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

Michael A. Boreen and John Arnold*

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.^{1,2} 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.³

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.⁴ 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.⁵ Aqueous uranium(V)

typically disproportionates into uranium(VI) and uranium(IV), while aqueous uranium(III) is unstable toward oxidation.⁵ In non-aqueous media, a wide range of stable uranium(III) and uranium(V) complexes have been isolated, however, ligands are often found to 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;^{6–11} oxidation of uranium(III) starting materials to uranium(IV) products may therefore occur during a reaction without clear identification of an oxidant.^{12–14}

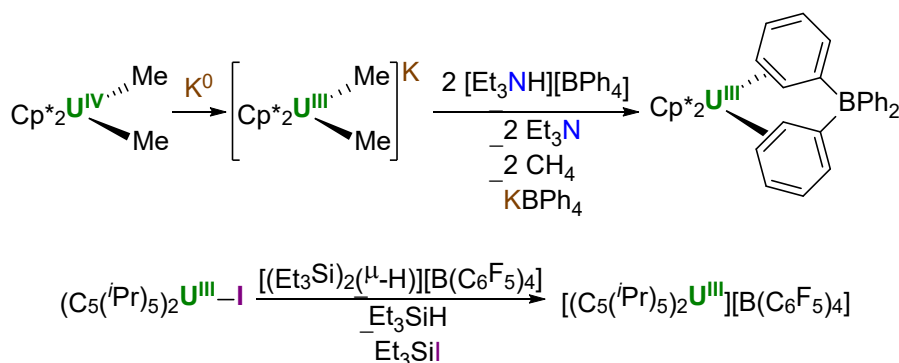
Recently, the redox chemistry of uranium was extended to the formal uranium(II) state with the isolation of [K(2.2.2-cryptand)][C₅H₄SiMe₃]₃U,¹⁵ although this oxidation state still remains quite rare for uranium. Molecular solution-phase or solid-state uranium(I) or uranium(0) species have not been reported, but a computational study suggested that a monovalent uranium complex may be synthetically accessible.¹⁶ Additionally, the UFe(CO)₃[−] anion was observed in the gas-phase and assigned as containing uranium(I).¹⁷

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.^{18–26}

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.²⁶ 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

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Scheme 2 Synthetic routes to uranium(III) metallocene 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).^{62,68}

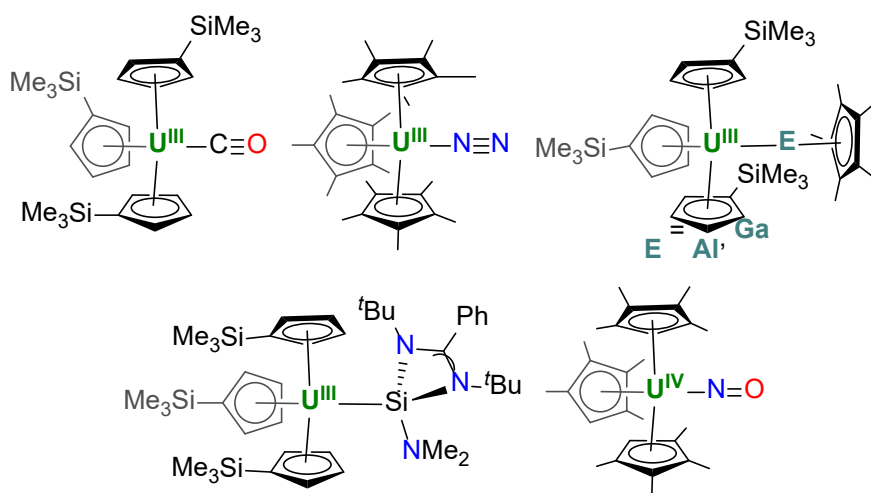


Chart 1 Selected examples of adducts formed with $(\text{Cp}^{\text{R}})_3\text{U}$ fragments.^{80,84–87,135}

observed, with ν_{CO} values of 1969, 1880, and 1922 cm^{-1} , respectively, in the solid-state. 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.⁸³ Back-bonding from uranium 5f to isocyanide π^* orbitals has also been studied in adducts of $(\text{Cp}^{\text{R}})_3\text{U}$ species.⁵⁹

Tris(Cp^{R}) uranium(III) fragments have proven capable of forming other uncommon motifs, including an end-on dinitrogen adduct,⁸⁴ unsupported U–Al and U–Ga bonds^{85,86} and uranium-silylenes (Chart 1).⁸⁷ Side-on dinitrogen binding has also been observed in the diuranium(III) species $[\text{U}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^t\text{BuMe}_2)_3\}]_2(\mu-\eta^2-\eta^2-\text{N}_2)$.⁸⁸

Since the first report in 1971,⁸⁹ several unsupported η^6 -arene complexes of uranium(III) have been characterized.^{90–93} Bridging η^6 -arene interactions were also observed in the dimeric solid-state structure of $[\text{U}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_3]_2$.³⁸ More recently, the chemistry of tris(aryloxy) ligands with tethered arene moieties has been developed;^{77,94–98} 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^{77,94} and in electrocatalytic water reduction.⁹⁷ Another tethered arene ligand was used with uranium(III) to isolate an

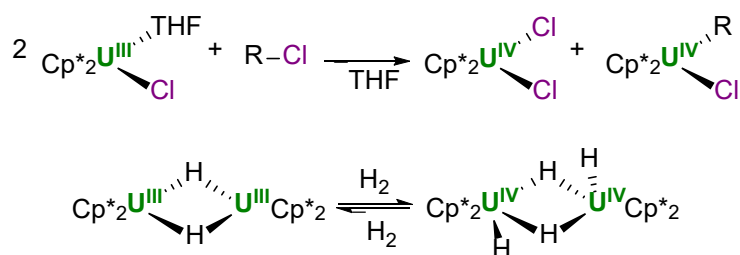
unsupported U–Fe bond, but significant δ back-bonding was not found in computational studies of this system.⁹⁹

Finally, crystallographic evidence for $\eta^2\text{-C,H}$ coordination of an alkane to the uranium(III) tris(aryloxy) complex $((^t\text{Bu},^t\text{BuArO})_3\text{tacn})\text{U}$ ($(^{\text{R},\text{R}'}\text{ArOH})_3\text{tacn} = 1,4,7\text{-tris}((2\text{-hydroxy-3-R-5-R}'\text{-phenyl)methyl)-1,4,7\text{-triazacyclononane})$) was reported in 2003;¹⁰⁰ a more recent study attributed alkane binding to London dispersion interactions with the $((^t\text{Bu},^t\text{BuArO})_3\text{tacn})^3-$ ligand.¹⁰¹

3.2. Redox Reactions

3.2.1. General Comments. The redox chemistry of uranium is characterized by a propensity to undergo one-electron steps.^{19,23} 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 $\text{Cp}^*_2\text{U}(\text{Cl})(\text{THF})$ and alkyl halides (RCl), which leads to uranium(IV) products $\text{Cp}^*_2\text{UCl}_2$ and $\text{Cp}^*\text{U}(\text{R})(\text{Cl})$ (Scheme 3, top).^{102,103} In this type of reaction, the overall two-electron process—a bimetallic oxidative addition—occurs with one-



Scheme 3 Selected examples of bimetallic oxidative addition with uranium(III) complexes. *Top*: reaction of Cp*₂U(III)(THF) yields uranium(IV) products Cp*₂UCl₂ and Cp*₂U(R)Cl (R = alkyl); *bottom*: reversible addition of H₂ to [Cp*₂U(III)(μ-H)]₂ to form [Cp*₂U(IV)(H)(μ-H)]₂.^{102–104}

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.²³ Similarly, the solution-state equilibrium between diuranium(IV) species [Cp*₂U(H)(μ-H)]₂ and diuranium(III) complex [Cp*₂U(μ-H)]₂ occurs via bimetallic reductive elimination and oxidative addition reactions (Scheme 3, bottom).¹⁰⁴ Recently (and in contrast to the one-electron step paradigm for uranium(III) reactivity), the unimolecular, two-electron oxidative addition of H₂O by the uranium(III) complex ((^{Ad},^{Me}ArO)₃Mes)U was reported as a step in the mechanism for water reduction, representing the first case of this kind of oxidative addition occurring across the uranium(III/V) redox couple.⁹⁷

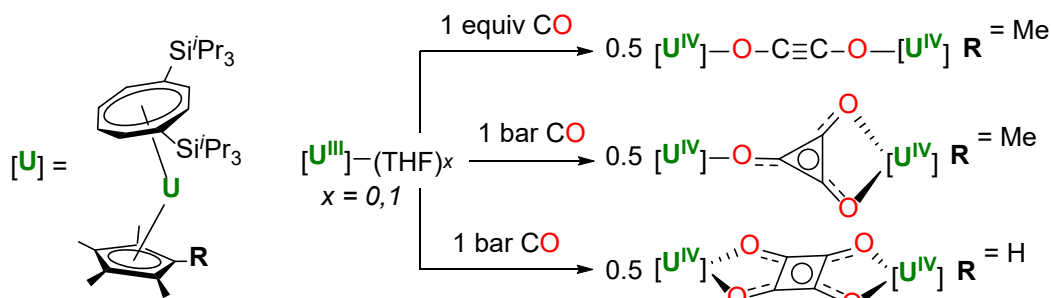
While the potential of the uranium(III/IV) redox couple can shift considerably based on the ligands coordinated to the uranium center,^{8,105} uranium(III) species are generally quite reducing and can therefore be oxidized to uranium(IV) even with mild oxidants. Through one-electron oxidation reactions, uranium(III) species have found use as precursors for uranium(IV) complexes with a wide range of ligand types.^{54,106} Some uranium(III) species have even been observed to cleave aryl C–F bonds to form uranium(IV) fluorides.^{107–109} 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.^{105,110}

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(η⁸-1,4-(SiⁱPr₃)₂C₈U₄) as well as the uranium(III) tris(aryloxides) U(O-2,6-^tBu₂C₆H₃)₃ and U(O-2,4,6-^tBu₃C₆H₂)₃ reversibly bound dinitrogen to form species assigned as diuranium(IV) bridged by a side-on N₂²⁻ unit.^{33,39} Interestingly, heating was necessary to eliminate N₂ from the latter aryloxide, but the other two systems favored the non-adduct species at ambient conditions under 1 atm of N₂.^{33,39} Stirring the trivalent complexes U[N(^tBu)(3,5-Me₂C₆H₃)₃](THF) and Mo[N(^tBu)(Ph)]₃ in a nitrogen atmosphere led to formation of [(^tBu)(3,5-Me₂C₆H₃)N]₃U(μ-η¹:η¹-N₂)Mo[N(^tBu)(Ph)]₃ in which both metal centers were assigned as tetravalent with a bridging linear N₂²⁻ ligand.¹⁴ 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 (η¹-N₂)Mo[N(^tBu)(Ph)]₃.¹⁴ Recently, nitride-bridged diuranium(III) siloxide species were found to bind and

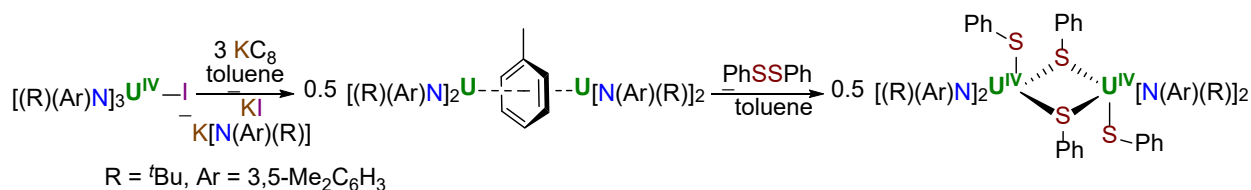
reduce N₂ to form diuranium(V) complexes with N₂⁴⁻ fragments that could subsequently be functionalized by several means.^{111,112} Direct cleavage of dinitrogen was achieved by reduction of the uranium(III) complex [K(DME)][(Et₆-calix[4]tetrapyrrole)U(DME)] with potassium naphthalenide under an N₂ atmosphere, resulting in a mixed-valent bis(μ-nitrido) diuranium(IV/V) complex.¹¹³

As observed with N₂, uranium(III) complexes with minor differences in supporting ligands have exhibited large differences in reactivity toward CO₂. Reductive binding of CO₂ by ((^{Ad},^tBu)ArO)₃tacn)U was reported to form a complex assigned as containing a uranium(IV) center exhibiting η¹-O coordination to the CO₂⁻ radical anion.¹¹⁴ In contrast, reaction of ((^tBu,^tBu)ArO)₃tacn)U with CO₂ led to two-electron reduction of CO₂ with C–O bond cleavage to form the μ-oxo diuranium(IV) complex with accompanying evolution of CO. Similarly, reactions of (Me₃SiC₅H₄)₃U with CO₂ or N₂O were both found to yield the corresponding μ-oxo diuranium(IV) species.¹¹⁵ Reductive disproportionation of CO₂ to form CO₃²⁻ and CO has been observed with more than one uranium(III) system,^{116,117} although multiple different product outcomes are possible between uranium(III) species and CO₂.^{24,118} Similarly, a variety of reactivity modes have been observed between CS₂ and uranium(III) species, including reduction to form bridging CS₂²⁻ species, reductive dimerization, and reductive disproportionation.^{49,117,119–121}

A diverse range of reduction products have also been observed between uranium(III) complexes and CO.¹²² 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 μ-η¹:η¹-CO⁻ ligand.¹²³ Reductive coupling to form C–C bonds has been observed with multiple systems. Exposure of U[N(SiMe₃)₂]₃, U(O-2,6-^tBu₂C₆H₃)₃, or U(O-2,4,6-^tBu₃C₆H₂)₃ to CO led to formation of diuranium(IV) species bridged by the linear ynediolate dianion, [OCCO]²⁻.^{39,124} The stoichiometric reaction of CO with mixed sandwich complex Cp*U(η⁸-1,4-(SiⁱPr₃)₂C₈H₆)(THF) yielded the ynediolate-bridged diuranium(IV) species (Scheme 4, top),¹²⁵ while use of excess CO yielded a diuranium(IV) species bridged by the deltatate dianion, C₃O₃²⁻ (Scheme 4, middle).¹²⁶ Remarkably, reaction of the extremely similar starting material (C₅Me₄H)U(η⁸-1,4-(SiⁱPr₃)₂C₈H₆)(THF) with excess CO led to a diuranium(IV) complex bridged by the squarate dianion, C₄O₄²⁻ (Scheme 4, bottom).¹²⁷ Further work has been carried out to correlate steric properties of related uranium(III) mixed sandwich complexes with reactivity



Scheme 4 Synthesis of diuranium(IV) yndiolate (top), deltate (middle), and squarate (bottom) complexes from uranium(III) mixed sandwich compounds.^{125–127}



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.¹³⁷

outcomes toward CO and CO₂.^{128,129}

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(η^{8-1,4}-(SiⁱPr₃)₂C₈H₆) with one equiv of CO followed by two equiv of H₂ led to isolation of a uranium(IV) methoxide complex.¹³⁰ Notably, addition of one equiv of CO to diuranium(IV) dihydride K₂[[U(OSi(O^tBu)₃)₂(μ-O)(μ-H)₂], formed by addition of H₂ to the corresponding diuranium(III) precursor, produced a complex with a bridging oxomethylene dianion [CH₂O²⁻] that yielded methoxide upon further reaction with H₂.¹³¹ Furthermore, treatment of Cp*U(η^{8-1,4}-(SiⁱPr₃)₂C₈H₆) 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.^{132,133}

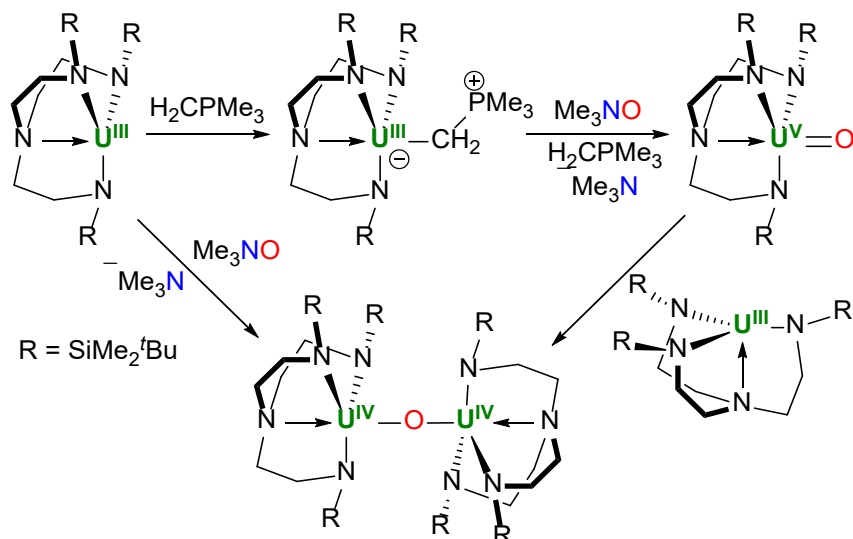
Beyond this reactivity, reports of reactions of NO with trivalent uranium are limited. The nature of the bonding in the NO adduct of Cp₃U was predicted in 1989.¹³⁴ Reaction of (C₅Me₄H)₃U with one equiv of NO led to isolation of (C₅Me₄H)₃UNO (Chart 1), formally containing singly reduced NO⁻ coordinated in a linear fashion to a uranium(IV) center, as was predicted for Cp₃UNO.^{134,135} 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) η¹-ONNO⁻ intermediate.¹³⁶ The same oxo complex was isolated by reaction of U(O-2,6-Ad₂-4-MeC₆H₂)₃ with N₂O.¹³⁶

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.^{12,117,137–147} Reaction of [(^tBu)(3,5-Me₂C₆H₃)N]₃U with three equiv of KC₈ in toluene yielded the toluene-bridged species {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}₂(μ-η⁶:η⁶-C₆H₅Me) (Scheme

5).¹³⁷ 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;¹³⁷ in fact, δ-bonding is a common and important stabilizing feature of this class of complexes.¹⁴⁰ Furthermore, reaction of {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}(μ-η⁶:η⁶-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.¹³⁷

While this four-electron reactivity might formally be described as {[(^tBu)(3,5-Me₂C₆H₃)N]₂U}(μ-η⁶:η⁶-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-η⁶:η⁶-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.¹³⁸ Multiple other examples of arene-bridged diuranium complexes have been assigned as diuranium(III) with a dianionic arene,^{12,144–146,148} but exceptions include mixed-valent species^{142,147} and uranium(IV) or uranium(V) species with tetraanionic toluene bridges.^{117,139,143,149}

Reaction of (Cp*₂U)₂(μ-η⁶:η⁶-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-η³:η³-C₈H₈) (containing three C₈H₈²⁻ ligands) along with neutral (C₅Me₅)₂ and free benzene.¹³⁸ 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 C₅Me₅²⁻/C₅Me₅ process.¹³⁸ This use of electrons derived from the C₅Me₅²⁻/C₅Me₅ process for reductive reactivity at the uranium center is an example of a sterically induced reduction, which has been studied extensively



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).¹⁷⁸

in both lanthanides and actinides.^{18,138,150–156}

Beyond reduced arenes and $C_5Me_5^-$, 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 $^{\cdot-}$,^{69,157–160} terpy $^{\cdot-}$,^{67,160} or ketyl ($OCPh_2^{\cdot-}$)¹⁶¹ 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,^{157,162,163} sometimes with accompanying radical coupling to the bipy ligand.^{69,159} Similar multi-electron reductive behavior has been observed in uranium(III) benzyl,^{162,164–168} hydride,^{169,170} and tetraphenylborate species.^{171,172} 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.¹⁷³

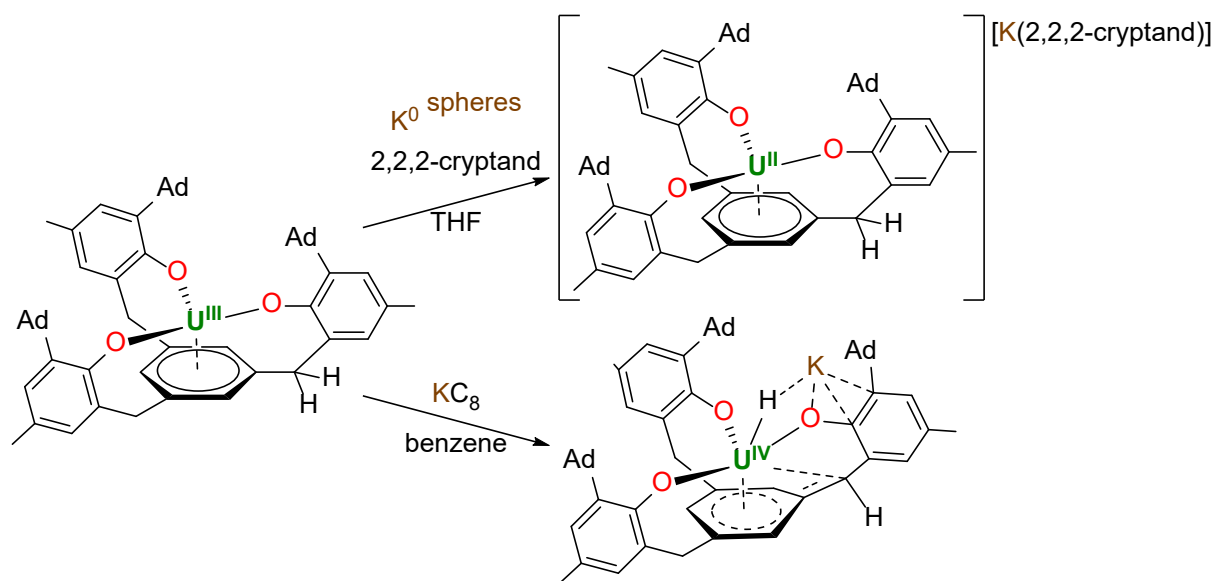
3.2.4. Formation of Uranium–Ligand Multiple Bonds.

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.^{174–177} Uranium(V) terminal oxo,^{178–186} terminal imido,^{178,187–192} and alkali metal-capped terminal nitride^{179,192–194} 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.^{195,196}

The two electrons for these transformations may derive from the uranium(III/V) 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,^{123,178,180} sulfide,^{197–200} selenide,^{197–200} telluride,^{197,200} imido,^{137,201} and nitride^{202–206} 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,^{178,207–209} although mechanisms involving only single-electron steps may also be possible in certain cases.^{197,210} 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.²¹¹ 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).^{178,207}

A variety of strategies have been developed to prepare uranium(IV) species with terminal metal–ligand multiple bonds



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*).^{77,96}

from uranium(III) starting materials. Addition of $\text{K}(\text{C}_5\text{H}_5)_2$ ($\text{E} = \text{O}, \text{S}$) 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.²⁰⁹ 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 $[\text{Ph}_3\text{PCH}_3][\text{U}(\text{E})\{\text{N}(\text{SiMe}_3)_2\}_3]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$).²⁰⁷ 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.²¹² Recently, oxidative deprotonation of a uranium(III) anilido complex was demonstrated as a method to form uranium(IV) imidos.²¹³ 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).^{157,163,164,167,168}

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.^{148,171} 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).⁷¹ 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.^{214,215} This method provided access to the uranium(VI) tris(imido) complex $\text{U}(\text{NDipp})_3(\text{THF})_3$ ($\text{Dipp} = 2,6\text{-}(\text{Pr})_2\text{C}_6\text{H}_3$) via reaction of $\text{U}(\text{I})_3(\text{THF})_4$ with three equiv of Dipp-N_3 and three equiv of KC_8 , an overall six-electron process.²¹⁴ 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 $\text{U}(\text{NAr})_2(\text{THF})_3$ ($\text{Ar} = \text{Ph}, 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3, \text{Dipp}$).^{216,217} 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 .²¹⁶

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. In general, uranium(II) species are expected to be very strong reductants,⁵ and 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) $(\text{Cp}^R)_3\text{U}$ starting materials.^{15,76} 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.⁷⁶ 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.⁷⁶ 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 $[(\text{K}(2.2.2\text{-cryptand}))][(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_3(\eta^1\text{-C}_5\text{H}_4\text{SiMe}_3)\text{U}]$.⁷⁶ Another example of a one-electron oxidation was the generation of cationic uranium(III)

complex $[U(NHAr^{iPr6})_2][B(3,5-(CF_3)_2-C_6H_3)_4]$ by reaction of $U(NHAr^{iPr6})_2$ with $[Cp_2Fe][B(3,5-(CF_3)_2-C_6H_3)_4]$.⁷⁸

While reduction of $((^{Ad,Me}ArO)_3Mes)U$ with potassium and 2,2,2-cryptand enabled isolation of the uranium(II) complex $[(^{Ad,Me}ArO)_3Mes)U]^-$ (Scheme 7, top),⁷⁷ reaction of $((^{Ad,Me}ArO)_3Mes)U$ 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).⁹⁶ While this reaction potentially occurred via the formal oxidative addition of a C–H bond, the resultant U–C_{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.⁹⁶

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 $((^{Ad,Me}ArO)_3Mes)U$ hints that uranium(II) complexes may be capable of mononuclear, two-electron oxidative addition reactions across the uranium(II/IV) redox couple,⁹⁶ 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 has been observed across the uranium(III/V) redox couple in only one case: the oxidative addition of H₂O by $((^{Ad,Me}ArO)_3Mes)U$.⁹⁷

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. 79 and 218.

§ Electrochemical measurements of the uranium(II/III) redox couple in $((^{Ad,Me}ArO)_3Mes)U$ and $(C_5(Pr)_5)_2U$ in THF gave values of –2.495 and –2.327 V vs $[Cp_2Fe]/[Cp_2Fe]^+$, respectively (see ref. 79 and 96). 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 $[Cp_2Fe]/[Cp_2Fe]^+$ in THF (see ref. 219), 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.

- 1 “Abundance of Elements in the Earth’s Crust and in the Sea,” in *CRC Handbook of Chemistry and Physics*, ed. J. R. Rumble, CRC Press/Taylor & Francis, Boca Raton, 101st edn. (Internet Version), 2020.
- 2 B. F. Parker, Z. Zhang, L. Rao and J. Arnold, *Dalton Trans.*, 2018, **47**, 639.
- 3 N. E. Holden, “Table of the Isotopes,” in *CRC Handbook of Chemistry and Physics*, ed. J. R. Rumble, CRC Press/Taylor & Francis, Boca Raton, 101st edn. (Internet Version), 2020.
- 4 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1976, **32**, 751.
- 5 C. J. Rodden, in *Analysis of Essential Nuclear Reactor Materials*, U. S. Atomic Energy Commission, Washington, D. C., 1964, ch. 1, pp 1–158.
- 6 S. Hohloch, M. E. Garner, B. F. Parker and J. Arnold, *Dalton Trans.*, 2017, **46**, 13768.
- 7 M. A. Boreen, B. F. Parker, S. Hohloch, B. A. Skeel and J. Arnold, *Dalton Trans.*, 2018, **47**, 96.
- 8 M. A. Boreen, D. J. Lussier, B. A. Skeel, T. D. Lohrey, F. A. Watt, D. K. Shuh, J. R. Long, S. Hohloch and J. Arnold, *Inorg. Chem.*, 2019, **58**, 16629.
- 9 C. R. Graves and J. L. Kiplinger, *Chem. Commun.*, 2009, 3831.
- 10 A. C. Behrle, A. J. Myers, P. Rungthanaphatsophon, W. W. Lukens, C. L. Barnes and J. R. Walensky, *Chem. Commun.*, 2016, **52**, 14373.
- 11 T. R. Boussie, R. M. Moore, Jr., A. Streitwieser, A. Zalkin, J. Brennan and K. A. Smith, *Organometallics*, 1990, **9**, 2010.
- 12 A. J. Wooles, W. Lewis, A. J. Blake and S. T. Liddle, *Organometallics*, 2013, **32**, 5058.

- 13 M. A. Boreen, O. A. Groß, S. Hohloch and J. Arnold, *Dalton Trans.*, 2020, **49**, 11971.
- 14 A. L. Odom, P. L. Arnold and C. C. Cummins, *J. Am. Chem. Soc.*, 1998, **120**, 5836.
- 15 M. R. MacDonald, M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 13310.
- 16 J.-N. Tian, M. Zheng, L. Li, G. Schreckenbach, Y.-R. Guo and Q.-J. Pan, *New J. Chem.*, 2019, **43**, 1469.
- 17 C. Chi, J.-Q. Wang, H. Qu, W.-L. Li, L. Meng, M. Luo, J. Li and M. Zhou, *Angew. Chem., Int. Ed.*, 2017, **56**, 6932.
- 18 W. J. Evans and S. A. Kozimor, *Coord. Chem. Rev.*, 2006, **250**, 911.
- 19 S. T. Liddle, *Angew. Chem., Int. Ed.*, 2015, **54**, 8604.
- 20 M. Ephritikhine, *Dalton Trans.*, 2006, 2501.
- 21 M. Ephritikhine, *Organometallics*, 2013, **32**, 2464.
- 22 P. L. Arnold, *Chem. Commun.*, 2011, **47**, 9005.
- 23 E. Lu and S. T. Liddle, *Dalton Trans.*, 2015, **44**, 12924.
- 24 L. Barluzzi, M. Falcone and M. Mazzanti, *Chem. Commun.*, 2019, **55**, 13031.
- 25 I. Castro-Rodríguez and K. Meyer, *Chem. Commun.*, 2006, 1353.
- 26 R. J. Baker, *Coord. Chem. Rev.*, 2012, **256**, 2843.
- 27 M. A. Boreen, T. D. Lohrey, G. Rao, R. D. Britt, L. Maron and J. Arnold, *J. Am. Chem. Soc.*, 2019, **141**, 5144.
- 28 D. L. Clark, A. P. Sattelberger, S. G. Bott and R. N. Vrtis, *Inorg. Chem.*, 1989, **28**, 1771.
- 29 L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248.
- 30 M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031.
- 31 C. D. Carmichael, N. A. Jones and P. L. Arnold, *Inorg. Chem.*, 2008, **47**, 8577.
- 32 W. J. Evans, S. A. Kozimor, J. W. Ziller, A. A. Fagin and M. N. Bochkarev, *Inorg. Chem.*, 2005, **44**, 3993.
- 33 F. G. N. Cloke and P. B. Hitchcock, *J. Am. Chem. Soc.*, 2002, **124**, 9352.
- 34 J. D. Corbett and A. Simon, in *Inorganic Syntheses*, ed. S. L. Holt, Jr., John Wiley & Sons, New York, 2007, vol. 22, pp. 31–36.
- 35 R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 1507.
- 36 D. C. Moody and J. D. Odom, *J. Inorg. Nucl. Chem.*, 1979, **41**, 533.
- 37 H. S. La Pierre, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2014, **50**, 3962.
- 38 W. G. Van der Sluys, C. J. Burns, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1988, **110**, 5924.
- 39 S. M. Mansell, N. Kaltsayannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2011, **133**, 9036.
- 40 M. Roger, N. Barros, T. Arliguie, P. Thuéry, L. Maron and M. Ephritikhine, *J. Am. Chem. Soc.*, 2006, **128**, 8790.
- 41 P. L. Arnold, N. A. Potter, C. D. Carmichael, A. M. Z. Slawin, P. Roussel and J. B. Love, *Chem. Commun.*, 2010, **46**, 1833.
- 42 S. J. Zuend, O. P. Lam, F. W. Heinemann and K. Meyer, *Angew. Chem., Int. Ed.*, 2011, **50**, 10626.
- 43 C. A. P. Goodwin, F. Tuna, E. J. L. McInnes, S. T. Liddle, J. McMaster, I. J. Vitorica-Yrezabal and D. P. Mills, *Chem. - Eur. J.*, 2014, **20**, 14579.
- 44 W. G. Van Der Sluys, C. J. Burns and A. P. Sattelberger, *Organometallics*, 1989, **8**, 855.
- 45 M. A. Boreen, B. F. Parker, T. D. Lohrey and J. Arnold, *J. Am. Chem. Soc.*, 2016, **138**, 15865.
- 46 F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 6th edn., 1999.
- 47 M. Sharma and M. S. Eisen, in *Organometallic and Coordination Chemistry of the Actinides*, ed. T. E. Albrecht-Schmitt, Springer, Berlin, Heidelberg, 2008, vol. 127, pp. 1–85.
- 48 D. Seyferth, *Organometallics*, 2004, **23**, 3562.
- 49 J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1986, **25**, 1756.
- 50 W. J. Evans, D. J. Wink and D. R. Stanley, *Inorg. Chem.*, 1982, **21**, 2565.
- 51 C. J. Windorff and W. J. Evans, *Organometallics*, 2014, **33**, 3786.
- 52 A. Formanui, A.-M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes and D. P. Mills, *Nat. Chem.*, 2017, **9**, 578.
- 53 J. J. Kiernicki, B. S. Newell, E. M. Matson, N. H. Anderson, P. E. Fanwick, M. P. Shores and S. C. Bart, *Inorg. Chem.*, 2014, **53**, 3730.
- 54 S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 1623.
- 55 D. G. Karkaker and J. A. Stone, *Inorg. Chem.*, 1972, **11**, 1742.
- 56 J.-C. Berthet, J.-F. Le Maréchal and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1991, 360.
- 57 C. Apostolidis, M. S. Dutkiewicz, A. Kovács and O. Walter, *Chem. - Eur. J.*, 2018, **24**, 2841.
- 58 M. del Mar Conejo, J. S. Parry, E. Carmona, M. Schultz, J. G. Brennann, S. M. Beshouri, R. A. Andersen, R. D. Rogers, S. Coles and M. B. Hursthouse, *Chem. - Eur. J.*, 1999, **5**, 3000.
- 59 W. W. Lukens, M. Speldrich, P. Yang, T. J. Duignan, J. Autschbach and P. Kögerler, *Dalton Trans.*, 2016, **45**, 11508.
- 60 W. J. Evans, K. J. Forrestal and J. W. Ziller, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 774.
- 61 N. A. Siladke, J. W. Ziller and W. J. Evans, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2347.
- 62 W. J. Evans, G. W. Nyce, K. J. Forrestal and J. W. Ziller, *Organometallics*, 2002, **21**, 1050.
- 63 J. W. Bruno, D. G. Kalina, E. A. Mintz and T. J. Marks, *J. Am. Chem. Soc.*, 1982, **104**, 1860.
- 64 P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood, W. E. Hunter and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1394.
- 65 W. W. Lukens, S. M. Beshouri, A. L. Stuart and R. A. Andersen, *Organometallics*, 1999, **18**, 1247.
- 66 L. R. Avens, C. J. Burns, R. J. Butcher, D. L. Clark, J. C. Gordon, A. R. Schake, B. L. Scott, J. G. Watkin and B. D. Zwick, *Organometallics*, 2000, **19**, 451.
- 67 E. J. Schelter, R. Wu, B. L. Scott, J. D. Thompson, D. E. Morris and J. L. Kiplinger, *Angew. Chem., Int. Ed.*, 2008, **47**, 2993.
- 68 F.-S. Guo, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, *Angew. Chem., Int. Ed.*, 2019, **58**, 10163.
- 69 A. Mohammad, D. P. Cladis, W. P. Forrest, P. E. Fanwick and S. C. Bart, *Chem. Commun.*, 2012, **48**, 1671.
- 70 A. B. Altman, A. C. Brown, G. Rao, T. D. Lohrey, R. D. Britt, L. Maron, S. G. Minasian, D. K. Shuh and J. Arnold, *Chem. Sci.*, 2018, **9**, 4317.
- 71 B. P. Warner, B. L. Scott and C. J. Burns, *Angew. Chem., Int. Ed.*, 1998, **37**, 959.
- 72 P. J. Fagan, J. M. Manriquez, T. J. Marks, C. S. Day, V. W. Day, S. H. Vollmer and V. W. Day, *Organometallics*, 1982, **1**, 170.
- 73 W. J. Evans, S. A. Kozimor, W. R. Hillman and J. W. Ziller, *Organometallics*, 2005, **24**, 4676.
- 74 S. J. Connelly, W. Kaminsky and D. M. Heinekey, *Organometallics*, 2013, **32**, 7478.
- 75 D. N. Huh, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2018, **57**, 11809.
- 76 C. J. Windorff, M. R. MacDonald, K. R. Meihaus, J. W. Ziller, J. R. Long and W. J. Evans, *Chem. - Eur. J.*, 2016, **22**, 772.
- 77 H. S. La Pierre, A. Scheurer, F. W. Heinemann, W. Hieringer and K. Meyer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7158.
- 78 B. S. Billow, B. N. Livesay, C. C. Mokhtarzadeh, J. McCracken, M. P. Shores, J. M. Boncella and A. L. Odom, *J. Am. Chem. Soc.*, 2018, **140**, 17369.

- 79 F.-S. Guo, N. Tsoureas, G.-Z. Huang, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, *Angew. Chem., Int. Ed.*, 2020, **59**, 2299.
- 80 J. G. Brennan, R. A. Andersen and J. L. Robbins, *J. Am. Chem. Soc.*, 1986, **108**, 335.
- 81 J. Parry, E. Carmona, S. Coles and M. Hursthouse, *J. Am. Chem. Soc.*, 1995, **117**, 2649.
- 82 W. J. Evans, S. A. Kozimor, G. W. Nyce and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 13831.
- 83 L. Maron, O. Eisenstein and R. A. Andersen, *Organometallics*, 2009, **28**, 3629.
- 84 W. J. Evans, S. A. Kozimor and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 14264.
- 85 S. G. Minasian, J. L. Krinsky, V. A. Williams and J. Arnold, *J. Am. Chem. Soc.*, 2008, **130**, 10086.
- 86 S. G. Minasian, J. L. Krinsky, J. D. Rinehart, R. Copping, T. Tyliczszak, M. Janousch, D. K. Shuh and J. Arnold, *J. Am. Chem. Soc.*, 2009, **131**, 13767.
- 87 I. J. Brackbill, I. Douair, D. J. Lussier, M. A. Boreen, L. Maron and J. Arnold, *Chem. - Eur. J.*, 2020, **26**, 2360.
- 88 P. Roussel and P. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 1070.
- 89 M. Cesari, U. Pedretti, Z. Zazzetta, G. Lugli and W. Marconi, *Inorg. Chim. Acta*, 1971, **5**, 439.
- 90 F. A. Cotton, W. Schwotzer and C. Q. Simpson, II, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 637.
- 91 F. A. Cotton and W. Schwotzer, *Organometallics*, 1987, **6**, 1275.
- 92 A. V. Garbar, M. R. Leonov, L. N. Zakharov and Y. T. Struchkov, *Russ. Chem. Bull.*, 1996, **45**, 451.
- 93 D. Baudry, E. Bulot, P. Charpin, M. Ephritikhine, M. Lance, M. Nierlich and J. Vigner, *J. Organomet. Chem.*, 1989, **371**, 155.
- 94 S. C. Bart, F. W. Heinemann, C. Anthon, C. Hauser and K. Meyer, *Inorg. Chem.*, 2009, **48**, 9419.
- 95 O. P. Lam, S. C. Bart, H. Kameo, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2010, **46**, 3137.
- 96 H. S. La Pierre, H. Kameo, D. P. Halter, F. W. Heinemann and K. Meyer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7154.
- 97 D. P. Halter, F. W. Heinemann, L. Maron and K. Meyer, *Nat. Chem.*, 2018, **10**, 259.
- 98 D. P. Halter, F. W. Heinemann, J. Bachmann and K. Meyer, *Nature*, 2016, **530**, 317.
- 99 S. Fortier, J. R. Aguilar-Calderón, B. Vlasisvljevich, A. J. Metta-Magaña, A. G. Goos and C. E. Botez, *Organometallics*, 2017, **36**, 4591.
- 100 I. Castro-Rodriguez, H. Nakai, P. Gantzel, L. N. Zakharov, A. L. Rheingold and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 15734.
- 101 J. Jung, S. T. Löffler, J. Langmann, F. W. Heinemann, E. Bill, G. Bistoni, W. Scherer, M. Atanasov, K. Meyer and F. Neese, *J. Am. Chem. Soc.*, 2020, **142**, 1864.
- 102 R. G. Finke, Y. Hirose and G. Gaughan, *J. Chem. Soc., Chem. Commun.* 1981, 232.
- 103 R. G. Finke, D. A. Schiraldi and Y. Hirose, *J. Am. Chem. Soc.*, 1981, **103**, 1875.
- 104 P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650.
- 105 D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez and J. L. Kiplinger, *Organometallics*, 2004, **23**, 5142.
- 106 L. R. Avens, D. M. Barnhart, C. J. Burns, S. D. McKee and W. H. Smith, *Inorg. Chem.*, 1994, **33**, 4245.
- 107 M. Weydert, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 8837.
- 108 C. L. Clark, J. J. Lockhart, P. E. Fanwick and S. C. Bart, *Chem. Commun.*, 2015, **51**, 14084.
- 109 M. A. Boreen, K. N. McCabe, T. D. Lohrey, F. A. Watt, L. Maron, S. Hohloch and J. Arnold, *Inorg. Chem.*, 2020, **59**, 8580.
- 110 R. K. Thomson, B. L. Scott, D. E. Morris and J. L. Kiplinger, *C. R. Chim.*, 2010, **13**, 790.
- 111 M. Falcone, L. Chatelain, R. Scopelliti, I. Živković and M. Mazzanti, *Nature*, 2017, **547**, 332.
- 112 M. Falcone, L. Barluzzi, J. Andrez, F. F. Tirani, I. Zivkovic, A. Fabrizio, C. Corminboeuf, K. Severin and M. Mazzanti, *Nat. Chem.*, 2019, **11**, 154.
- 113 I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 2002, **41**, 3433.
- 114 I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757.
- 115 J.-C. Berthet, J.-F. Le Maréchal, M. Nierlich, M. Lance, J. Vigner and M. Ephritikhine, *J. Organomet. Chem.*, 1991, **408**, 335.
- 116 O. T. Summerscales, A. S. P. Frey, F. G. N. Cloke and P. B. Hitchcock, *Chem. Commun.*, 2009, 198.
- 117 V. Mougel, C. Camp, J. Pécaut, C. Copéret, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem., Int. Ed.*, 2012, **51**, 12280.
- 118 N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777.
- 119 O. P. Lam, F. W. Heinemann and K. Meyer, *Angew. Chem., Int. Ed.*, 2011, **50**, 5965.
- 120 O. P. Lam, L. Castro, B. Kosog, F. W. Heinemann, L. Maron and K. Meyer, *Inorg. Chem.*, 2012, **51**, 781.
- 121 C. Camp, O. Cooper, J. Andrez, J. Pécaut and M. Mazzanti, *Dalton Trans.*, 2015, **44**, 2650.
- 122 P. L. Arnold and Z. R. Turner, *Nat. Rev. Chem.*, 2017, **1**, 0002.
- 123 I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242.
- 124 P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci.*, 2011, **2**, 77.
- 125 A. S. Frey, F. G. N. Cloke, P. B. Hitchcock, I. J. Day, J. C. Green and G. Aitken, *J. Am. Chem. Soc.*, 2008, **130**, 13816.
- 126 O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *Science*, 2006, **311**, 829.
- 127 O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *J. Am. Chem. Soc.*, 2006, **128**, 9602.
- 128 R. J. Kahan, J. H. Farnaby, N. Tsoureas, F. G. N. Cloke, P. B. Hitchcock, M. P. Coles, S. M. Roe and C. Wilson, *J. Organomet. Chem.*, 2018, **857**, 110.
- 129 N. Tsoureas, O. T. Summerscales, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2013, **32**, 1353.
- 130 A. S. P. Frey, F. G. N. Cloke, M. P. Coles, L. Maron and T. Davin, *Angew. Chem., Int. Ed.*, 2011, **50**, 6881.
- 131 M. Falcone, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2019, **141**, 9570.
- 132 A. S. P. Frey, F. G. N. Cloke, M. P. Coles and P. B. Hitchcock, *Chem. - Eur. J.*, 2010, **16**, 9446.
- 133 C. E. Kefalidis, A. S. P. Frey, S. M. Roe, F. G. N. Cloke and L. Maron, *Dalton Trans.*, 2014, **43**, 11202.
- 134 B. E. Bursten, L. F. Rhodes and R. J. Strittmatter, *J. Am. Chem. Soc.*, 1989, **111**, 2758.
- 135 N. A. Siladke, K. R. Meihaus, J. W. Ziller, M. Fang, F. Furche, J. R. Long and W. J. Evans, *J. Am. Chem. Soc.*, 2012, **134**, 1243.
- 136 C. J. Hoerger, H. S. La Pierre, L. Maron, A. Scheurer, F. W. Heinemann and K. Meyer, *Chem. Commun.*, 2016, **52**, 10854.
- 137 P. L. Diaconescu, P. L. Arnold, T. A. Baker, D. J. Mindiola and C. C. Cummins, *J. Am. Chem. Soc.*, 2000, **122**, 6108.
- 138 W. J. Evans, S. A. Kozimor, J. W. Ziller and N. Kaltsoyannis, *J. Am. Chem. Soc.*, 2004, **126**, 14533.
- 139 D. Patel, F. Moro, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2011, **50**, 10388.
- 140 S. T. Liddle, *Coord. Chem. Rev.*, 2015, **293–294**, 211.
- 141 P. L. Diaconescu and C. C. Cummins, *J. Am. Chem. Soc.*, 2002, **124**, 7660.
- 142 P. L. Diaconescu and C. C. Cummins, *Inorg. Chem.*, 2012, **51**, 2902.

- 143 D. Patel, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Dalton Trans.*, 2013, **42**, 5224.
- 144 D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2011, **3**, 454.
- 145 M. J. Monreal, S. I. Khan, J. L. Kiplinger and P. L. Diaconescu, *Chem. Commun.*, 2011, **47**, 9119.
- 146 P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nat. Chem.*, 2012, **4**, 668.
- 147 A. J. Wooles, D. P. Mills, F. Tuna, E. J. L. McInnes, G. T. W. Law, A. J. Fuller, F. Kremer, M. Ridgway, W. Lewis, L. Gagliardi, B. Vlaisavljevich and S. T. Liddle, *Nat. Commun.*, 2018, **9**, 2097.
- 148 W. J. Evans, C. A. Traina and J. W. Ziller, *J. Am. Chem. Soc.*, 2009, **131**, 17473.
- 149 C. Camp, V. Mougél, J. Pécaut, L. Maron and M. Mazzanti, *Chem. - Eur. J.*, 2013, **19**, 17528.
- 150 W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119.
- 151 W. J. Evans, *J. Organomet. Chem.*, 2002, **647**, 2.
- 152 W. J. Evans, J. R. Walensky, F. Furche, J. W. Ziller, A. G. DiPasquale and A. L. Rheingold, *Inorg. Chem.*, 2008, **47**, 10169.
- 153 W. J. Evans, G. W. Nycé and J. W. Ziller, *Angew. Chem., Int. Ed.*, 2000, **39**, 240.
- 154 W. J. Evans, *Coord. Chem. Rev.*, 2000, **206–207**, 263.
- 155 W. J. Evans, *J. Alloys Compd.*, 2009, **488**, 493.
- 156 W. J. Evans, G. W. Nycé, M. A. Johnston and J. W. Ziller, *J. Am. Chem. Soc.*, 2000, **122**, 12019.
- 157 G. Zi, L. Jia, E. L. Werkema, M. D. Walter, J. P. Gottfriedsen and R. A. Andersen, *Organometallics*, 2005, **24**, 4251.
- 158 S. J. Kraft, P. E. Fanwick and S. C. Bart, *Inorg. Chem.*, 2010, **49**, 1103.
- 159 L. Zhang, C. Zhang, G. Hou, G. Zi and M. D. Walter, *Organometallics*, 2017, **36**, 1179.
- 160 T. Mehdoui, J.-C. Berthet, P. Thuéry, L. Salmon, E. Rivière and M. Ephritikhine, *Chem. - Eur. J.*, 2005, **11**, 6994.
- 161 E. M. Matson, J. J. Kiernicki, N. H. Anderson, P. E. Fanwick and S. C. Bart, *Dalton Trans.*, 2014, **43**, 17885.
- 162 J. J. Kiernicki, R. F. Higgins, S. J. Kraft, M. Zeller, M. P. Shores and S. C. Bart, *Inorg. Chem.*, 2016, **55**, 11854.
- 163 S. J. Kraft, J. Walensky, P. E. Fanwick, M. B. Hall and S. C. Bart, *Inorg. Chem.*, 2010, **49**, 7620.
- 164 E. M. Matson, M. G. Crestani, P. E. Fanwick and S. C. Bart, *Dalton Trans.*, 2012, **41**, 7952.
- 165 E. M. Matson, M. D. Goshert, J. J. Kiernicki, B. S. Newell, P. E. Fanwick, M. P. Shores, J. R. Walensky and S. C. Bart, *Chem. - Eur. J.*, 2013, **19**, 16176.
- 166 E. M. Matson, P. E. Fanwick and S. C. Bart, *Eur. J. Inorg. Chem.*, 2012, **2012**, 5471.
- 167 C. J. Tatebe, M. Zeller and S. C. Bart, *Inorg. Chem.*, 2017, **56**, 1956.
- 168 E. M. Matson, W. P. Forrest, P. E. Fanwick and S. C. Bart, *Organometallics*, 2013, **32**, 1484.
- 169 W. J. Evans, K. A. Miller, S. A. Kozimor, J. W. Ziller, A. G. DiPasquale and A. L. Rheingold, *Organometallics*, 2007, **26**, 3568.
- 170 W. J. Evans, K. A. Miller and J. W. Ziller, *Angew. Chem., Int. Ed.*, 2008, **47**, 589.
- 171 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Chem. Commun.*, 2005, 4681.
- 172 W. J. Evans, K. A. Miller, W. R. Hillman and J. W. Ziller, *J. Organomet. Chem.*, 2007, **692**, 3649.
- 173 P. K. Pal, S. Chowdhury, M. G. B. Drew and D. Datta, *New J. Chem.*, 2002, **26**, 367.
- 174 M. A. Boreen and J. Arnold, Multiple Bonding in Actinide Chemistry, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, ed. R. A. Scott, Wiley, Hoboken, 2018, DOI: 10.1002/9781119951438.eibc2535.
- 175 T. W. Hayton, *Dalton Trans.*, 2010, **39**, 1145.
- 176 T. W. Hayton, *Chem. Commun.*, 2013, **49**, 2956.
- 177 D. M. King and S. T. Liddle, *Coord. Chem. Rev.*, 2014, **266–267**, 2.
- 178 P. Roussel, R. Boaretto, A. J. Kingsley, N. W. Alcock and P. Scott, *J. Chem. Soc., Dalton Trans.*, 2002, 1423.
- 179 N. Tsoureas, A. F. R. Kilpatrick, C. J. Inman and F. G. N. Cloke, *Chem. Sci.*, 2016, **7**, 4624.
- 180 S. Fortier, J. L. Brown, N. Kaltsoyannis, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2012, **51**, 1625.
- 181 S. Fortier, N. Kaltsoyannis, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 14224.
- 182 D. M. King, F. Tuna, J. McMaster, W. Lewis, A. J. Blake, E. J. L. McInnes and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2013, **52**, 4921.
- 183 A.-C. Schmidt, F. W. Heinemann, W. W. Lukens, Jr. and K. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 11980.
- 184 D. S. J. Arney and C. J. Burns, *J. Am. Chem. Soc.*, 1993, **115**, 9840.
- 185 S. M. Franke, B. L. Tran, F. W. Heinemann, W. Hieringer, D. J. Mindiola and K. Meyer, *Inorg. Chem.*, 2013, **52**, 10552.
- 186 O. Cooper, C. Camp, J. Pécaut, C. E. Kefalidis, L. Maron, S. Gambarelli and M. Mazzanti, *J. Am. Chem. Soc.*, 2014, **136**, 6716.
- 187 J. G. Brennan and R. A. Andersen, *J. Am. Chem. Soc.*, 1985, **107**, 514.
- 188 P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood and H. Zhang, *Inorg. Chim. Acta*, 1987, **139**, 13.
- 189 A. Zalkin, J. G. Brennan and R. A. Andersen, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 1553.
- 190 I. Castro-Rodriguez, K. Olsen, P. Gantzel and K. Meyer, *J. Am. Chem. Soc.*, 2003, **125**, 4565.
- 191 S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, **130**, 12536.
- 192 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2013, **5**, 482.
- 193 D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717.
- 194 D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes and S. T. Liddle, *Nat. Commun.*, 2016, **7**, 13773.
- 195 A. R. Fox and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 5716.
- 196 M. A. Boreen, G. Rao, D. G. Villarreal, F. A. Watt, R. D. Britt, S. Hohloch and J. Arnold, *Chem. Commun.*, 2020, **56**, 4535.
- 197 J. G. Brennan, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1986, **25**, 1761.
- 198 C. Camp, M. A. Antunes, G. García, I. Ciofini, I. C. Santos, J. Pécaut, M. Almeida, J. Marçalo and M. Mazzanti, *Chem. Sci.*, 2014, **5**, 841.
- 199 O. P. Lam, F. W. Heinemann and K. Meyer, *Chem. Sci.*, 2011, **2**, 1538.
- 200 J. L. Brown, G. Wu and T. W. Hayton, *Organometallics*, 2013, **32**, 1193.
- 201 J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2008, **2008**, 5455.
- 202 W. J. Evans, S. A. Kozimor and J. W. Ziller, *Science*, 2005, **309**, 1835.
- 203 W. J. Evans, K. A. Miller, J. W. Ziller and J. Greaves, *Inorg. Chem.*, 2007, **46**, 8008.
- 204 G. Nocton, J. Pécaut and M. Mazzanti, *Angew. Chem., Int. Ed.*, 2008, **47**, 3040.
- 205 L. Barluzzi, L. Chatelain, F. Fadaei-Tirani, I. Zivkovic and M. Mazzanti, *Chem. Sci.*, 2019, **10**, 3543.
- 206 S. Fortier, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2010, **132**, 6888.
- 207 J. L. Brown, S. Fortier, R. A. Lewis, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2012, **134**, 15468.
- 208 J. G. Brennan, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1988, **110**, 4554.

- 209 D. E. Smiles, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2014, **136**, 96.
- 210 J. Andrez, J. Pécaut, R. Scopelliti, C. E. Kefalidis, L. Maron, M. W. Rosenzweig, K. Meyer and M. Mazzanti, *Chem. Sci.*, 2016, **7**, 5846.
- 211 B. M. Gardner and S. T. Liddle, *Chem. Commun.*, 2015, **51**, 10589.
- 212 S. Fortier, J. R. Walensky, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2011, **133**, 6894.
- 213 D. Perales, S. A. Ford, S. R. Salpage, T. S. Collins, M. Zeller, K. Hanson and S. C. Bart, *Inorg. Chem.*, 2020, DOI: 10.1021/acs.inorgchem.0c01704.
- 214 N. H. Anderson, H. Yin, J. J. Kiernicki, P. E. Fanwick, E. J. Schelter and S. C. Bart, *Angew. Chem., Int. Ed.*, 2015, **54**, 9386.
- 215 M. A. Boreen and J. Arnold, *Polyhedron*, 2018, **155**, 149.
- 216 T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista and P. J. Hay, *Science*, 2005, **310**, 1941.
- 217 T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista and P. J. Hay, *J. Am. Chem. Soc.*, 2006, **128**, 10549.
- 218 J. Maynadié, N. Barros, J.-C. Berthet, P. Thuéry, L. Maron and M. Ephritikhine, *Angew. Chem., Int. Ed.*, 2007, **46**, 2010.
- 219 I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, *J. Phys. Chem. B*, 1999, **103**, 6713.