\text{E} = \text{O}, \text{S}$) to $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$, followed by addition of 18-crown-6, led to isolation of uranium(IV) terminal chalcogenide complexes $[\text{K}(18\text{-crown-6})][\text{U}(\text{E})\{\text{N}(\text{SiMe}_3)_2\}_3]$ by mechanisms involving reductive cleavage (for KOCPh_3) or radical cleavage (for KSCPh_3) of the trityl group.²³² Addition of elemental sulfur, selenium, or tellurium to uranium(III) ylide adduct $\text{U}(\text{CH}_2\text{PPh}_3)[\text{N}(\text{SiMe}_3)_2]_3$ yielded uranium(IV) products $[\text{Ph}_3\text{PCH}_3][\text{U}(\text{E})\{\text{N}(\text{SiMe}_3)_2\}_3]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$).²³⁰ This same uranium(III) ylide adduct was found to convert to a uranium(IV) carbene complex $\text{U}(\text{CHPPH}_3)[\text{N}(\text{SiMe}_3)_2]_3$ likely via intermolecular hydrogen atom

transfer between ylide ligands.²³⁴ Recently, oxidative deprotonation of a uranium(III) anilido complex was demonstrated as a method to form uranium(IV) imidos.²³⁵ Reaction of oxo-transfer reagents or organic azides with uranium(III) complexes containing benzyl or singly reduced bipy ligands has also led to uranium(IV) oxos and imidos (see section 3.2.3).^{184,190,191,194,195}

Uranium(III) precursors have even provided direct access to complexes containing more than one imido group. Redox-active ligands have enabled mono- or dinuclear uranium(III) complexes to act as four- or eight-electron reductants, respectively, to form uranium(VI) *cis*-bis(imido) species by reactions with azobenzene or organic azides.^{178,198} Furthermore, an external reducing agent such as sodium amalgam, combined with a uranium(III) species, can facilitate similar four-electron processes to form uranium(VI) *cis*-bis(imidos).⁹⁶ In fact, solvates of $\text{U}(\text{I}_3)$ can be used to form imido species directly by addition of organic azides and external reductants.^{236,237} This method provided access to the uranium(VI) tris(imido) complex $\text{U}(\text{NDipp})_3(\text{THF})_3$ (Dipp = 2,6-(*i*Pr)₂C₆H₃) via reaction of $\text{U}(\text{I}_3)(\text{THF})_4$ with three equiv of Dipp-N₃ and three equiv of $\text{K}(\text{C}_8)$, an overall six-electron process.²³⁶ A very different method, namely the one-pot reaction of $\text{U}(\text{I}_3)(\text{THF})_4$ with two equiv of a primary amine, 1.5 equiv of iodine, and four equiv of an amine base yielded uranium(VI) *trans*-bis(imido) species $\text{U}(\text{N}^t\text{Bu})_2(\text{THF})_2$ and $\text{U}(\text{NAr})_2(\text{THF})_3$ (Ar = Ph, 3,5-(CF₃)₂C₆H₃, Dipp).^{238,239} Intriguingly, $\text{U}(\text{N}^t\text{Bu})_2(\text{THF})_2$ could also be prepared directly from uranium turnings by reaction with six equiv of $^t\text{BuNH}_2$ and three equiv of I_2 .²³⁸

3.2.5. Uranium(II). In large part due to the scarcity of isolated uranium(II) compounds, very little reactivity has been reported for uranium in this oxidation state. The principal challenge in isolating uranium(II) species is that, in general, such complexes act as very strong reductants. Moreover, decomposition pathways such as C–H bond activation may be a common aspect of uranium(II) reactivity, which adds further



Scheme 7 Reduction of $((^{\text{Ad,Me}}\text{ArO})_3\text{Mes})\text{U}$ with K^0 in THF in the presence of 2,2,2-cryptand yielded an isolable uranium(II) complex (top), while reduction with KC_8 in benzene generated the uranium(IV) hydride product via benzylic C–H bond activation (bottom).^{109,127}

challenges in finding suitable supporting ligands and solvents for application to uranium(II) chemistry. While reactions involving one-electron oxidation to uranium(III) have been observed in several cases, it also may be possible for the uranium(II/IV) redox couple to mediate two-electron reductions.

Uranium(II) complexes $[\text{K}(2,2,2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}]$ and $[\text{K}(18\text{-crown-6})(\text{THF})_2][\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}_3\text{U}]$ were found to react with H_2 or PhSiH_3 to form the uranium(III) hydrides $[\text{K}(2,2,2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{UH}]$ and $[\text{K}(18\text{-crown-6})(\text{THF})_2][\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}_3\text{UH}]$; these hydrides were synthesized independently by addition of KH and 2,2,2-cryptand or 18-crown-6 to the corresponding uranium(III) $(\text{Cp}^{\text{R}})_3\text{U}$ starting materials.^{22,108} Reactions of the same uranium(II) complexes with two equiv of C_8H_8 led to formation of the uranium(IV) compound uranocene, $(\text{C}_8\text{H}_8)_2\text{U}$, as well as the potassium salts of the corresponding Cp^{R} ligands, however, uranium(III) byproducts $[\text{K}(2,2,2\text{-cryptand})][(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_3(\eta^1\text{-C}_5\text{H}_4\text{SiMe}_3)\text{U}]$ or $\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}_3\text{U}$ were also observed for both systems.¹⁰⁸ While it is possible that reduction of C_8H_8 to $\text{C}_8\text{H}_8^{2-}$ occurred as a two-electron step via the uranium(II/IV) redox couple, the presence of uranium(III) products suggests that one-electron steps (i.e. uranium(II/III) redox processes) were also operative in the course of the reaction.¹⁰⁸ Reaction of $[\text{K}(2,2,2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}]$ with 0.5 equiv of $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Pb}$ also led to one-electron oxidation to $[\text{K}(2,2,2\text{-cryptand})][(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_3(\eta^1\text{-C}_5\text{H}_4\text{SiMe}_3)\text{U}]$.¹⁰⁸ Another example of a one-electron oxidation was the generation of cationic uranium(III) complex $[\text{U}(\text{NHAr}^{\text{iPr6}})_2][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$ by reaction of $\text{U}(\text{NHAr}^{\text{iPr6}})_2$ with $[\text{Cp}_2\text{Fe}][\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$.¹¹¹

While reduction of $((^{\text{Ad,Me}}\text{ArO})_3\text{Mes})\text{U}$ with potassium and 2,2,2-cryptand enabled isolation of the uranium(II) complex $[(^{\text{Ad,Me}}\text{ArO})_3\text{MesU}]^-$ (Scheme 7, top),¹⁰⁹ reaction of $((^{\text{Ad,Me}}\text{ArO})_3\text{Mes})\text{U}$ with potassium graphite or sodium in the absence of a chelating agent led to formation of a uranium(IV)

hydride complex via activation of a benzylic C–H bond by a uranium(II) intermediate (Scheme 7, bottom).¹²⁷ While this reaction potentially occurred via the formal oxidative addition of a C–H bond, the resultant $\text{U}\text{-C}_{\text{benzylic}}$ distance (2.946(6) Å in the crystallographically characterized product) is quite long,[‡] and, furthermore, the exact mechanism of this process has not been characterized.¹²⁷

Reduction of uranium(III) compounds $\text{Cp}^*_2\text{U}[\text{N}(\text{SiMe}_3)_2]$ or $\text{Cp}^*\text{U}[\text{N}(\text{SiMe}_3)_2]_2$ with KC_8 likely led to uranium(II) intermediates; however, in both cases, cyclometalated uranium(III) products resulting from C–H bond activation formed readily at low temperatures.²⁴⁰ It was proposed that these uranium(II) intermediates activated C–H bonds with concomitant elimination of H_2 ;²⁴⁰ a similar mechanism was proposed for the cyclometallation of uranium(III) compounds $\text{U}(\text{Tren}^{\text{R}})$ ($\text{Tren}^{\text{R}} = \text{N}(\text{CH}_2\text{CH}_2\text{NR}, \text{R} = \text{SiMe}_2\text{tBu}$ or $\text{Si}^{\text{iPr}}\text{Pr}_3$) under photolytic conditions.²⁴¹ In an additional possible case of uranium(II)-mediated C–H bond activation, reduction of $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ with KC_8 in the presence of 18-crown-6 led to crystallographic characterization of bimetallic uranium(III) hydride decomposition product $[\text{K}(18\text{-crown-6})(\text{OEt}_2)][\{(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}\}_2(\mu\text{-H})]$; the origin of the hydride ligand was not determined but was likely the solvent.¹⁰⁸

4. Conclusions

The varied and unusual reactivity observed with low-valent uranium has attracted considerable attention in recent years. Much of this progress was facilitated by advances in synthetic routes to uranium(III) starting materials. Moreover, the development of new ligand systems has greatly expanded the types of reactivity now known to be possible with trivalent uranium. For example, despite the tendency of uranium-mediated redox reactions to occur via one-electron steps, uranium(III) complexes have found extensive application as

precursors to complexes containing uranium–ligand multiple bonds, and many of these syntheses involve direct oxidation (with concurrent group transfer) to uranium(V). Additionally, use of redox-active ligands or multinuclear complexes has enabled uranium(III) species to act as multi-electron reductants for a range of transformations. Undoubtedly, many new modes of reactivity have yet to be discovered for trivalent uranium.

In contrast to the extensive studies of uranium(III), the chemistry of uranium(II) is drastically less developed due in large part to its tendency to be extremely reducing. Only a handful of different ligand types have been shown to be capable of stabilizing uranium(II) to yield isolable complexes, and reactivity studies are quite limited. It is therefore an open question if the uranium(II/IV) redox couple may directly mediate certain reactions. In other words, do reactions with uranium(II) occur exclusively via one-electron steps, or are two-electron steps possible? The generation of a uranium(IV) hydride via reduction of ((^{Ad},MeArO)₃Mes)U hints that uranium(II) complexes may be capable of mononuclear, two-electron oxidative addition reactions across the uranium(II/IV) redox couple,¹²⁷ although further mechanistic analysis and follow-up studies with other systems will be necessary to confirm this notion. As noted above, mononuclear, two-electron oxidative addition across the uranium(III/V) redox couple has been proposed in only two cases: the oxidative addition of PhNNPh and H₂O by U(Ts^{Xy}) and ((^{Ad},MeArO)₃Mes)U, respectively.^{128,133}

One of the pervasive challenges in studying low-valent uranium is that subtle variations between ligands may lead to dramatic differences in reactivity. Combined with the generally labile nature of low-valent uranium, this often means that it is difficult to predict the outcome of reactions, particularly in the area of small molecule activation. Systematic reactivity studies, coupled with computational analysis, will continue to provide insight into how to predict and control reactivity with different substrates.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

† Bent metallocene geometries have exclusively been observed for uranium(III), but linear metallocenes have been reported with uranium(II), uranium(IV) and uranium(V). See ref. 112 and 242.

§ Electrochemical measurements of the uranium(II/III) redox couple in ((^{Ad},MeArO)₃Mes)U and (C₅(ⁱPr)₅)₂U in THF gave values of –2.495 and –2.327 V vs [Cp₂Fe]/[Cp₂Fe]⁺, respectively (see ref. 127 and 112). For the latter complex, Cp*₂Fe was used as an internal reference, so the measured reduction potential of [Cp*₂Fe]/[Cp*₂Fe]⁺, –0.427 V versus [Cp₂Fe]/[Cp₂Fe]⁺ in THF (see ref. 243), was used as a conversion factor.

‡ The other two crystallographic U–C_{benzylic} distances are much longer, however, with values of 3.767(5) and 3.993(6) Å.

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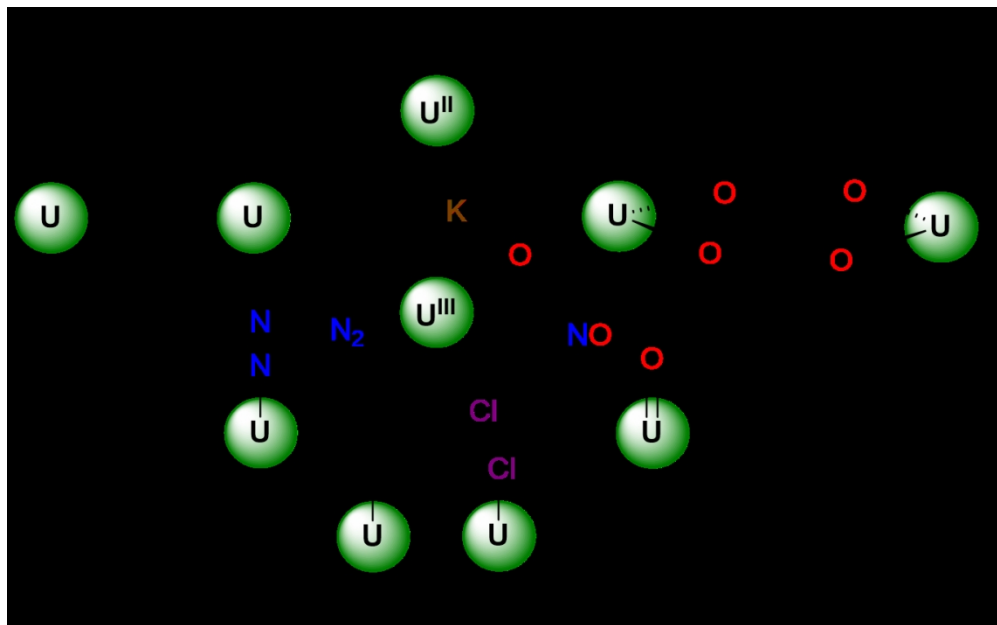
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This synthesis and diverse reactivity of uranium(III) and uranium(II) complexes is discussed.



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