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Review

Expanding the chemistry of U^{3+} reducing agents

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Abstract

The U^{3+} ion offers many opportunities for developing new actinide reaction chemistry. This review surveys the traditional non-aqueous U^{3+} reduction chemistry in the literature and summarizes recent attempts to combine U^{3+} reduction with ligand-based reductions to achieve multi-electron reduction with complexes of this ion. The purpose of this analysis is to better identify new possibilities for further expansion of the reduction chemistry of U^{3+}.

Keywords: Uranium; Reduction; Sterically induced reduction; Multi-electron reduction; Actinide; Organometallic; Cyclopentadienyl

1. Purpose

Redox reactions constitute one of the most general classes of chemical reactions. Traditionally, metal complexes containing f element ions have not displayed extensive redox chemistry because relatively few oxidation states are available. For example, the trivalent oxidation state is the only oxidation state readily accessible under normal conditions for many of the lanthanides and the heavy actinides [1–3]. In molecular lanthanide complexes, oxidation chemistry has been traditionally limited to Ce^{4+} [4,5] and reduction chemistry to Eu^{2+}, Yb^{2+} and Sm^{2+} [6].

Recently, however, the molecular divalent reduction chemistry available to the lanthanides has expanded dramatically in several ways [7–9]. The first molecular complexes of Tm^{2+} [10], Dy^{2+} [11] and Nd^{2+} [12] have been fully characterized by X-ray crystallography and shown to have useful chemistry [9,11,13–18]. Organometallic La^{2+} and Ce^{2+} complexes of arene monoanions have also been structurally characterized [19,20]. A LnZ_3/K reduction system (Z = anion) that mimics divalent reactivity has been identified [21–23]. Finally, divalent-like reduction chemistry has been observed with sterically crowded $(C_5Me_5)_3Ln$ complexes in a process called sterically induced reduction (SIR) [7,8,24–26].

In contrast to the lanthanides and heavy actinides, the light actinide elements, and particularly uranium, have a more extensive set of available oxidation states [2,3]. Due to the difficulty in handling the more radioactive elements, much more is known about the reactivity of uranium and thorium than the other early actinides. It seemed possible that in light of the recent developments in reductive lanthanide chemistry, a more expanded U^{3+} reduction chemistry might also be possible. Since U^{3+} is already a reactive and widely investigated reducing agent and since the results of these reductions are scattered throughout the literature, it is more difficult to identify the opportunities for expansion. To help in this regard, we review here the current state of knowledge on U^{3+} reduction chemistry. Traditional U^{3+} reductions are summarized as well as recent reports combining ligand-based reductions, including sterically induced reduction, with U^{3+} reduction to achieve multi-electron reductions.

2. Scope

U^{3+} reduction chemistry has been addressed in previous reviews including those by Marks and Ernst [27,28], Raymond and Eigenbrot [29], Takats [30], Pires de Matos and co-workers [31], Edelmann [32], Berthet and Ephritikhine [33,34], and Seyferth [35] as part of larger reviews of actinide chemistry in general. This manuscript differs from the previous reviews in that it focuses on a single aspect of uranium chemistry, the oxidation/reduction reactions involving U^{3+} in non-aqueous solution. In order to present the entire scope of U^{3+} redox chemistry, information from these past reviews is also included in an attempt to be as comprehensive as possible in this review. If any relevant papers have been missed, please contact the authors and an addendum will be made available via the internet.

3. Organization

This review begins with a section on U^{3+} electrochemistry and is followed by sections divided on the basis of the number of electrons transferred per U^{3+} starting material. Within each of these sections, the review is organized by the class of uranium reducing agent used. The order of presentation of topics within each section has been chosen to provide an introduction to typical U^{3+} chemistry with the complexes for which the most reductive chemistry is known. Only representative redox reactions will be discussed in the text.

4. U^{3+} electrochemistry

Electrochemical studies of the strongly reducing ions of the f elements are difficult to carry out. The range of unreactive solvents is limited and the high reactivity of the species involved requires extreme purity in the supporting electrolyte and solvent. Potentials can vary depending on the concentration of the electrolyte [36] and ligand redistribution reactions can be enhanced under the conditions necessary to obtain electrochemical data [37]. In the past, electrochemical data on U^{3+} has been published sporadically [36–51], but recently a detailed study of the electrochemistry of U^{4+} complexes has been published that reviews this area and adds a substantial amount of new data [51]. In light of this comprehensive treatment, U^{3+} electrochemistry only needs to be summarized here.

The data show that U^{3+} is a substantial reductant and the reduction potentials can vary significantly depending on the specific ligands surrounding the metal. It has been estimated [51] "that the potential for the U^{4+}/U^{3+} couple lies between ~ -1.5 and -2.2 V versus $[(C_5H_5)_2Fe]^{1+/0}$ in all studies". Several studies have shown that U^{3+} becomes more reducing as the electron donating ability of the ligands increases, e.g. $(C_5Me_5)^{1-} > (C_5H_5)^{1-} > Cl^{1-}$ [45] and $(C_5H_5)^{1-} > (BH_4)^{1-}$ [36]. However, as noted by Morris et al. [51], this correlation is not always perfect as exemplified by the $(C_5H_4R)_3UCl/[(C_5H_4R)_3UCl]^{1-}$ series, in which the U^{3+} component becomes more reducing in the order $R = SiMe_3 < H < CMe_3 < Me$ [48].

The subtle importance of local environment is emphasized by comparing the results on some related bis(cyclopentadienyl) uranium chloride complexes. $(C_5Me_5)_2UCl(THF)$ has an irreversible oxidation at -0.7 V versus SCE in THF [40]. However, starting with the tetravalent $(C_5Me_5)_2UCl_2$, a reversible $(C_5Me_5)_2UCl_2/[(C_5Me_5)_2UCl_2]^{1-}$ U^{4+}/U^{3+} redox couple is observed at -1.3 V versus SCE in MeCN and -1.2 V in THF. In comparison, an alternative tetravalent precursor, $(C_5Me_4H)_3UCl$, displayed an irreversible reduction peak at -2.35 V versus $[(C_5H_5)_2Fe]^{1+/0}$ in THF [46].

Cyclopentadienyl free U^{3+} complexes have also been investigated electrochemically. $(2,6\text{-}^tBu_2C_6H_3O)_3U$ displays reversible one electron oxidation at -1.22 V versus $[(C_5H_5)_2Fe]^{1+/0}$ in THF [47] and $[(Me_3Si)_2N]_3U$ has a similar potential in THF, -1.24 V versus $[(C_5H_5)_2Fe]^{1+/0}$ [47].

5. U^{3+} to U^{4+} transformations

This section addresses the most common reduction reaction of U^{3+} complexes [47], i.e. reactions involving the one electron redox couple, U^{4+}/U^{3+}. Since single electron reductions generate odd electron products which can subsequently be further reduced by a second equivalent of U^{3+} starting materials, many of the reactions involve two equivalents of the U^{3+} reagent. Since these two electron reductions are affected by two equivalents of the U^{3+} reagent, i.e. only one electron is provided per monometallic U^{3+} reductant, they are included in this section. Section 6 describes two electron reactivity via the U^{5+}/U^{3+} redox couple.

5.1. $(C_5Me_5)_2UCl(THF)$

The bis(pentamethylcyclopentadienyl) uranium chloride THF adduct, $(C_5Me_5)_2UCl(THF)$ [52,53], provides a good starting point to examine trivalent uranium reduction chemistry. This complex has been studied electrochemically [40], its reduction chemistry has been studied mechanistically with a variety of substrates [53–55], and it involves a bis(pentamethylcyclopentadienyl) metallocene coordination environment that is often favorable for isolating products.

$(C_5Me_5)_2UCl(THF)$ reduces alkyl and aryl halides, RX and ArX (X = halide), at exceptionally fast reaction rates [54,55]. These reactions typically give mixtures of products that include the halide abstraction product, $(C_5Me_5)_2UClX$, as well as products formed from the radical remaining after $(C_5Me_5)_2UClX$ is formed. These include $(C_5Me_5)_2U(R)Cl$, R–R, R(–H) and RH. The generalized stoichiometry presented in the literature for this reaction is shown in Eq. (1) [55]. When only $(C_5Me_5)_2UCl_2$ is formed

$$\begin{aligned}&(a+2b)(C_5Me_5)_2UCl(THF) + (a+b)RCl\\&\quad\rightarrow (a+b)(C_5Me_5)_2UCl_2 + b(C_5Me_5)_2U(R)Cl\\&\qquad + a[R\text{–}R, RH, R(\text{–}H)] + (a+2b)THF\end{aligned} \tag{1}$$

and the resulting alkyl radical terminates by reacting with another radical, the half reaction for the one electron reduction involving uranium is shown in Eq. (2).

$$(C_5Me_5)_2UCl(THF) \rightarrow [(C_5Me_5)_2UCl]^{1+} + 1e^{1-} + THF \tag{2}$$

When $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2U(R)Cl$ are formed from two equivalents of $(C_5Me_5)_2UCl(THF)$, the transformation involves a two electron reduction for the uranium species.

The ratio of $(C_5Me_5)_2UCl_2$ to $(C_5Me_5)_2U(R)Cl$ in the product mixtures is highly variable depending on R. In some cases, e.g. $R = {}^tBu$ and CH_2Ph, $(C_5Me_5)_2UCl_2$ is the only isolated uranium complex, with no $(C_5Me_5)_2U(R)Cl$ observed [54]. However, for R = Me, a 6.4/1 ratio is reported [53] and for $R = {}^nBu$, a 1/0.55 ratio is observed. When mixtures are formed, these reactions are often not useful preparatively, since the alkyl and halide products can be difficult to separate. In the reaction of methyl *iodide*, the product mixture is even more complicated [54]. It contains 0.31 mol of $(C_5Me_5)_2UCl_2$, 0.25 mol of $(C_5Me_5)_2UCl(I)$, 0.03 mol of $(C_5Me_5)_2UI_2$, 0.19 mol of $(C_5Me_5)_2UMeCl$ and 0.22 mol of $(C_5Me_5)_2UMeI$. The isolation of $(C_5Me_5)_2UI_2$ indicates that ligand redistribution occurs under the reaction conditions. This will be seen repeatedly throughout this review.

The order of reactivity of RX substrates, i.e. benzyl ~ tertiary > secondary > primary > neopentyl, and $^nBuI > {}^nBuBr > {}^nBuCl$, is consistent with halogen–carbon bond cleavage in the rate determining step to make $(C_5Me_5)_2UClX$ and $R^\bullet$ radicals. Further support for a radical mechanism was obtained using radical traps such as cyclopropylcarbinyl chloride. This formed a significant amount of ring opened product [55].

The reaction rates were found to be dependent on THF concentration and a pre-equilibrium was postulated involving the dissociation of THF. The data are consistent with an inner sphere process involving halide abstraction, Scheme 1 [55].

$$(C_5Me_5)_2UCl(THF) \rightleftharpoons (C_5Me_5)_2UCl + THF$$

$$(C_5Me_5)_2UCl + RX \rightleftharpoons (C_5Me_5)_2UCl(X) + R\cdot$$

$$R\cdot \longrightarrow R\text{-}R + RH + R(\text{-}H)$$

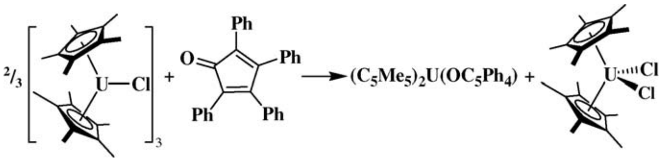
$$R\cdot + (C_5Me_5)_2UCl \longrightarrow (C_5Me_5)_2U(R)Cl$$

Scheme 1.

5.2. *[(C$_5$Me$_5$)$_2$UCl]$_3$*

The related unsolvated bis(pentamethylcyclopentadienyl) chloride complex, $[(C_5Me_5)_2UCl]_3$, which exists as a toluene insoluble trimer in the solid state [52], reacts similarly with alkyl halides as expected based on the initial step of desolvation from $(C_5Me_5)_2UCl(THF)$, Scheme 1. However, the U^{3+} reduction chemistry of this complex with *halide-free* organic substrates is somewhat different [53]. With the substrates discussed below, the reductive reactivity of $[(C_5Me_5)_2UCl]_3$ involves a two electron reduction of a single substrate molecule effected by two equivalents of the monomeric $(C_5Me_5)_2UCl$ unit.

In reactions with tetraphenylcyclopentadienone, 9,10-phenanthrenequinone and diphenylacetylene, two equivalents of $(C_5Me_5)_2UCl$ deliver two electrons to make dianions from the substrates [53]. Additionally, an equivalent of the tetravalent dichloride, $(C_5Me_5)_2UCl_2$, is formed as a byproduct in each case [53]. Eqs. (4) and (5) show examples in which tetravalent uranium complexes of the oxygen-containing dianions $(OC_5Ph_4)^{2-}$ and $(O_2C_{14}H_8)^{2-}$ are generated. With PhC≡CPh, two electron reductive coupling occurs to form the $(C_4Ph_4)^{2-}$ dianion and a metallacyclopentadiene product as shown in Eq. (6) [53].



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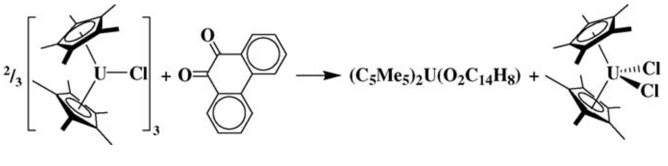

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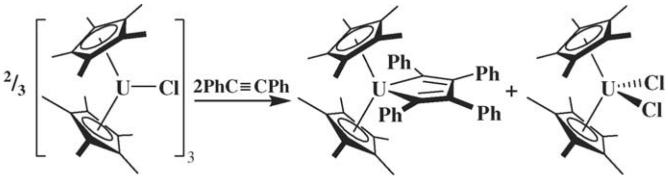


(6)

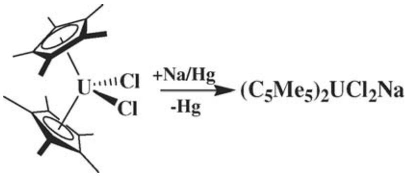
The formal half reaction for the two electron transformations in Eqs. (4)–(6) is shown in Eq. (7). This half reaction is related to the previously described $(C_5Me_5)_2UCl/[(C_5Me_5)_2UCl]^{1+}$ reaction in Eq. (2) except that the chloride ligands of the $[(C_5Me_5)_2UCl]^{1+}$ product of Eq. (2) undergo a ligand redistribution to form a mixture of $(C_5Me_5)_2UCl_2$ and formally the $[(C_5Me_5)_2U]^{2+}$ cation. In this sense, it was recognized that $[(C_5Me_5)_2UCl]_3$ acts like a divalent species of formula $(C_5Me_5)_2U$ in that it delivers two electrons and the $[(C_5Me_5)_2U]^{2+}$ cation [53]. One problem with this type of U^{3+} reduction is that the product is generated as part of a mixture containing soluble $(C_5Me_5)_2UCl_2$, a byproduct that is often difficult to separate.

$$\tfrac{2}{3}[(C_5Me_5)_2UCl]_3 \rightarrow [(C_5Me_5)_2U]^{2+} + 2e^{1-} + (C_5Me_5)_2UCl_2 \qquad (7)$$

Formation of $(C_5Me_5)_2UCl_2$ from $[(C_5Me_5)_2UCl]_3$ could be facile, since each uranium ion in both the products and reactants is already ligated by two $(C_5Me_5)^{1-}$ ligands and two chlorides. However, the details of the sequence of electron transfer are unknown. One could imagine the oxygen containing substrates of Eqs. (4) and (5) breaking up the $[(C_5Me_5)_2U(\mu\text{-}Cl)]_3$ trimer and coordinating to the uranium as in the inner sphere mechanism postulated by Finke [54,55] for $(C_5Me_5)_2UCl$, Scheme 1. The resulting $(C_5Me_5)_2ClU(\mu\text{-}Cl)U(C_5Me_5)_2$(substrate) intermediate would have the composition necessary to make the $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2U$(dianion) products. However, such a sequence is more difficult to imagine when PhC≡CPh is a substrate.

5.3. *(C$_5$Me$_5$)$_2$UCl$_2$Na*

Another variation of the "$(C_5Me_5)_2UCl$" reduction system involves the NaCl adduct, $(C_5Me_5)_2UCl_2Na$. This trivalent "ate" salt is obtained by sodium amalgam reduction of $(C_5Me_5)_2UCl_2$, Eq. (8) [53]. Since reductions with this complex still involve the odd electron U^{4+}/U^{3+}redox couple, two electron reductions by $(C_5Me_5)_2UCl_2Na$ require two equivalents of this complex and yield $(C_5Me_5)_2UCl_2$ as a byproduct, Eq. (9) [53]. The formal half reaction for this process is shown in Eq. (10).



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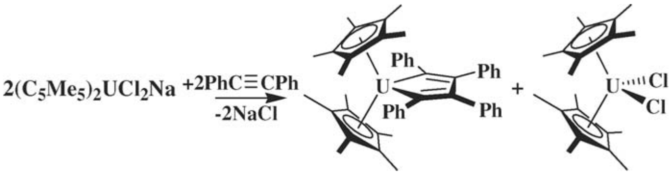

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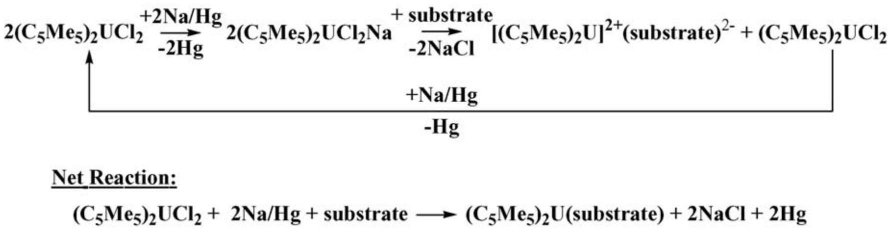
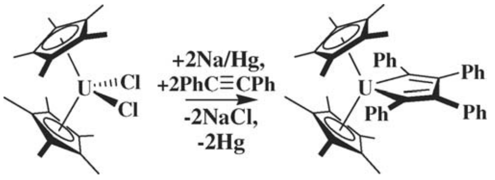


Scheme 2.

$$2(C_5Me_5)_2UCl_2Na \rightarrow [(C_5Me_5)_2U]^{2+} + 2e^{1-} + (C_5Me_5)_2UCl_2 + 2NaCl \quad (10)$$

This is similar to Eq. (7) for $[(C_5Me_5)_2UCl]_3$ except that NaCl is also present.

Although stoichiometric reactions of $(C_5Me_5)_2UCl_2Na$ can effect reduction, this U^{3+} reductant also has the problem that a product mixture is formed containing $(C_5Me_5)_2UCl_2$ as shown in Eq. (9). However, since the $(C_5Me_5)_2UCl_2$ byproduct can be reduced to the starting material with Na/Hg, as shown in Eq. (8) [53], the use of $(C_5Me_5)_2UCl_2Na$ with an external reductant-like Na/Hg can remove the byproduct and cleanly provide only the desired product, Eq. (11) and Scheme 2 [53].



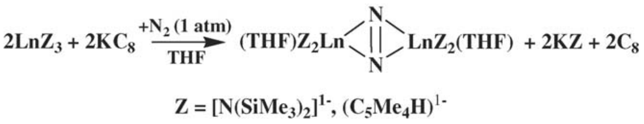
(11)

The formal half reaction for this process is given in Eq. (12). The net reaction starts with

$$(C_5Me_5)_2UCl_2 + 2Na/Hg \rightarrow [(C_5Me_5)_2U]^{2+} + 2e^{1-} + 2NaCl + 2Hg \quad (12)$$

tetravalent $(C_5Me_5)_2UCl_2$, involves two equivalents of external reductant, effects a two electron reduction, and returns a tetravalent uranium product. Starting with $(C_5Me_5)_2UCl_2$ [56] is advantageous since it avoids the multi-step synthesis of $[(C_5Me_5)_2UCl]_3$ [52,53].

The overall reactions in Eqs. (11) and (12) are similar to the LnZ_3/K and LnZ_2Z'/K reactions recently developed for lanthanides, Eqs. (13) and (14) [21–23]. The reduction



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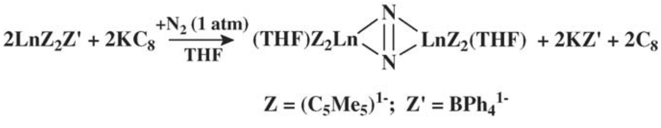


(14)

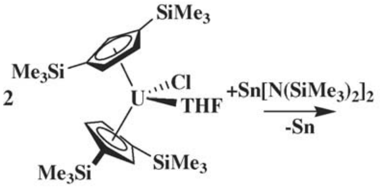
capacity is provided by the alkali metal and an alkali metal salt is eliminated.

Other types of U^{3+} alkali metal "ate" salts are known and participate in U^{3+}-based reductive chemistry. A phosphide analog of $(C_5Me_5)_2UCl_2Na$, namely $(C_5Me_5)_2U(PPh_2)_2K$, obtained from $(C_5Me_5)_2U(PPh_2)_2$ and KH, reduces $TlBPh_4$ to form Tl and the $(C_5Me_5)_2U(PPh_2)_2$ precursor [165]. The mixed metal complex, $[K(18\text{-crown-}6)]\{(C_5Me_5)_2U(Cl)[ReH_6(PPh_3)_2]\}$, obtained from $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$ and $[(C_5Me_5)_2UCl]_3$ [57], also has a U^{3+}/U^{4+} redox couple and reduces $TlBPh_4$ to form Tl and $\{(C_5Me_5)_2U(Cl)[ReH_6(PPh_3)_2]\}[BPh_4]$ [57].

The U^{3+} thiolate analogs of $(C_5Me_5)_2UCl_2Na$, namely $(C_5Me_5)_2U(SR)_2Na$, (R = Me, ^{i}Pr, ^{t}Bu, Ph), obtained from $(C_5Me_5)_2U(SR)_2$ by Na(Hg) reduction, have an interesting chemistry involving both C–S and C–H bond cleavage [166,167]. Complexes such as $[Na(18\text{-crown-}6)][(C_5Me_5)_2U(S^iPr)_2]$, which has been crystallographically characterized, react with $AgBPh_4$ to make their U^{4+} precursors, in this case $(C_5Me_5)_2U(S^iPr)_2$, as in the other systems above. However, upon heating to 65 °C, the $(C_5Me_5)_2U(SR)_2Na$ complexes can form U^{4+} sulfide and metallothiocyclopropane complexes, $[(18\text{-crown-}6)Na][(\mu\text{-}S)U(C_5Me_5)_2(S^tBu)]$, and $[Na(18\text{-crown-}6)(THF)_2][(C_5Me_5)_2U(SMe)(\eta^2\text{-}CH_2S)]$, respectively. Both complexes were crystallographically characterized, but mechanistic details were obscured by the formation of side products. Hydrocarbon side products such as isobutene and isobutane from the ^{t}BuS reactions, propene, propane, and 2,3-dimethylbutane from the ^{i}PrS reactions, and methane from the MeS reactions were observed. These U^{3+} thiolate complexes were much more reactive than their U^{4+} counterparts in terms of S-element activation reactions. The presence of 18-crown-6 was found to increase the stability of the U^{3+} ate salts.

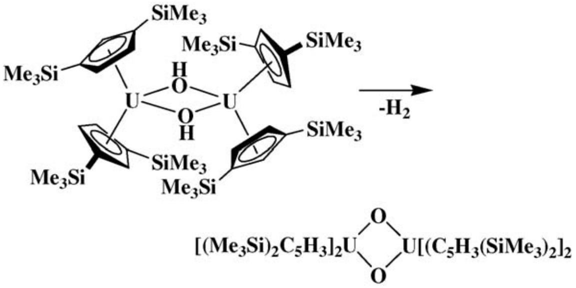
5.4. $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U(\mu\text{-}X)\}_x$

The entire series of $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U(\mu\text{-}X)\}_x$ (X = F, Cl, Br, I) [58–60] complexes is available as well as the aryloxide and hydroxide analogs, $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U[\mu\text{-}OC_6H_3{}^iPr_2\text{-}2,6](THF)$ [59] and $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U(\mu\text{-}OH)\}_x$ [61]. The reduction chemistry of these $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U(\mu\text{-}X)\}_x$ complexes has been less heavily studied than that of the $(C_5Me_5)^{1-}$ analogs. However, an unusual reduction of $Sn[N(SiMe_3)_2]_2$, a reagent that itself is usually a reductant, by $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UCl(THF)$ has been reported. The products of this reaction are $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2UCl[N(SiMe_3)_2]$ and presumably Sn metal, Eq. (15) [58,59].



(15)

The $\{[1,3\text{-}(Me_3Si)_2C_5H_3]_2U(\mu\text{-}OH)\}_2$ and $\{[1,3\text{-}(Me_3C)_2C_5H_3]_2U(\mu\text{-}OH)\}_2$ complexes [61] undergo an unusual oxidative elimination of hydrogen. Specifically, the trivalent uranium hydroxide $[U(\mu\text{-}OH)_2U]^{4+}$ unit is converted to a tetravalent uranium oxide $[U(\mu\text{-}O)_2U]^{4+}$ group and hydrogen, Eq. (16) [61]. Temperatures of 100 °C are needed to get reasonable rates for this reaction. The mechanism is not known, but a $[U(OH)_2U]^{4+}$ to $[(H)U(\mu\text{-}O)(\mu\text{-}OH)U]^{4+}$ conversion with a tetravalent hydride intermediate is postulated.



(16)

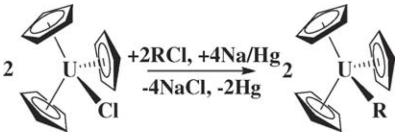
5.5. $(C_5H_4R)_3U$ and $(C_5Me_4H)_3U$

Another class of organometallic U^{3+} complexes whose reductive chemistry has been extensively investigated involves the $(C_5H_4R)_3U$ complexes (R = H [62,63], Me [64], CMe_3[65], and $SiMe_3$ [64]). In contrast to the $(C_5Me_5)_2UCl(THF)$ reductant, which makes bis(cyclopentadienyl) $(C_5Me_5)_2UClX$ and $(C_5Me_5)_2UClR$ products from alkyl halides, the $(C_5H_4R)_3U$ complexes often react in a 2:1 stoichiometry to make equimolar mixtures of tris(cyclopentadienyl) $(C_5H_4R)_3UX$ and $(C_5H_4R)_3UR$ compounds. With substrates that can be reduced to dianions, the $(C_5H_4R)_3U$ complexes form bridged bimetallic $[(C_5H_4R)_3U]_2$(substrate dianion) products instead of the mixtures of $(C_5Me_5)_2U$(reduced substrate) and $(C_5Me_5)_2UCl_2$ products, shown in Eqs. (4)–(6), which form from reactions using $(C_5Me_5)_2UCl(THF)$.

$(C_5H_5)_3U(THF)$ reacts with a variety of organic halides [66]. Since these reactions proceed slower in THF than in benzene, initial THF dissociation is postulated as in the $(C_5Me_5)_2UCl(THF)$ reactions, Scheme 1. Again a halide abstraction is thought to occur, in this case to form $(C_5H_5)_3UX$ and $R^{\bullet}$. In this tris(cyclopentadienyl) case, the radicals were found to react cleanly with additional starting material such that an equimolar mixture of $(C_5H_5)_3UX$ and $(C_5H_5)_3UR$ was obtained with MeI, ^{n}BuX (X = Cl, Br, I), $^{i}PrCl$, $PhCH_2Cl$, and allyl chloride, Eq. (17) [66].

(17)

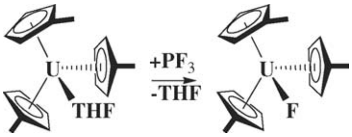
Since $(C_5H_5)_3U$ can be made from $(C_5H_5)_3UCl$ [67] and Na/Hg [68], the reductions in Eq. (17) can be effected by starting with the latter two reagents. When two equivalents of Na/Hg are used per $(C_5H_5)_3UCl$, the $(C_5H_5)_3UCl$ byproduct of Eq. (17) gets reduced. This provides a clean synthesis of $(C_5H_5)_3UR$ via the net reaction shown in Eq. (18) [66].



(18)

The use of two equivalents of an external reductant with a tetravalent precursor is similar to Scheme 2.

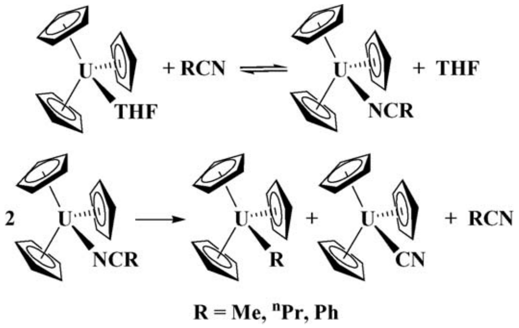
A more unusual route to a tris(cyclopentadienyl) uranium halide was found in the reaction of $(C_5H_4Me)_3U(THF)$ with PF_3, Eq. (19) [69]. The $(C_5H_4Me)_3UF$ product was synthesized in 19% yield by this route.



(19)

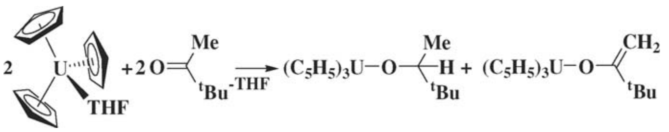
Tris(cyclopentadienyl) uranium complexes also reduce nitriles such as PhCN and MeCN to form mixtures of the alkyl $(C_5H_5)_3UR$ and cyanide $(C_5H_5)_3U(CN)$ products, Scheme 3 [70]. Since cyanide is a pseudohalide, these reactions may be closely related to the alkyl halide reactions.

The reactivity of $(C_5H_5)_3U(THF)$ with a variety of ketones, such as acetone, cyclohexanone, and *tert*-butyl methyl ketone, has been examined and provides another example of a case in which single electron transfer to coordinated substrate can occur [71]. The products of these reactions are mixtures of uranium alkoxides and uranium enolates, Eq. (20) [71]. These products



Scheme 3.

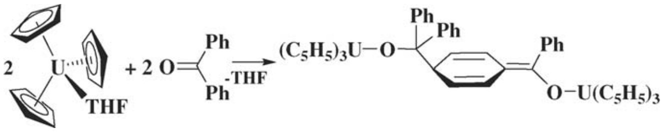
can arise as the result of radical



(20)

disproportionation of the U^{4+} complex of the radical anion, $(RR'CO\bullet)^{1-}$, initially formed. Reactions similar to Eq. (20) were also observed with acetone and cyclohexanone [71].

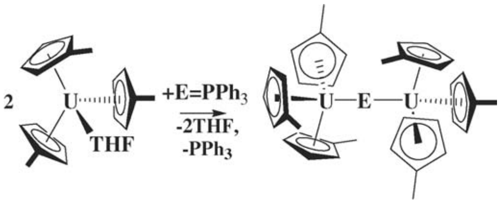
With aromatic ketones, such as benzophenone, $(C_5H_5)_3U(THF)$ reacts to form a carbon–carbon coupling product, Eq. (21) [72]. Reactions of $(C_5H_5)_3U(THF)$ with



(21)

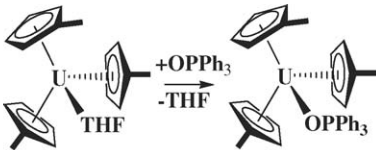
benzaldehyde and with aryl ketones, PhCOR (R = H, Me, ^{i}Pr, ^{t}Bu), are similar [72].

Reactions of $(C_5H_4Me)_3U$ with E=PPh$_3$ substrates (E = S, Se, Te) effect E=P cleavage to form bimetallic $[(C_5H_4Me)_3U]_2(\mu\text{-}E)$ complexes of the E^{2-} ion, Eq. (22) [73].



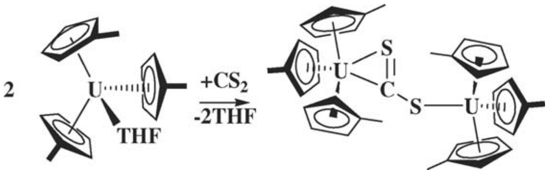
(22)

Although the analogous product of the O=PPh$_3$ reaction would have favorable U–O bonds, this reagent only forms an adduct in the room temperature reaction, Eq. (23) [73].



(23)

Two equivalents of $(C_5H_4Me)_3U$ will form an identical $[(C_5H_4Me)_3U]_2(\mu\text{-}S)$ product from OCS [73], but the reaction with CS$_2$ forms an unusual carbon disulfide dianion product, $[(C_5H_4Me)_3U]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CS_2)$ Eq. (24) [64]. $(C_5H_4SiMe_3)_3U$ reacts similarly with CS$_2$ [64].

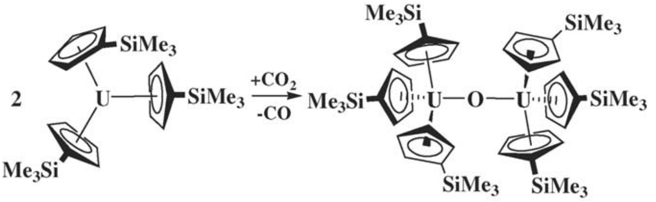


(24)

In a reaction similar to Eq. (24), $(C_5H_4Me)_3U$ reduces PhNCO by two electrons to generate a bimetallic $(PhNCO)^{2-}$ product, Eq. (25) [74].

(25)

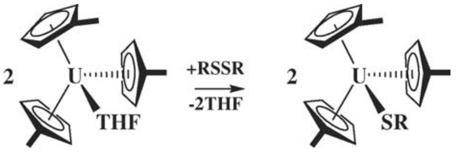
In contrast to these reactions, $(C_5H_4SiMe_3)_3U$ reacts with CO$_2$ to make the oxide $[(C_5H_4SiMe_3)_3U]_2(\mu\text{-}O)$, Eq. (26) [75]. The same oxide product was isolated from the reduction of N$_2$O.



(26)

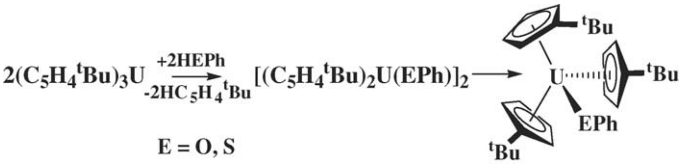
The analogous $[(C_5H_5)_3U]_2(\mu\text{-}O)$ oxide has been made by gentle oxidation of $(C_5H_5)_3U(THF)$ with a stoichiometric amount of anhydrous O$_2$ [76]. $[(C_5H_5)_3U]_2(\mu\text{-}O)$ can also be made by rapid sublimation of $(C_5H_5)_3U(OH)$ or from a reaction between $(C_5H_5)_4U$ and half an equivalent of H$_2$O [76].

$(C_5H_4Me)_3U$ complexes also form uranium chalcogen complexes by reductive cleavage of S–S bonds of disulfides, RSSR (R = ^{i}Pr, ^{t}Bu, Ph) Eq. (27) [77].



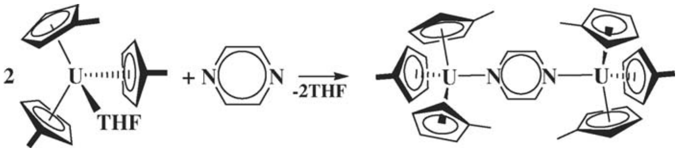
(27)

$(C_5H_4Me)_3U(SR)$ thiolates, as well as the analogous aryloxide products, can also be accessed using REH (E = S, O) substrates [65]. The reaction of $(C_5H_4{}^tBu)_3U$ with HEPh is proposed to involve protonation of the $(C_5H_4{}^tBu)^{1-}$ anion to form a bimetallic bridged dimer, $[(C_5H_4{}^tBu)_2U(SPh)]_2$, that undergoes a subsequent ligand redistribution to form $(C_5H_4{}^tBu)_3U(SPh)$, Eq. (28) [65].



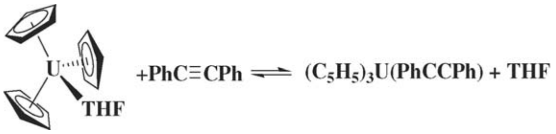
(28)

Another example of the use of two equivalents of $(C_5H_4R)_3U(THF)$ effecting two electron reductions involves pyrazine as a substrate. In this case, bridging pyrazine dianions are formed, Eq. (29) [78].



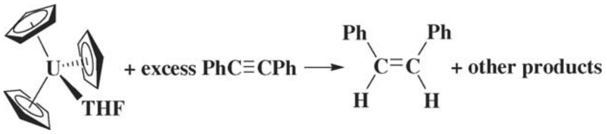
(29)

In the reaction of $(C_5H_5)_3U(THF)$ with PhC≡CPh, an alkyne complex of formula $(C_5H_5)_3U(PhC{\equiv}CPh)$ is observed by NMR spectroscopy to be in equilibrium with the starting material, Eq. (30) [79]. In the presence of excess PhC≡CPh, the system



(30)

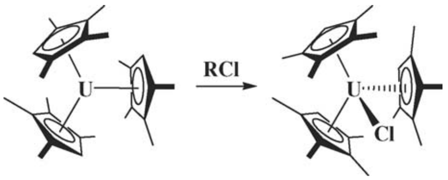
generates *cis*-stilbene and an undefined uranium complex, Eq. (31). Labeling



(31)

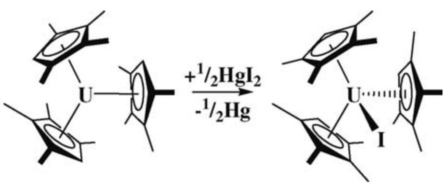
experiments indicated that the solvent does not provide the hydrogen that was added to the PhC≡CPh substrate. Abstraction of hydrogen from a $(C_5H_5)^{1-}$ ligand is suggested to explain the reactivity [79].

The tetramethylcyclopentadienyl analog of the complexes discussed above, $(C_5Me_4H)_3U$, reacts with ^{t}BuCl and PhX (X = Cl, I) to form the $(C_5Me_4H)_3UX$ products as opposed to 1:1 mixtures of uranium halides and alkyls, Eq. (32) [80]. With the



(32)

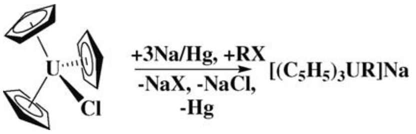
halobenzene substrates, biphenyl was observed as the major byproduct. The $(C_5Me_4H)_3UX$ complexes can also be synthesized by reduction of mercuric halides, Eq. (33) [80].



(33)

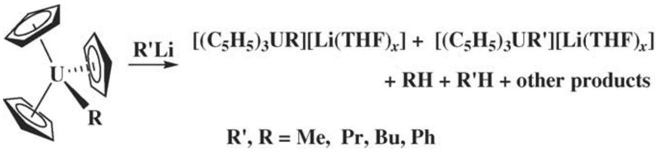
5.6. $[(C_5H_5)_3UR]^{1-}$

A class of compounds that is a hybrid of the $(C_5Me_5)_2UCl_2Na$ and $(C_5H_4R)_3U$ series involves the U^{3+} alkyl anions, $[(C_5H_5)_3UR]^{1-}$. These complexes are made by (a) Na/Hg reduction of $(C_5H_5)_3UR$ [68], (b) the reduction of $(C_5H_5)_3UCl$ with three equivalents of Na/Hg in the presence of RX, Eq. (34), (see Eq. (18)) [66] and (c)



(34)

addition of LiR to $(C_5H_4R)_3U$ [81,82] or $(C_5H_5)_3UR$ [83,84]. The last starting material is particularly interesting in that it shows that reductants such as butyl anions can generate U^{3+} complexes with the proper ligand set, Eq. (35). NMR studies show that



(35)

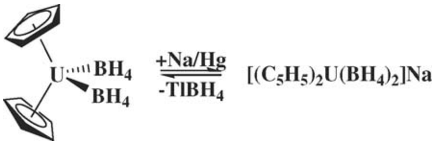
these $[(C_5H_5)_3UR]^{1-}$ complexes react with alkyl halides, R′X, to make $(C_5H_5)_3UR$ and $(C_5H_5)_3UR'$ products and presumably MX. Despite the halophilicity of organo-f-element complexes, no $(C_5H_5)_3UX$ complexes were observed, Eq. (36) [85].

$$[(C_5H_5)_3UR]Na + R'X \rightarrow (C_5H_5)_3UR' + (C_5H_5)_3UR + \text{other products} \qquad (36)$$

$[(C_5H_4R)_3UR']^{1-}$ complexes in which R′ = H are also known [86,87,168] and undergo redox chemistry with oxidants. Hence, $[Na(18\text{-crown-}6)][(C_5H_4R)_3UH]$ reacts with $TlBPh_4$ to make $(C_5H_4R)_3UH$ (R = $SiMe_3$ and CMe_3) [87]. The azide analog, $[Na(18\text{-crown-}6)][(C_5H_4SiMe_3)_3U(N_3)]$, is also known and reduces $TlBPh_4$ to make the analogous tetravalent product, $(C_5H_4SiMe_3)_3U(N_3)$ [169]. In the azide case, a bimetallic U^{3+} bridged complex, $[Na(18\text{-crown-}6)][C_5H_4SiMe_3)_3U(N_3)U(C_5H_4SiMe_3)_3]$, is known that will reduce $TlBPh_4$ to the mixed valent product, $(C_5H_4SiMe_3)_3U(N_3)U(C_5H_4SiMe_3)_3$.

5.7. $[(C_5H_5)_2U(BH_4)_2]^{1-}$

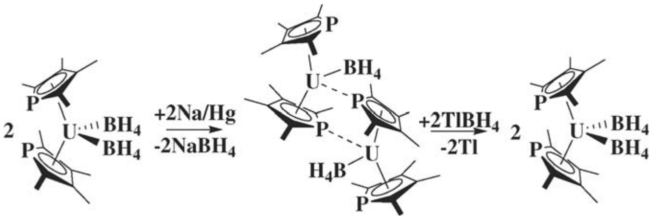
Another anionic cyclopentadienyl complex of trivalent uranium known to react as a one electron reductant is the sodium salt of bis(cyclopentadienyl)uranium bis(tetrahydroborate), $[(C_5H_5)_2U(BH_4)_2]Na$ [88]. Like the bis-chloride sodium "ate" salt analog, $(C_5Me_5)_2UCl_2Na$, the $(C_5H_5)_2U(BH_4)_2Na$ complex can be prepared by reduction $(C_5H_5)_2U(BH_4)_2$ with sodium amalgam, Eq. (37). These $[(C_5H_5)_2U(BH_4)_2]^{n-}$ complexes are



(37)

special in that they represent a rare case of uranium metallocenes of simple $(C_5H_5)^{1-}$ ligands that are stable to ligand redistribution. This may be related to the nature of the polydentate $(BH_4)^{1-}$ ligands. The $(C_5H_5)_2U(BH_4)_2Na$ complex reacts as a one electron reductant with $TlBH_4$ to regenerate the precursor $(C_5H_5)_2U(BH_4)_2$, Eq. (37) [88].

In contrast, the peralkylated phosphorus analogue, $(C_4Me_4P)_2U(BH_4)_2$, is reduced with Na/Hg to $[(C_4Me_4P)_2U(BH_4)]_2$ and the $NaBH_4$ adduct is not retained, Eq. (38) [89].

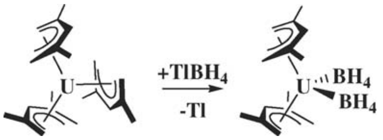


(38)

This trivalent complex can also be oxidized with $TlBH_4$ to reform $(C_4Me_4P)_2U(BH_4)_2$, Eq. (38) [89].

5.8. 2,4-Dimethylpentadienyl complexes

The homoleptic open dimethylpentadienyl U^{3+} complex, $[CH_2C(Me)CHC(Me)CH_2]_3U$, reduces Tl^{1+} to Tl^0 with the formation of a U^{4+} product, Eq. (39). However, in this case, the isolated reduction product is not a tris(pentadienyl) compound but rather a bis(pentadienyl) complex, evidently formed by ligand redistribution [88,90].



(39)

5.9. $(C_5Me_5)(C_8H_8)U(THF)$

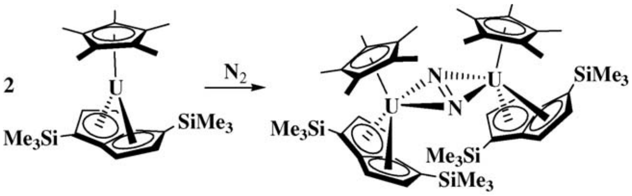
$(C_5Me_5)(C_8H_8)U(THF)$ [91] is a mixed ligand U^{3+} metallocene that also has the potential to react in a manner similar to $(C_5Me_5)_2UCl(THF)$. In this complex, one of the ancillary ligands is a dianion and the analogous Cl^{1-} ligand redistribution reactions described earlier in Eqs. (4)–(7) are not possible. However, it seems likely that $(C_8H_8)^{2-}$ redistribution reactions to form the stable tetravalent $(C_8H_8)_2U$ complex [35,92] could occur following reduction. Interestingly, when $(C_5Me_5)(C_8H_8)U(THF)$ reacts with 1,3,5,7-C_8H_8, it does not form $(C_8H_8)_2U$, but $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$ is isolated instead, Eq. (40) [93]. Under these conditions, this product does not ligand redistribute to $(C_8H_8)_2U$.

(40)

Although the THF ligand in $(C_5Me_5)U(C_8H_8)(THF)$ can be displaced with dimethylbipyridine, no evidence for reduction was observed [91]. The reaction of $(C_5Me_5)(C_8H_8)U(THF)$ with CS_2 to form a $(CS_2)^{2-}$ product, $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CS_2)$, has also been mentioned in the literature [94].

5.10. $(C_5Me_5)U[C_8H_4(SiMe_3)_2]$

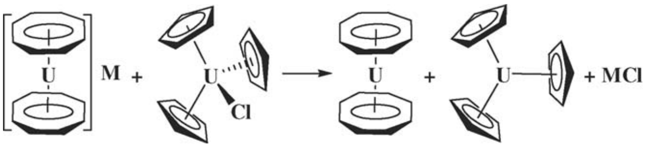
The pentamethylcyclopentadienyl bis(tri-isopropylsilyl)-pentalene complex, $(C_5Me_5)U(C_8H_4R_2)$ ($R = Si^iPr_3$), is a potent enough U^{3+} reductant to reduce dinitrogen. A bimetallic complex is formed, $[(C_5Me_5)U(C_8H_4R_2)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, that has an NN distance of 1.23(1) Å, Eq. (41) [95]. This structural feature along with a DFT calculation indicates that the product is a U^{4+} complex of an $(N_2)^{2-}$ ligand [96]. Hence, a two electron reduction of dinitrogen has been accomplished by the two U^{3+} centers. An unusual feature of this reduction product is that the complex loses the dinitrogen ligand to revert back to the U^{3+} starting material. This is not uncommon in lanthanide dinitrogen reduction chemistry [97–99], but it is only rarely observed in U^{4+}/U^{3+} chemistry (e.g. references [56,100,101]).



(41)

5.11. $[(C_8H_8)_2U]^{1-}$

Highly reactive bis(cyclooctatetraenyl) complexes of trivalent uranium, $[(C_8H_8)_2U]M$ (M = Li, K), can be obtained from reduction of uranocene [35,92] using lithium naphthalenide [102] or potassium [103]. The reduction chemistry of these complexes has not been extensively investigated perhaps because oxidation of $[(C_8H_8)_2U]M$ typically forms $(C_8H_8)_2U$ rather than a U^{4+} complex that can incorporate a reduced substrate. The lithium naphthalenide/$U(C_8H_8)_2$ reduction product has been reported to reduce $(C_5H_5)_3UCl$ to $(C_5H_5)_3U$, which demonstrates that U^{3+} in a cyclooctatetraenyl environment is more reducing than it is in a tris(cyclopentadienyl) environment [102], e.g. Eq. (42) (M = Li).



(42)

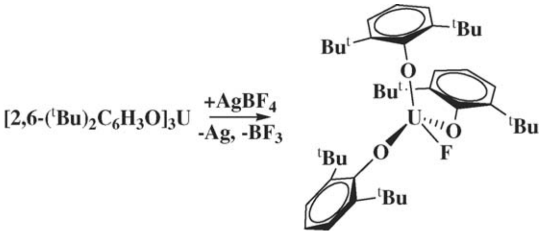
5.12. *$(C_5Me_5)UI_2(THF)_3$*

Bridging the transition from U^{3+} complexes of cyclopentadienyl, cyclooctatetraenyl, and related ligands to compounds supported solely by inorganic ligands is the mono(cyclopentadienyl) diiodide complex, $(C_5Me_5)UI_2(THF)_3$, that can be synthesized from KC_5Me_5 and $UI_3(THF)_4$ [104]. $(C_5Me_5)UI_2(THF)_3$ reduces CS_2 and is proposed to initially form $[(C_5Me_5)UI_2(THF)_3]_2S$. This intermediate decomposes to form the cluster $[(C_5Me_5)UI]_3(\mu\text{-}I)_3(\mu_3\text{-}I)(\mu_3\text{-}S)$, Eq. (43) [94].

$$(C_5Me_5)UI_2(THF)_3 \xrightarrow{CS_2} [(C_5Me_5)UI_2]_2S \rightarrow [(C_5Me_5)UI]_3(\mu\text{-}I)_3(\mu_3\text{-}I)(\mu_3\text{-}S) \quad (43)$$

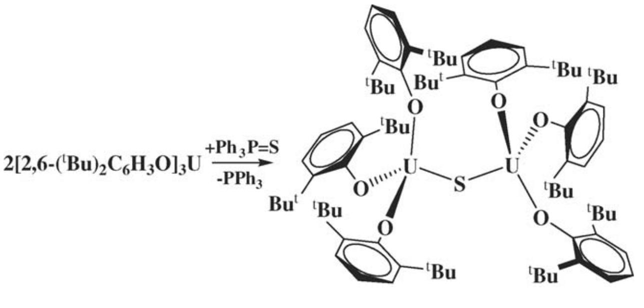
5.13. *$(2,6\text{-}^tBu_2C_6H_3O)_3U$*

Like the tris(cyclopentadienyl) complexes described above, the homoleptic aryloxide complex, $(2,6\text{-}^tBu_2C_6H_3O)_3U$, reduces substrates to form both mono and bimetallic products [47]. One equivalent of this compound reacts with $AgBF_4$ to produce $(2,6\text{-}^tBu_2C_6H_3O)_3UF$ via a one electron process, Eq. (44). $(2,6\text{-}^tBu_2C_6H_3O)_3U$ will also reduce benzyl chloride, $AgPF_6$, PCl_5, AgBr, CBr_4, PBr_5, and I_2 to form the corresponding $(2,6\text{-}^tBu_2C_6H_3O)_3UX$ products (X = F, Cl, Br, I). In the case of CI_4, the product isolated is the diiodide, $(2,6\text{-}^tBu_2C_6H_3O)_2UI_2(THF)$, which is thought to form through ligand redistribution involving a $(2,6\text{-}^tBu_2C_6H_3O)_3UI$ intermediate.



(44)

Two equivalents of $(2,6\text{-}^tBu_2C_6H_3O)_3U$ reduce reagents containing sulfur, such as COS and $Ph_3P{=}S$, to the $(S)^{2-}$ dianion [47]. Reagents containing oxygen, e.g. N_2O, NO, Me_3NO, pyNO are reduced to complexes of the $(O)^{2-}$ oxide ligand. $[(2,6\text{-}^tBu_2C_6H_3O)_3U]_2E$ (E = S, O) complexes are isolated from these reactions, e.g. Eq. (45).

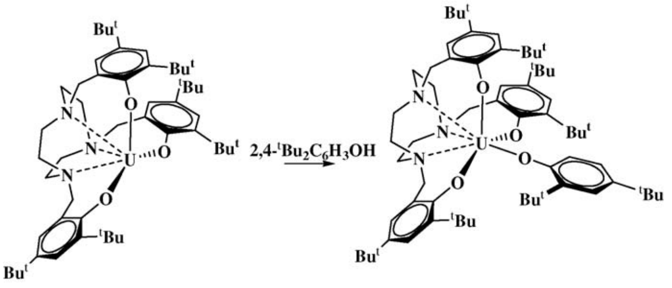


(45)

5.14. *$[(ArO)_3tacn]U$*

Another type of tris(aryloxide) uranium coordination environment is available using the triazacyclononane anchored ligands, 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (abbreviated $[(^tBu_2C_6H_2O)_3tacn]$) [105] and its analog with an adamantyl group replacing the *tert*-butyl in the 3 position (abbreviated $\{[(^tBu)(Ad)C_6H_2O]_3tacn\}U$) [106]. These ligands provide three aryloxide groups ligated to U^{3+} as well as three more distant chelated nitrogen donor atoms which block one side of the metal. As a result, the U^{3+} ion is most easily accessed by substrates along a single axial site.

Attempts to crystallize the $[(^tBu_2C_6H_2O)_3tacn]U$ complex from Et_2O and THF resulted in the formation of a di-*tert*-butyl aryloxide U^{4+} derivative, $[(^tBu_2C_6H_2O)_3tacn]U(OC_6H_2{}^tBu_2)$, Eq. (46), and the bimetallic oxide $\{[(^tBu_2C_6H_2O)_3tacn]U\}_2O$, Eq. (47) [107]. Since the latter, bridged-oxo complex can be isolated, it appears that the steric bulk of the $[(^tBu_2C_6H_2O)_3 tacn]^{3-}$ ligand is not sufficient to prevent dimerization. In this sense, it is similar to the tris-aryloxide ligand set in $[(2,6\text{-}^tBu_2C_6H_3O)_3U]_2(\mu\text{-}E)$, E = O, Se [47], discussed above. Similar bimetallic, oxide-bridged U^{4+} complexes containing the $[N(CH_2CH_2NSiMe_2{}^tBu)_3]^{3-}$ [108] ligand or three $(C_5H_5)^{1-}$ [76] or $(C_5H_4SiMe_3)^{1-}$ [75] ligands per uranium have also been isolated.



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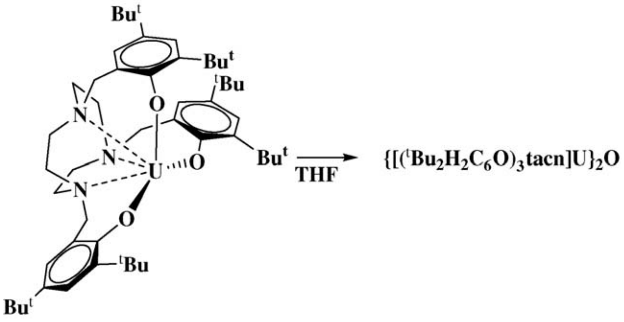
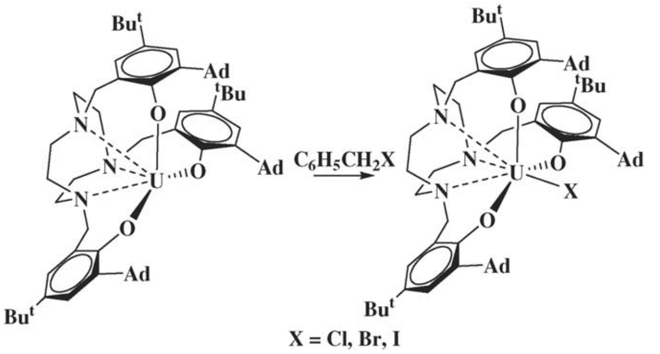


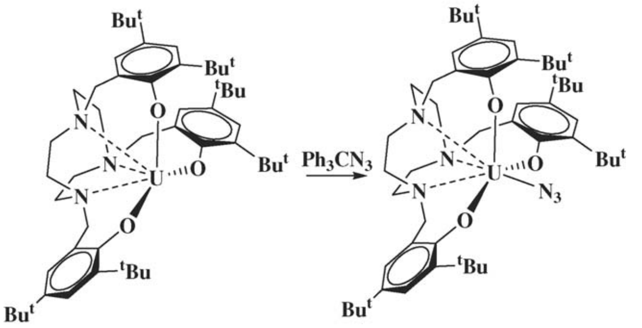
(47)

The adamantyl derivative, $\{[(^tBu)(Ad)C_6H_2O]_3tacn\}U$ reacts with benzyl chloride, benzyl bromide, and iodine to make the U^{4+} halides, $\{[(^tBu)(Ad)C_6H_2O]_3tacn\}UX$ (X = Cl, Br, I), Eq. (48) [109].



(48)

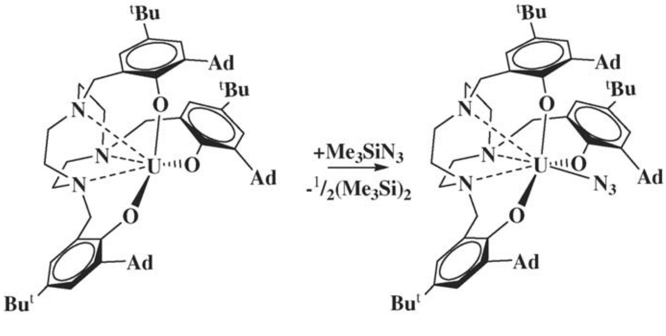
The reactions of [(ArO)$_3$tacn]U complexes with organic azides are heavily dependent on the identity of the organic azide as well as the substituents of the aryloxide. The di-*tert*-butyl substituted complex, [(^{t}Bu$_2$C$_6$H$_2$O)$_3$tacn]U, reacts with trityl azide to form the U^{4+} azide product, [(^{t}Bu$_2$C$_6$H$_2$O)$_3$tacn]U(N$_3$), as depicted in Eq. (49) [110].



(49)

However, reaction of [(^{t}Bu$_2$C$_6$H$_2$O)$_3$tacn]U with trimethylsilylazide makes a mixture of the uranium azide, [(^{t}Bu$_2$C$_6$H$_2$O)$_3$tacn]U(N$_3$), and a U^{5+} imido complex, [(^{t}Bu$_2$C$_6$H$_2$O)$_3$tacn]U[N(SiMe$_3$)]. The latter complex, which is the major product, forms by a two electron process that is discussed in Section 6.

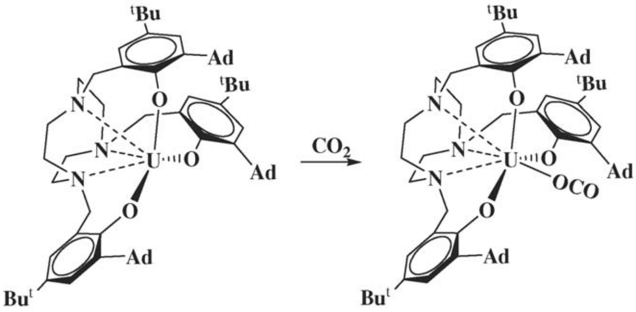
When the steric bulk of the aryloxide substituents is increased by using {[(^{t}Bu)(Ad)C$_6$H$_2$O]$_3$tacn}U, the reaction with Me$_3$SiN$_3$ forms the uranium azide complex, {[(^{t}Bu)(Ad)C$_6$H$_2$O]$_3$tacn}U(N$_3$) along with (Me$_3$Si)$_2$, Eq. (50) [109].



(50)

The two azide products in Eqs. (49) and (50) are unusual in that the di-*tert*-butyl complex has a U–N–N angle of 145.9(9)°, but the *tert*-butyl adamantyl analog has a 175.6(3)° angle.

The most spectacular chemistry obtained to date for this ligand system involves the reaction of {[(^{t}Bu)(Ad)C$_6$H$_2$O]$_3$tacn}U with CO$_2$, Eq. (51), [109].

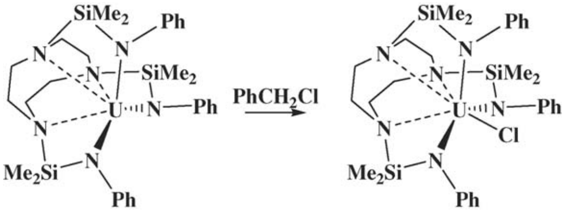


(51)

The product of this reaction, {[(^{t}Bu)(Ad)C$_6$H$_2$O]$_3$tacn}U(OCO), analyzes as a U^{4+} complex of a (OCO)$^{1-}$ monoanion. This complex represents the first example of a linear (OCO)$^{1-}$ anionic complex [109].

5.15. [(PhNSiMe$_2$)$_3$tacn]U

The triazacyclononane skeleton has also been used to make a trisamido coordination geometry [111] used to ligate the U^{3+} ion [112]. This [(PhNSiMe$_2$)$_3$tacn]U complex reacts with benzyl chloride to make [(PhNSiMe$_2$)$_3$tacn]UCl, Eq. (52), and with iodine to make the [(PhNSiMe$_2$)$_3$tacn]UI [112].



(52)

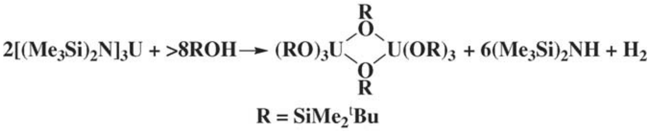
The chloride complex can be made in much higher yield by the reaction of [(PhNSiMe$_2$)$_3$tacn]Na$_3$ with UCl$_4$.

5.16. [(Me$_3$Si)$_2$N]$_3$U

Relatively few reductions have been done with [(Me$_3$Si)$_2$N]$_3$U despite that fact that it was one of the earliest identified U^{3+} complexes [113]. Perhaps, it has been assumed that the steric bulk of the bis(trimethylsilylamide) ligand provides steric crowding that might interfere with the formation of [(Me$_3$Si)$_2$N]$_3$UX complexes. However, the isolation of the *N*-heterocyclic carbene complex, [(Me$_3$Si)$_2$N]$_3$U[C(NMeCMe)$_2$] [106], and the tetrakis(amide), {[(Me$_3$Si)$_2$N]$_4$U}[K(THF)$_6$] [22], shows that there is ample space to coordinate a fourth bulky ligand to a uranium ion that is already ligated by three [(Me$_3$Si)$_2$N]$^{1-}$ anions.

It has been reported that [(Me$_3$Si)$_2$N]$_3$U will reduce AgF to make [(Me$_3$Si)$_2$N]$_3$UF [47]. Additionally, reaction of

$[(Me_3Si)_2N]_3U$ with excess $HOSiMe_2{}^tBu$ results in the formation of the U^{4+} containing bimetallic siloxide complex, $[({}^tBuMe_2SiO)_3U(\mu\text{-}OSiMe_2{}^tBu)]_2$, Eq. (53) [114]. Hydrogen is assumed to be the byproduct in this reaction.



(53)

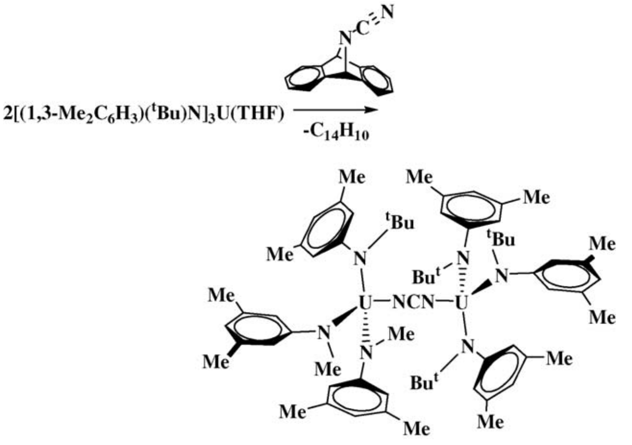
5.17. $[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3U(THF)$

In contrast to the reaction between $UI_3(THF)_4$ and $KN(SiMe_3)_2$ that affords the trivalent $[(Me_3Si)_2N]_3U$ complex, a similar reaction between $UI_3(THF)_4$ and the arylamide $LiN({}^tBu)(C_6H_3Me_2\text{-}3,5)$ generates the tetravalent complex, $[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3UI$ [115]. A disproportionation reaction to form one equivalent of uranium metal and three U^{4+} ions is inferred from the optimized stoichiometry for this reaction as depicted in Eq. (54). Despite this complication the trivalent uranium amide,

$$\tfrac{4}{3}UI_3(THF) + 3LiN({}^tBu)(C_6H_3Me_2\text{-}1,3) \rightarrow [(1,3\text{-}Me_2H_3C_6)({}^tBu)N]_3UI + \tfrac{1}{3}U^0 + 3LiI \quad (54)$$

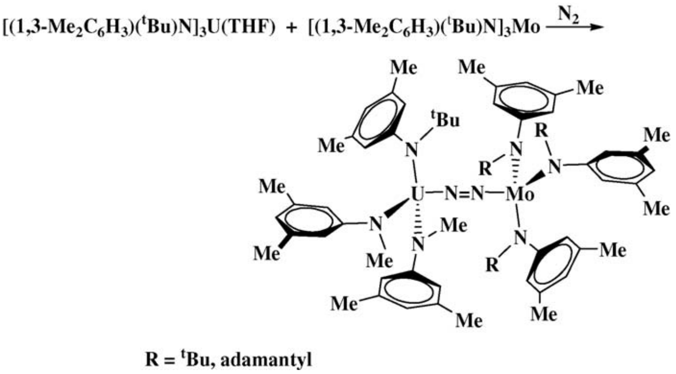
$[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]U(THF)$, was successfully isolated upon reduction of $[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3UI$ with Na/Hg.

The reaction of two equivalents of $[(3,5,\text{-}Me_2C_6H_3)({}^tBu)N]_3U$ with the cyanoimide transfer reagent, $(NCN)C_{14}H_{10}$, generates a bimetallic tetravalent uranium complex of the unusual $(\mu\text{-}\eta^1{:}\eta^1\text{-}NCN)^{2-}$ ligand, $\{[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3U\}_2(NCN)$, and anthracene, Eq. (55) [116].



(55)

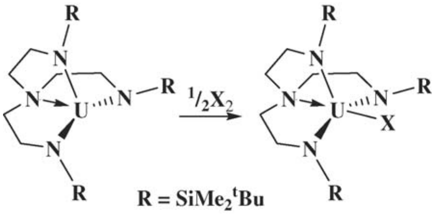
Although no detectable reactivity of $[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3U(THF)$ was observed with dinitrogen, hetrodinuclear complexes of N_2 form upon addition of $[(3,5\text{-}Me_2C_6H_3)RN]_3Mo$ (R = ${}^tBu$, adamantyl), Eq. (56) [115]. The structural parameters and infrared spectroscopy of the resulting $[(3,5\text{-}Me_2C_6H_3)({}^tBu)N]_3U\text{-}(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)\text{-}Mo[NR(C_6H_3Me_2\text{-}3,5)]_3$ complexes were consistent with the formation of U^{4+} and Mo^{4+} accompanied by reduction of dinitrogen to $(N_2)^{2-}$ [115].



(56)

5.18. $[N(CH_2CH_2NSiMe_2{}^tBu)_3]U$

U^{3+} reduction chemistry has also been explored with the polydentate amide/amine coordination environment provided by the trianionic ligand, $[N(CH_2CH_2NSiMe_2{}^tBu)_3]^{3-}$, abbreviated $(NN'_3)^{3-}$ [117]. This U^{3+} system seems to be very sensitive to the substituents since $[N(CH_2CH_2NR)_3]^{3-}$ ligands in which R = Me_3Si and $MePh_2Si$ did not lead to trivalent species [117]. $(NN'_3)U$ reacts with oxidizing agents such as Cl_2, Br_2, and I_2 to form $(NN'_3)UX$ (X = Cl, Br, I), Eq. (57) [108]. $(NN'_3)UCl$ can also be prepared by reduction of chloroform, Eq. (58) [108]. Although $(NN'_3)U$ reacts with alkyl and aryl disulfides and diselenides, REER, specific $(NN'_3)UER$ products were not identified among the mixture of products [108]. $(NN'_3)U$ reacts with half an equivalent of Me_3NO to form the oxide-bridged bimetallic $[(NN'_3)U]_2O$, Eq. (59) [108].



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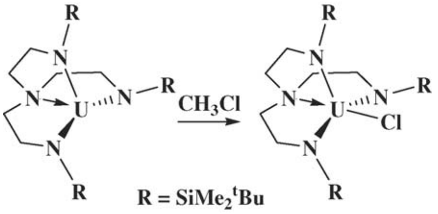

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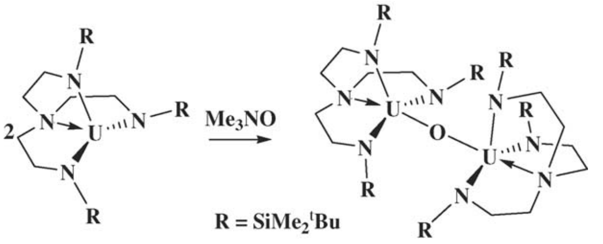
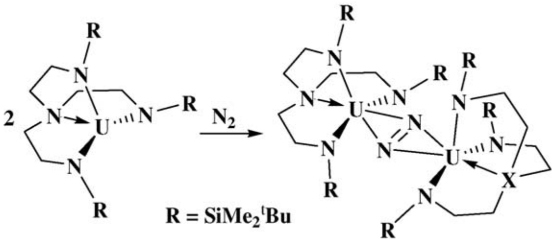


(59)

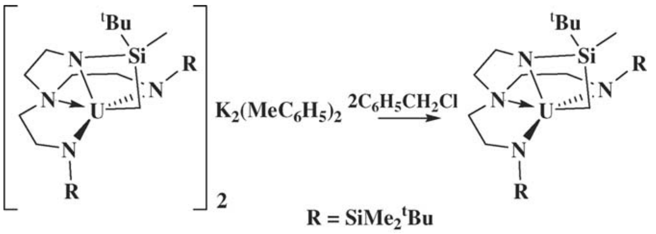
$(\mathrm{NN'}_3)\mathrm{U}$ also reacts with dinitrogen and forms a product with a $\mathrm{U}_2(\mu\text{-}\eta^2{:}\eta^2\text{-N}_2)$ structure, Eq. (60) [118]. As opposed to the $[(\mathrm{C}_5\mathrm{Me}_5)\mathrm{U}(\mathrm{C}_8\mathrm{H}_4\mathrm{R}_2)]_2\mathrm{N}_2$ complex formed in Eq. (41) [95], the 1.109 Å NN distance in $[(\mathrm{NN'}_3)\mathrm{U}]_2(\mathrm{N}_2)$ is not much different from that of free dinitrogen, i.e. little reduction has occurred. This complex also loses dinitrogen readily (see Section 5.10). These observations suggest that a U^{3+} coordination complex of N_2 has formed, as does the UV/vis spectra and magnetic data. As such this reaction does not formally fall into the area covered by this review. However, to the extent that electron density is transferred from the U^{3+} ion to the N_2 ligand, as indicated by the DFT calculation [119], this reaction represents some degree of reduction and is appropriate to be included.



(60)

A similar situation occurs in the reaction of $(\mathrm{NN'}_3)\mathrm{U}$ with pyridine. It is also difficult to determine if coordination or reduction occurs with this substrate. The UV/vis/NIR spectrum of the product was similar to that of the starting material, but the $^1\mathrm{H}$ NMR spectrum was more similar to a U^{4+} product [108].

A U^{3+} complex containing a closely related ligand has been identified as $[\mathrm{K}(\mathrm{MeC}_6\mathrm{H}_5)]_2\{\mathrm{N}[\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}(\mathrm{SiMe}_2{}^t\mathrm{Bu})]_2[\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}(\mathrm{SiMe}^t\mathrm{BuCH}_2)]\mathrm{U}\}_2$ [120]. In this compound, one of the $-\mathrm{SiMe}_2{}^t\mathrm{Bu}$ arms of the $(\mathrm{NN'}_3)^{3-}$ ligand has been metallated to form a tetranionic ligand containing a tethered alkyl $\{\mathrm{N}[\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}(\mathrm{SiMe}_2{}^t\mathrm{Bu})]_2[\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}(\mathrm{SiMe}^t\mathrm{BuCH}_2)]\}^{4-}$, which is abbreviated $(bit\text{-}\mathrm{NN'}_3)^{4-}$. The $[\mathrm{K}(\mathrm{MeC}_6\mathrm{H}_5)]_2[(bit\text{-}\mathrm{NN'}_3)\mathrm{U}]_2$ complex exists as a dimer connected by C–H···K interactions. This compound reacts with benzyl chloride to form $(bit\text{-}\mathrm{NN'}_3)\mathrm{U}$ and presumably KCl, Eq. (61) [120]. This is an unusual U^{3+} reaction in that the product does not contain any part of the substrate, benzyl chloride, and both C–H activation and reduction occur in the reaction.



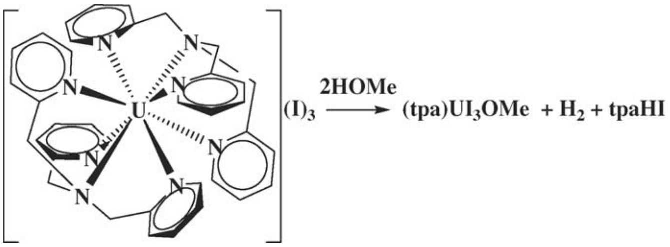
(61)

5.19. *Tris[(2-pyridyl)methyl]amine complexes of uranium*

The tris[(2-pyridyl)methyl]amine ligand, tpa, provides a neutral tripodal N-donor ligand from which the reduction chemistry of U^{3+} has been explored [121]. Starting from $\mathrm{UI}_3(\mathrm{THF})_4$, both a neutral mono(tpa) complex, $(\mathrm{tpa})\mathrm{UI}_3\mathrm{L}$ (L = MeCN or pyridine), and a bis(tpa) species, $\{[(\mathrm{tpa})_2\mathrm{U}]_2\}^{3+}$, have been isolated. The mono complex, $(\mathrm{tpa})\mathrm{UI}_3(\mathrm{CNMe})$, reacts in acetonitrile with methanol to give the U^{4+} product, $(\mathrm{tpa})\mathrm{UI}_3(\mathrm{OMe})$, Eq. (62) [121]. Hydrogen is suggested to be the byproduct in this reaction.

$$(\mathrm{tpa})\mathrm{UI}_3 \xrightarrow{\mathrm{HOMe}} (\mathrm{tpa})\mathrm{UI}_3(\mathrm{OMe}) + \mathrm{H}_2 \tag{62}$$

In contrast, the bis(tpa) complex, $[(\mathrm{tpa})_2\mathrm{U}]_2(\mathrm{I})_3$, in which all of the I^{1-} ligands are outer sphere, reacts with methanol to form a mono(tpa) U^{4+} product, $(\mathrm{tpa})\mathrm{UI}_2(\mathrm{OMe})_2$. One equivalent of tpa is lost as the tpaHI salt and H_2 is evolved, Eq. (63). The reaction of $[(\mathrm{tpa})_2\mathrm{U}](\mathrm{I})_3$ with $\mathrm{H}_2\mathrm{O}$ results in the formation of the trimetallic tetravalent $\{[(\mathrm{tpa})\mathrm{UI}(\mu\text{-O})]_3(\mu_3\text{-I})\}\mathrm{I}_2$ complex [121].



(63)

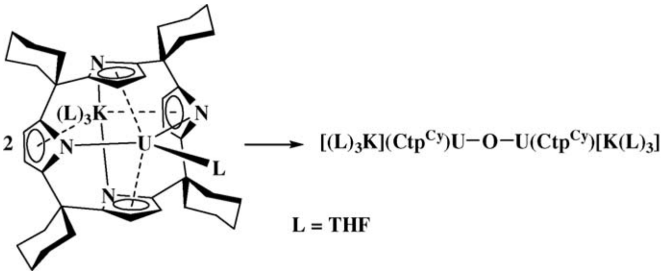
5.20. *[(terpy)$_2$UX$_2$](X) (X = I, OSO$_2$CF$_3$)*

The $[(\mathrm{terpy})_2\mathrm{UX}_2](\mathrm{X})$ ($\mathrm{X} = \mathrm{I}, \mathrm{OSO}_2\mathrm{CF}_3$; terpy = 2,2′:6′,2″-terpyridine) system offers soluble trivalent uranium complexes that have been used to study the coordination chemistry of uranium with triflate [122] versus halides. The U^{3+} ions in these complexes can be oxidized with trace amounts of water to give polynuclear uranium oxide complexes [123]. $[(\mathrm{terpy})_2\mathrm{UI}_2](\mathrm{I})$ is oxidized to form $\{(\mathrm{terpy})_2\mathrm{UI}(\mu\text{-O})\}_2[(\mathrm{terpy})\mathrm{UI}_2]\}^{4+}$ and $[(\mathrm{terpy})_2\mathrm{U}(\mathrm{OSO}_2\mathrm{CF}_3)_2](\mathrm{OSO}_2\mathrm{CF}_3)$ complex is oxidized to $\{[(\mathrm{terpy})_2\mathrm{U}(\mathrm{OSO}_2\mathrm{CF}_3)(\mu\text{-O})(\mu\text{-OSO}_2\mathrm{CF}_3)\mathrm{U}(\mathrm{terpy})]_2(\mu\text{-OSO}_2\mathrm{CF}_3)_2(\mu\text{-O})\}^{4+}$ [123].

5.21. *Calix[4]tetrapyrrole complexes*

Another polydentate ligand that confers high reactivity on U^{3+} is the porphyrinogen or calix(tetrapyrrole) ligand system [124,125]. This class of complexes represents another type of “ate”-salt since the compounds contain the tetraanionic calix[4]tetrapyrrole ligands, and have alkali metal cations present to balance the charge with U^{3+}. Two types of calix[4]tetrapyrrole ligands have been used with U^{3+}: one with eight ethyl groups on the ligand periphery, which will be abbreviated here as $(\mathrm{Ctp^{Et}})^{4-}$ for the ethyl substituted *c*alix*t*etra*p*yrrole, and one with four pairs of these eight positions occupied by pentamethylene units. With the carbon in the Ctp backbone, these $–(\mathrm{CH_2})_5–$ units generate four cyclohexyl rings in the ligand periphery. This ligand will be designated here as $(\mathrm{Ctp^{Cy}})^{4-}$.

The reduction chemistry of the $[\mathrm{L}_x\mathrm{M}][(\mathrm{Ctp^{Cy}})\mathrm{U}]$ complexes (M = alkali metal and L = an ether) has not been extensively investigated perhaps due to their instability toward oxide formation [126]. Hence, like the $[({}^t\mathrm{Bu_2C_6H_2O})_3\mathrm{tacn}]\mathrm{U}$ complexes described above, simple addition of the $[\mathrm{L}_x\mathrm{M}]_4[(\mathrm{Ctp^{Cy}})]$ reagent to U^{3+} reagents generates complexes that decompose in ether solvents to form oxides. For example, the reaction of $\mathrm{UI_3(THF)_4}$ with $[(\mathrm{THF})\mathrm{K}]_4[(\mathrm{Ctp^{Cy}})]$ in THF leads to the isolation of the tetravalent oxide, $\{[(\mathrm{THF})_3\mathrm{K}][(\mathrm{Ctp^{Cy}})\mathrm{U}]_2(\mu\text{-O})$, Eq. (64) [126], in which the oxygen is believed to originate from THF. The reactions are highly dependent on the U^{3+} precursor, the alkali metal, and the substitution of the calix[4]tetrapyrrole. The analogous reaction starting with the lithium salt $[(\mathrm{THF})\mathrm{Li}]_4(\mathrm{Ctp^{Cy}})$ gives intractable materials, but a 2:1 mixture of the tetralithium salt and $\mathrm{UI_3(THF)_4}$ generates a tetravalent product in which one pyrrole carbon was deprotonated and metallated by uranium to make a diuranium complex of formula $\{[(\mathrm{THF})_2\mathrm{Li}](\mathrm{Ctp^{Cy}}\text{-H})\mathrm{U}\}_2$, Eq. (65) [126]. A reaction using $\mathrm{UCl_3}$ (made in situ from $\mathrm{UCl_4}$/potassium naphthalenide) [127] led to an ethoxide fragmentation product of THF, namely $[(\mathrm{THF})_2\mathrm{Li}](\mathrm{Ctp^{Cy}})\mathrm{U}(\mu\text{-OCH_2CH_3})$ [126].



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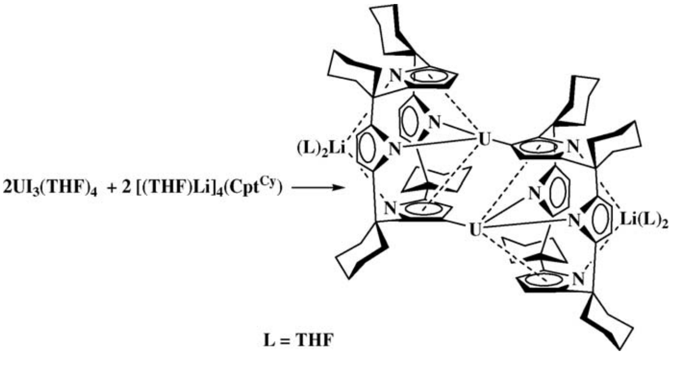
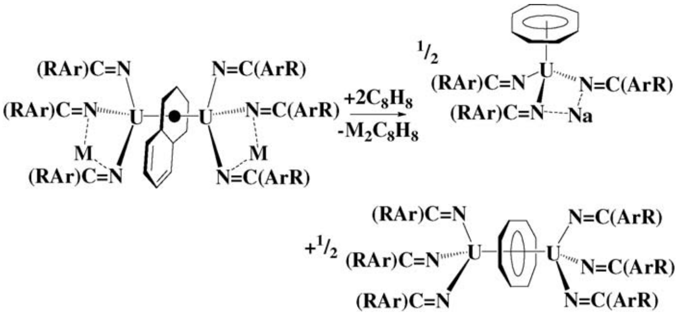


(65)

In contrast to these immediate decompositions, reaction of the dimethoxyethane solvated precursor, $\mathrm{UI_3(DME)_2}$, with the octaethylcalix[4]tetrapyrrole, $[(\mathrm{DME})_2\mathrm{K}_4](\mathrm{Ctp^{Et}})$, generated an isolable trivalent complex, $[(\mathrm{DME})\mathrm{K}](\mathrm{Ctp^{Et}})\mathrm{U}(\mathrm{DME})$ [128]. The redox chemistry of this U^{3+} complex with K(naphthalenide) has been studied. Reactions in ether solvents in the absence of $\mathrm{N_2}$ result in the formation of oxide products. Hence, DME cleavage is proposed to explain the formation of the mixed valent $\mathrm{U}^{3+}/\mathrm{U}^{4+}$ complex, $\{[(\mathrm{DME})\mathrm{K}](\mathrm{Ctp^{Et}})\mathrm{U}\}_2(\mu\text{-O})][\mathrm{K(DME)_4}]$ from a reaction between $\mathrm{K(C_{10}H_8)}$ and trivalent $[(\mathrm{DME})\mathrm{K}](\mathrm{Ctp^{Et}})\mathrm{U}(\mathrm{DME})$. This mixture of $[(\mathrm{DME})\mathrm{K}](\mathrm{Ctp^{Et}})\mathrm{U}(\mathrm{DME})$ and $\mathrm{K(C_{10}H_8)}$ is also reported to decompose silicon grease to make a tetravalent uranium $(\mathrm{Me_2SiO_2})^{2-}$ derivative, $\{[(\mathrm{DME})\mathrm{K}(\mathrm{Ctp^{Et}})\mathrm{U}]_2(\mathrm{O_2SiMe_2K})\}[\mathrm{K(DME)_4}]$ [128].

5.22. *Tris(ketimide) complexes*

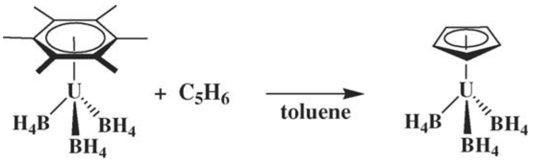
Reduction of the tetravalent uranium tris(ketimide) complexes, $[({}^t\mathrm{Bu})(2,4,6\text{-Me_3C_6H_2})\mathrm{C{=}N}]_3\mathrm{UI}$, by sodium and potassium naphthalenide represents a controllable system with which to do uranium reduction chemistry in conjunction with naphthalene [129]. This reaction results in the formation of the $\mathrm{M_2}\{[({}^t\mathrm{Bu})(2,4,6\text{-Me_3C_6H_2})\mathrm{C{=}N}]_3\mathrm{U}\}_2(\mathrm{C_{10}H_8})$ (M = Na, K) “ate”-complexes which are stable in ether solvents and can be used to reduce $1,3,5,7\text{-C_8H_8}$ to make the U^{4+} cyclooctatetraenyl products $(\mathrm{C_8H_8})\mathrm{U}[\mathrm{N{=}C}(2,4,6\text{-Me_3C_6H_2})({}^t\mathrm{Bu})]_3\mathrm{M}$ and $(\mathrm{C_8H_8})\{\mathrm{U}[\mathrm{N{=}C}(2,4,6\text{-Me_3C_6H_2})({}^t\mathrm{Bu})]_3\}_2$, Eq. (66) [129], $\mathrm{R} = {}^t\mathrm{Bu}$; Ar = $(2,4,6\text{-Me_3C_6H_2})$.



(66)

5.23. *$(\mathrm{MX_4})_3\mathrm{U}(\mathrm{arene})$ complexes*

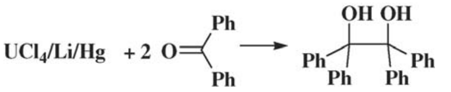
Another class of U^{3+} “ate” salts involves the tris(tetrahaloaluminate) and tris(tetrahydroborate) complexes of neutral arenes with the general formula $(\mathrm{MX_4})_3\mathrm{U}(\mathrm{arene})$, (X = halide, M = Al; X = hydride, M = B) [90,130–134]. $\mathrm{C_6Me_6}$ is the most commonly used π-bound arene in these complexes, but even $\mathrm{C_6H_6}$ complexes have been reported. Of these compounds, redox reactivity has only been reported for $(\mathrm{C_6H_3Me_3})\mathrm{U}(\mathrm{BH_4})_3$, which reacts with cyclopentadiene to make $(\mathrm{C_5H_5})\mathrm{U}(\mathrm{BH_4})_3$ in 80% yield. Hydrogen is presumed to be the byproduct, Eq. (67) [133].



(67)

5.24. *UCl4/alkali metal*

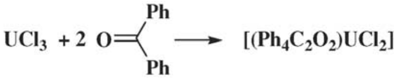
The reaction of UCl_4 and alkali metal amalgams has been used for pinacol coupling [135–139]. An example with benzophenone is provided in Eq. (68) [135].



$$UCl_4/Li/Hg + 2\,O{=}CPh_2 \rightarrow Ph_2C(OH){-}C(OH)Ph_2 \quad (68)$$

This reaction is in contrast to the reaction described in Eq. (21) between $(C_5H_5)_3U(THF)$ and benzophenone that results in a carbon–carbon coupling product [72].

A proposed pathway for the coupling in Eq. (68) involves the formation of a tetravalent uranium pinacolate dichloride intermediate, formulated as $(Ph_4C_2O_2)UCl_2$, that has been isolated and can be hydrolyzed to give the diol. The pinacolate was independently synthesized from UCl_3 and $Ph_2C{=}O$, Eq. (69) [135,136]. Aliphatic ketones



$$UCl_3 + 2\,O{=}CPh_2 \rightarrow [(Ph_4C_2O_2)UCl_2] \quad (69)$$

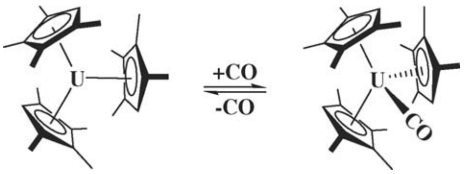
such as acetone can also be reductively coupled to diols with $UCl_4/M/Hg$ (M = Li, Na). The uranium products formed before hydrolysis are more complicated than the benzophenone reactions and the use of Li versus Na produces different results, such as aldolization. For the uranium pinacolate complexes formed from aliphatic and aryl ketones, addition of an added equivalent of alkali metal results in deoxygenation and production of alkenes, Eq. (70) [135]. In the presence of $AlCl_3$, the Li(Hg)-based reduction is reported to be catalytic in UCl_4 [170].

$$[(Ph_4C_2O_2)UCl_2] + 2Na(Hg) \rightarrow Ph_2C{=}CPh_2 + \text{other products} \quad (70)$$

5.25. *Reactions with CO and N2*

As described above in Sections 5.10 and 5.18, U^{3+} reacts with dinitrogen to make products that reversibly revert to the starting material. The extent of reduction by U^{3+} appears to be variable in these reactions as judged by the length of the NN bond in the products, i.e. these complexes are somewhere between being U^{3+} coordination complexes of neutral dinitrogen and U^{4+} complexes of reduced dinitrogen anions. Since some reduction occurs, these reactions are appropriate for this review. Another substrate that displays similar behavior is CO. Its reactions with U^{3+} complexes as well as an additional related N_2 reaction are reported in this section.

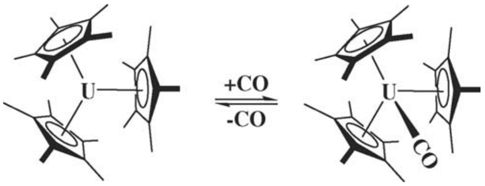
$(C_5H_4SiMe_3)_3U$ reacts with CO to make a complex identified as $(C_5H_4SiMe_3)_3U(CO)$[140] that displays a CO stretch at 1976 cm^{-1} indicative of reduction of the CO bond. Subsequently, the reaction of $(C_5Me_4H)_3U$ with CO was reported to give a crystallographically characterizable $(C_5Me_4H)_3U(CO)$ complex, Eq. (71) [141,142].



(71)

The tetramethylcyclopentadienyl CO complex has υ_{CO} at 1880 cm^{-1} which is consistent with the greater electron donating ability of the $(C_5Me_4H)^{1-}$ ligand relative to $(C_5H_4SiMe_3)^{1-}$.

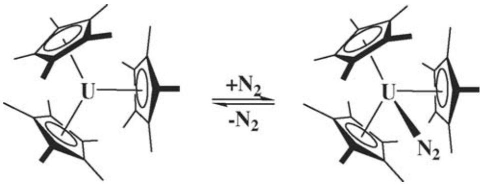
Surprisingly, the sterically crowded $(C_5Me_5)_3U$ [143] also reacts with CO to form an analogous complex, $(C_5Me_5)_3U(CO)$, Eq. (72) [144]. This complex differs from



(72)

$(C_5Me_4H)_3U(CO)$ in that the cyclopentadienyl rings do not bend back when CO coordinates. The tris(cyclopentadienyl) metal part of $(C_5Me_5)_3U(CO)$ is almost identical to that of the trigonal planar $(C_5Me_5)_3U$. All of the bond distances in $(C_5Me_5)_3U(CO)$ are long including the U-C(CO) distance, 2.485(9) Å which is 0.1 Å longer than the 2.383(6) Å length in $(C_5Me_4H)_3U(CO)$. The CO stretching frequency in $(C_5Me_5)_3U(CO)$, 1922 cm^{-1}, is higher than the 1880 cm^{-1} observed in $(C_5Me_4H)_3U(CO)$. This is not what is expected on the basis of the electron donating capacity of the cyclopentadienyl ligands, but it is consistent with the long U-C(CO) bond length.

$(C_5Me_5)_3U$ forms a complex analogous to $(C_5Me_5)_3U(CO)$ with dinitrogen, but N_2 pressure is necessary to obtain an isolable product. $(C_5Me_5)_3U(N_2)$ can be crystallographically characterized, Eq. (73), but readily reverts back to $(C_5Me_5)_3U$ [145].



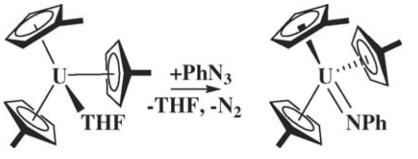
(73)

$(C_5Me_5)_3U(N_2)$ has a υ_{N2} stretching frequency at 2207 cm^{-1} (versus the 2331 cm^{-1} reported for free N_2 by Raman spectroscopy [146]) that again indicates that electron density has been transferred to the ligand.

6. U^{3+} to U^{5+} transformations

Since U^{5+} is not nearly as common an oxidation state as U^{4+}, fewer U^{3+} to U^{5+} transformations are known. Nonetheless, with the proper choice of reagents, such reactions can be observed. Interestingly, these reactions are found with many U^{3+} reagents when the product contains a $(NR)^{2-}$ imido ligand.

The most common U^{3+} to U^{5+} transformation involves the conversion of an organic azide, RN_3, to a U^{5+} imido complex. This was first demonstrated with the tris(cyclopentadienyl) complex, $(C_5H_4Me)_3U$, Eq. (74) [74]. The U^{3+} to U^{5+} imido transformation also occurs with $\{[C_5H_3(SiMe_3)_2]_2UCl\}_2$, Eq. (75) [59], and the triamidoamine complex, $(NN'_3)U$, $\{(NN'_3) = [N(CH_2CH_2NSiMe_2{}^tBu)_3]\}$, Eq. (76) [108].



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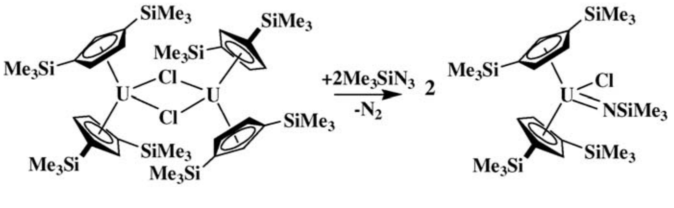

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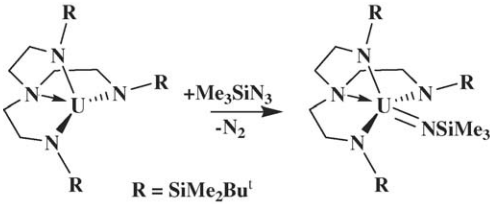
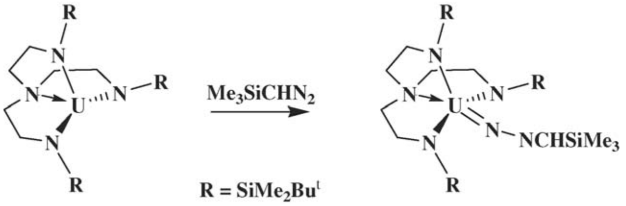


(76)

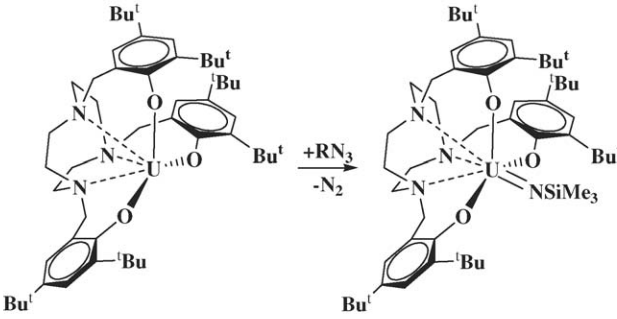
The mixed valent U^{3+}/U^{4+} complex $[(NN'_3)U]_2Cl$ reacts with Me_3SiN_3 to form a 1:1 mixture of $(NN'_3)U{=}NSiMe_3$ and $(NN'_3)UCl$ [117].

When $(NN'_3)U$ was treated with trimethylsilyldiazomethane, formal oxidation to U^{5+} also occurred. However, in this case a nitrogen-substituted imide, $(NN'_3)U{=}N{-}N{=}CHSiMe_3$, was obtained, Eq. (77) [108].



(77)

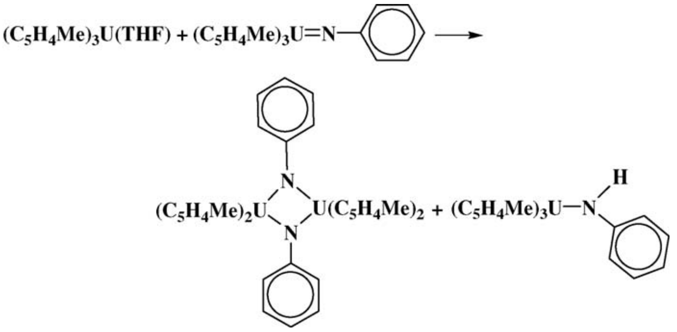
The tris(aryloxide)triazacyclononane system also forms U^{5+} imido complexes, but only with the di-*tert*-butyl substituted complex, $[({}^tBu_2C_6H_2O)_3tacn]U$, Eq. (78) [110].



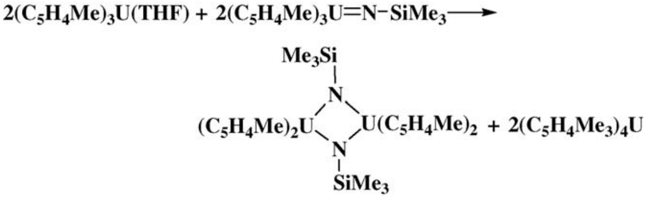
(78)

The formation of $[({}^tBu_2C_6H_2O)_3tacn]U({=}NSiMe_3)$ is accompanied by the formation of a small amount of $[({}^tBu_2C_6H_2O)_3tacn]U(N_3)$. In contrast, the more crowded analog, $\{[({}^tBu)(Ad)C_6H_2O]_3tacn\}U$, reacts to make a only the simple azide, Eq. (50), which suggests that there are some steric requirements for the organic azide to uranium imido transformation.

Subsequent studies of the reactivity of the cyclopentadienyl U^{5+} imido species, $(C_5H_4Me)_3U({=}NR)$ (R = Ph, $SiMe_3$), with trivalent $(C_5H_4Me)_3U$ showed that, as expected on the basis of aqueous reduction potentials, U^{3+} would reduce U^{5+} to U^{4+}. This generates bridging $(NR)^{2-}$ units that form bimetallic U^{4+} products, Eqs. (79) and (80) [147].



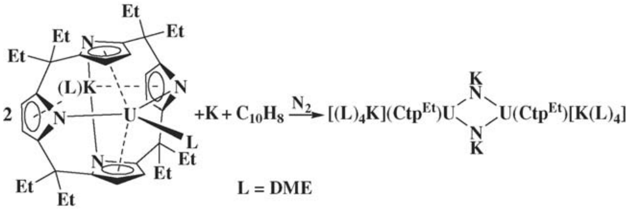
(79)



(80)

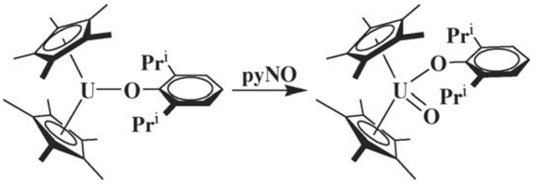
This is an alternative bonding arrangement between uranium and $(NR)^{2-}$ ligands (also see Section 7.3.1).

A more complicated U^{3+} to U^{5+} transformation involves the K(naphthalenide) reduction of the calix[4]tetrapyrrole $(DME)K(Ctp^{Et})U(DME)$ (Section 5.21) under dinitrogen [128]. This reaction is reported to form a mixed valent U^{4+}/U^{5+} product bridged by $(N)^{3-}$ nitride ligands. As discussed in Section 5.21, in the absence of dinitrogen, solvent and grease are attacked by this combination of U^{3+} and $(Ctp^{Et})^{4-}$ to form oxides and siloxides. Under dinitrogen, however, neither the solvent nor the grease react and the triply bridged nitride, $\{[(DME)K(Ctp^{Et})U]_2(\mu\text{-}NK)_2\}[K(DME)_4]$, was characterized by X-ray crystallography, Eq. (81) [128].



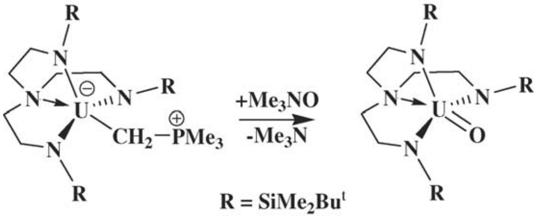
(81)

Another type of complex frequently formed from U^{3+} to U^{5+} reactions involves terminal $(O)^{2-}$ oxo ligands rather than terminal $(NR)^{2-}$ imido groups. As in the imido system, the formation of bridging species, i.e. U^{4+}–O–U^{4+} rather than U^{5+}=O, can complicate these reactions. $(C_5Me_5)_2U(OAr)$ reacts with pyridine *N*-oxide to make the U^{5+} oxo species, $(C_5Me_5)_2U(OAr)(=O)$, Eq. (82) [148]. U^{5+} oxo formation from U^{3+} was



(82)

also observed using a trimethylphosphorane adduct of a triamidoamine complex, $(NN'_3)U(CH_2PMe_3)$, which reacts with Me_3NO to form $(NN'_3)U$=O, Eq. (83) [108].



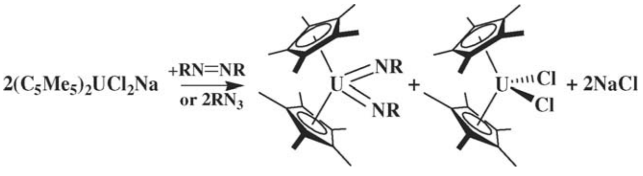
(83)

However, the latter complex can be converted to the tetravalent bridging oxide, $[(NN'_3)U]_2(\mu\text{-}O)$.

The $[(Me_3Si)_2N]_3U$ complex has also been observed to form U^{5+} oxo complexes. This complex reacts with both molecular oxygen and trimethylamine *N*-oxide to make $[(Me_3Si)_2N]_3U$=O, a product characterized by analytical and spectroscopic methods, but not by X-ray crystallography [113].

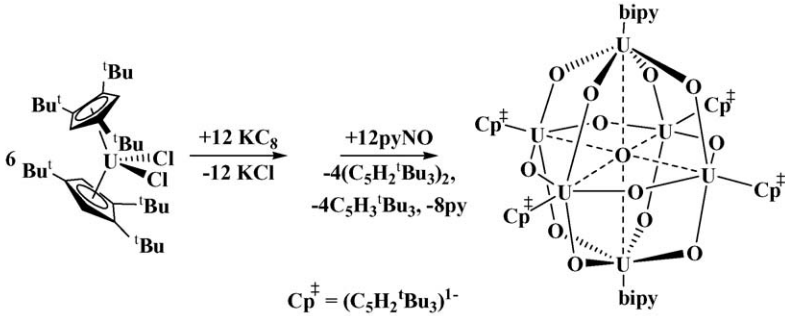
A more complicated oxo-forming reaction involving U^{5+} products occurs when the tetravalent tris(*tert*-butyl)-substituted cyclopentadienyl complex, $[1,3,5\text{-}(Me_3C)_3C_5H_2]_2UCl_2$, is reduced by KC_8 in THF followed by addition of pyridine *N*-oxide [149]. Although many of the trivalent uranium complexes discussed above react to form mono and bimetallic species, the product in this case is the hexametallic $[1,3,5\text{-}(Me_3C)_3C_5H_2]_4(bipy)_2U_6O_{13}$ (bipy = bipyridine) complex, Scheme 4. This cluster contains four $[1,3,5\text{-}(Me_3C)_3C_5H_2]UO_2$ units, two $(bipy)UO_2$ units, and a central oxide ligand. Both $[1,3,5\text{-}(Me_3C)_3C_5H_2]_2$ and $1,3,5\text{-}(Me_3C)_3C_5H_3$ are observed as byproducts. The formation of these byproducts is postulated to result from (a) the coupling of two $[1,3,5\text{-}(Me_3C)_3C_5H_2]$ radicals and (b) α-atom abstraction from the pyridine that is formed after reduction. Coupling of pyridine radicals is suggested to explain the formation of bipy. If the cluster is comprised of six $U^{5+}f^1$ ions, then there is charge balance with four $[1,3,5\text{-}(Me_3C)_3C_5H_2]^{1-}$ ligands and thirteen O^{2-} ligands. The magnetic data support this description [149].

Just as two U^{3+}/U^{4+} processes can be combined to effect a 2 electron reduction with two equivalents of U^{3+}, e.g. Scheme 2, it is possible to combine two of the two electron reactions of U^{3+} to effect four electron reduction with two equivalents of U^{3+}. The single example of this reaction does not involve conversion of two U^{3+} centers to two U^{5+} ions, but rather to a mixture of U^{4+} and U^{6+} products. Reaction of two equivalents of trivalent $(C_5Me_5)_2UCl_2Na$ with organic azides, RN_3 (R = phenyl, adamantyl), or with the azo compounds, PhN=NPh and $PhN{=}NSiMe_3$, effects four electron reductions of these substrates to make the U^{6+} bis(imido) complex, $(C_5Me_5)_2U(=NR)_2$, Eq. (84) [150].

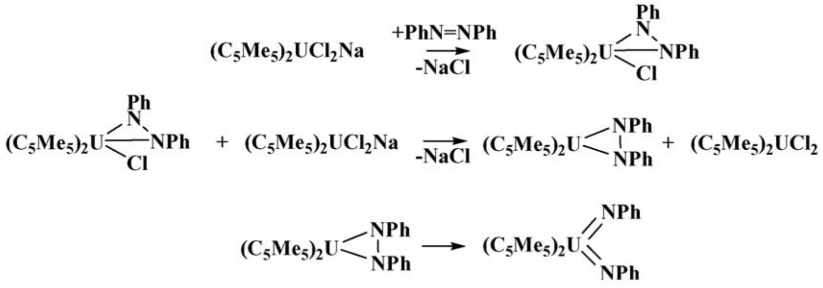


(84)

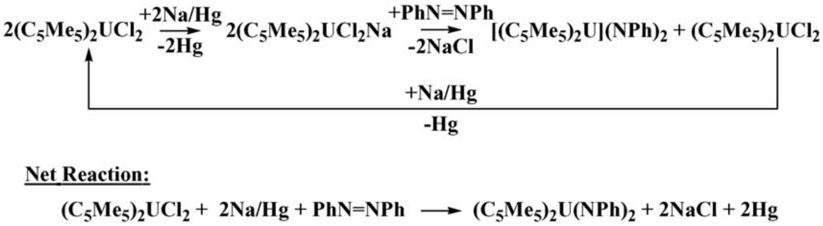
As in the one electron transformations discussed above with $(C_5Me_5)_2UCl_2Na$, Eq. (9), the byproduct of the reactions is the tetravalent dichloride, $(C_5Me_5)_2UCl_2$. The overall reaction involves the conversion of two U^{3+} centers to a mixture of U^{4+} and U^{6+} products. The reactions are thought to occur by formation of U^{5+} intermediates, $(C_5Me_5)_2UCl(=NR)$ and $(C_5Me_5)_2UCl(RNNR)$, that can conproportionate with additional $(C_5Me_5)_2UCl_2Na$ to make tetravalent $(C_5Me_5)_2UCl_2$ plus $(C_5Me_5)_2U(=NR)$ and $(C_5Me_5)_2U(RNNR)$, each of which is known to go on to make the final U^{6+} bis(imido) product, Scheme 5 [150]. $(C_5Me_5)_2U(=NR)_2$ can be generated cleanly by reducing the $(C_5Me_5)_2UCl_2$ byproduct with Na/Hg as described in Scheme 6. This set of reactions is analogous to the approach used in Scheme 2. The overall half reaction from $(C_5Me_5)_2UCl_2$



Scheme 4.



Scheme 5.



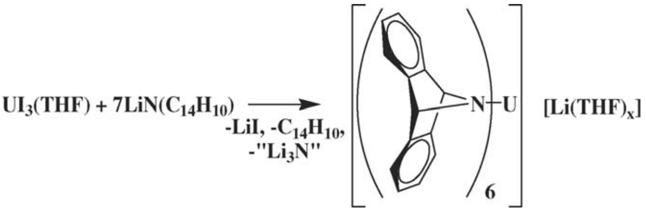
Scheme 6.

described in Eq. (85) is

$$(C_5Me_5)_2UCl_2 + 2Na/Hg \rightarrow [(C_5Me_5)_2U]^{4+} + 4e^{1-} + 2NaCl + 2Hg \quad (85)$$

another case in which the chemistry mimics that of the unknown divalent $(C_5Me_5)_2U$ [150]. In this case, four electrons are delivered and the $[(C_5Me_5)_2U]^{4+}$ cation forms.

An unusual transformation that generates U^{5+} products from U^{3+} starting materials is the reaction of $UI_3(THF)_4$ with the nitride delivery agent, $LiN(C_{14}H_{10})$, which can readily eliminate anthracene. In this case, the several equivalents of the ligand remain intact and a hexakis amido U^{5+} complex is isolated, $[Li(THF)_x]\{[(C_{14}H_{10})N]_6U\}$, Eq. (86) [151].



(86)

The derivative, $(PPh_4)\{[(C_{14}H_{10})N]_6U\}$, was structurally characterized. In this reaction, the U^{3+} to U^{5+} transformation was accompanied by formal loss of Li_3N and anthracene.

One final example of a U^{3+} to U^{5+} transformation comes from the $(C_5H_5)URM/R'X$ system (M = alkali metal; X = halide; R,R′ = alkyl), Section 5.6, in which U^{5+} $(C_5H_5)_3URR'$ intermediates are thought to be involved in Eq. (36) as shown in Eq. (87) [85]. This result could not be crystallographically confirmed because the U^{5+}

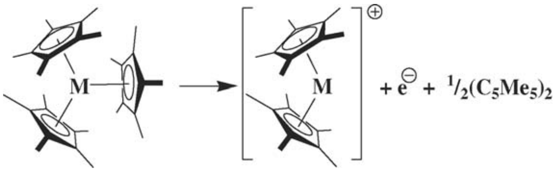
$$[(C_5H_5)_3UR]M + R'X \rightarrow (C_5H_5)_3URR' + MX \quad (87)$$

dialkyls were not sufficiently stable to isolate.

7. Combining ligand and U^{3+} redox chemistry to achieve multi-electron reduction

As described in the previous sections, U^{3+} can be used in two ways to achieve two electron reduction. In one case, the products are tetravalent and the reduction involves either (a) two equivalents of U^{3+} according to Eq. (7) or (b) two equivalents of an external reductant such as Na/Hg to make two equivalents of U^{3+}, Eq. (12). In the other case, U^{5+} products are obtained from a U^{3+} to U^{5+} transformation, Section 6. The latter reaction is most common when U^{5+} imido and oxo complexes are the products. This may have more to do with the special nature of the products than the reduction chemistry of U^{3+}. Reductions of organic azides and azo compounds, RN=NR, were also described that involve unusual U^{3+} to U^{6+} transformations, which again result in the isolation of uranium imido complexes.

An alternative method to achieve multi-electron reduction with U^{3+} is to couple the U^{3+} reduction with a ligand-based reduction. This approach to U^{3+} reductive chemistry was initiated by the discovery of the sterically crowded tris(pentamethylcyclopentadienyl) complexes, $(C_5Me_5)_3M$ [8]. These complexes are so sterically crowded that the $(C_5Me_5)^{1-}$ ligands cannot achieve their normal bond distances and electrostatic stabilization from the metal. Consequently, the traditionally inert $(C_5Me_5)^{1-}$ ligands become reactive. Among the reactions discovered for these complexes is the reduction shown in Eq. (88). This reaction is called sterically induced reduction



(88)

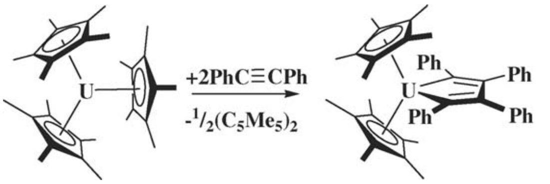
(SIR) because the $(C_5Me_5)^{1-}$ ligands do not exhibit this chemistry in sterically less crowded systems [7,8,24–26].

Since $(C_5Me_5)_3U$ [143] has more electron donating ligands than the previously discussed U^{3+} reductants, it was expected to be a good reducing agent. Since it is sufficiently crowded to do sterically induced reduction, it provided the opportunity to see how SIR could be combined with U^{3+} redox chemistry to allow a single equivalent of a U^{3+} complex to do two electron chemistry and generate U^{4+} products. As described in this section, $(C_5Me_5)_3U$ displays more than two electron reductive chemistry. Also included in this section is the multi-electron reduction chemistry obtainable by coupling other types of ligand-based reduction with U^{3+} processes. This appears to be a growing area of reductive U^{3+} chemistry.

7.1. $(C_5Me_5)_3U$

7.1.1. Two electron reduction

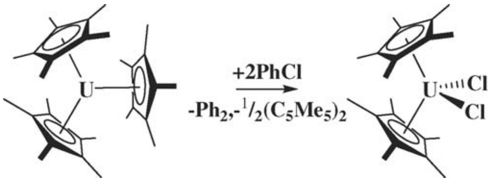
One equivalent of $(C_5Me_5)_3U$ functions as a two electron reductant with both aryl [101] halides and PhC≡CPh [152]. U^{3+} reduction of these substrates was described above in Eqs. (6) and (9) in which two equivalents of U^{3+} reagents were previously needed. The PhC≡CPh reaction, Eq. (89), involves the reduction of two equivalents of PhC≡CPh to



(89)

make the $(C_4Ph_4)^{2-}$ dianion [152]. This is the same metallocyclopentadiene product obtained from $[(C_5Me_5)_2UCl]_3$ in Eq. (6), a reaction that required two equivalents of U^{3+} and was accompanied by ligand redistribution. The half reactions for Eq. (89) are shown in Scheme 7.

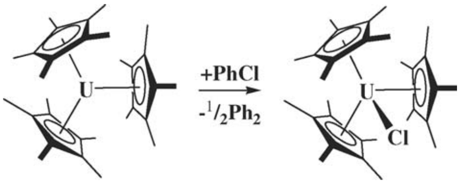
The two electron reduction of two equivalents of chlorobenzene by one equivalent of $(C_5Me_5)_3U$ results in the formation of $(C_5Me_5)_2UCl_2$ in good yield, Eq. (90) [101]. Like



(90)

the aryl and alkyl halide reductions described above, other byproducts can form in this reaction. For example, some small amounts of $(C_5Me_5)_2UCl(C_6H_5)$ are also observed.

Since Eq. (90) occurs in two steps, i.e. one equivalent of PhCl reacts quickly and the second more slowly, it was possible to determine which reductive half reaction occurred first, U^{3+} or $(C_5Me_5)^{1-}/(C_5Me_5)$. Initially, it was expected that SIR would occur first to make the well known $[(C_5Me_5)_2UCl]_3$ [52,53] as an intermediate. This U^{3+} complex would then do its usual chemistry with C_6H_5Cl (see Eq. (1) above) to form $(C_5Me_5)_2UCl_2$. The alternative order of reduction, i.e. U^{3+} first, would generate a tetravalent $(C_5Me_5)_3UCl$ complex expected to be much more crowded than the starting $(C_5Me_5)_3U$. However, as shown in Eq. (91), U^{3+} reduction does precede sterically induced



(91)

reduction in this case and $(C_5Me_5)_3UCl$ is isolated as an intermediate [101]. This was surprising since $(C_5Me_5)_3UCl$ represented the first example of a tris(pentamethylcyclopentadienyl) complex with an additional fourth ligand.

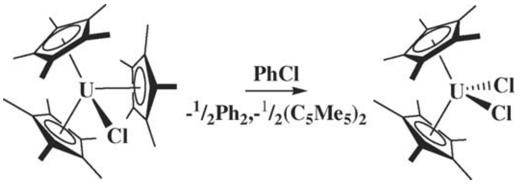
$$2PhC{\equiv}CPh + 2e^{1-} \longrightarrow (C_4Ph_4)^{2-}$$

$$U^{3+} \longrightarrow e^{1-} + U^{4+}$$

$$(C_5Me_5)^{1-} \longrightarrow e^{1-} + {}^{1}/_{2}(C_5Me_5)_2$$

Scheme 7.

$(C_5Me_5)_3UCl$ goes on to effect the second reduction via sterically induced reduction, Eq. (92), in which both the products and reactants are tetravalent [101]. This is



(92)

case in which sterically induced reduction mimics U^{3+} redox chemistry.

Once the existence of $(C_5Me_5)_3UCl$ was established, several alternative syntheses were discovered that utilized U^{3+} reductions, Eqs. (93)–(96) [80,101]. The isolation of

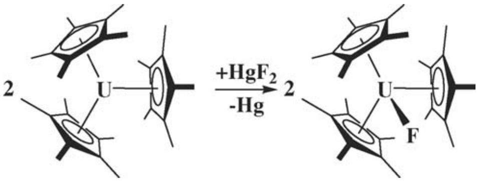
$$(C_5Me_5)_3U + (C_5Me_5)_2UCl_2 \rightarrow (C_5Me_5)_3UCl + \tfrac{1}{3}[(C_5Me_5)_2UCl]_3 \quad (93)$$

$$2(C_5Me_5)_3U + MCl_2 \xrightarrow[-M]{} 2(C_5Me_5)_3UCl \quad (M = Pb, Hg) \quad (94)$$

$$(C_5Me_5)_3U + {}^{t}BuCl \rightarrow (C_5Me_5)_3UCl + \text{other products} \quad (95)$$

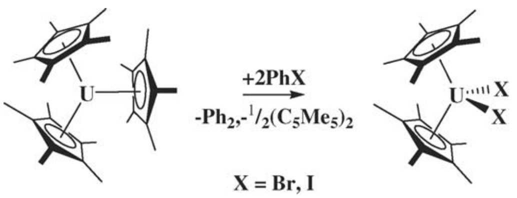
$$2[(C_5Me_5)_2UCl]_3 + 3Pb(C_5Me_5)_2 \xrightarrow[-3Pb]{} 6(C_5Me_5)_3UCl \quad (96)$$

$(C_5Me_5)_3UCl$ indicated that the fluoride analog was also sterically accessible and $(C_5Me_5)_3U$ was found to react with HgF_2 to form $(C_5Me_5)_3UF$, Eq. (97) [101].



(97)

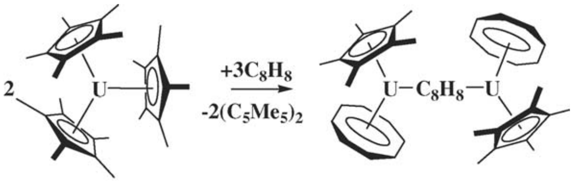
$(C_5Me_5)_3U$ also reacts with two equivalents of PhBr and PhI to make the corresponding $(C_5Me_5)_2UX_2$ products, Eq. (98) [101]. In these cases the expected intermediate complexes, $(C_5Me_5)_3UX$, have not yet yielded to crystallographic characterization. The red intermediates from the reactions of $(C_5Me_5)_3U$ with one equivalent of PhX do analyze as $(C_5Me_5)_3UX$ (X = Br, I). These complexes also react further with an additional equivalent of PhX to make $(C_5Me_5)_2UX_2$, in direct analogy with the $(C_5Me_5)_3UCl/PhCl$ system, Eq. (92).



(98)

7.1.2. Three electron reduction

The reaction of one equivalent of $(C_5Me_5)_3U$ with one equivalent of 1,3,5,7-C_8H_8 was examined to determine if a two electron reduction to form $C_8H_8{}^{2-}$ would occur [93]. The reaction run in a 1:1 stoichiometry formed $(C_5Me_5)_2$ and a new organouranium product, but residual $(C_5Me_5)_3U$ remained at the end of the reaction. Subsequently, it was determined that a 2:3 $(C_5Me_5)_3U/C_8H_8$ stoichiometry was necessary to achieve full consumption of the starting materials. As shown in Eq. (99), this reaction produces $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$, a product containing three $(C_8H_8)^{2-}$ dianions [93]. Hence, the two equivalents of $(C_5Me_5)_3U$ delivered a total of six electrons and $(C_5Me_5)_3U$ is a three electron reductant in this reaction. The half reactions for Eq. (99) are given in Scheme 8. In this case, two of the $(C_5Me_5)^{1-}$ ligands are lost from each $(C_5Me_5)_3U$ precursor to provide two electrons to go along with an electron provided by U^{3+}. Neither the sequence of these reductions nor the intermediates involved are known. There may be two intermediate species so sterically crowded that they will undergo SIR processes.



(99)

$$3C_8H_8 + 6e^{1-} \longrightarrow 3(C_8H_8)^{2-}$$

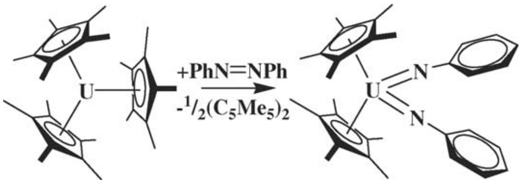
$$2U^{3+} \longrightarrow 2e^{1-} + 2U^{4+}$$

$$4(C_5Me_5)^{1-} \longrightarrow 4e^{1-} + 2(C_5Me_5)_2$$

Scheme 8.

7.1.3. Four electron reduction

$(C_5Me_5)_3U$ has also been observed to function as a four electron reductant by combining SIR with a U^{3+}/U^{6+} process. Hence, $(C_5Me_5)_3U$ reacts with PhN=NPh to form $(C_5Me_5)_2$ and the hexavalent uranium bis(imido) complex $(C_5Me_5)_2U(NPh)_2$, Eq. (100) [152].



(100)

Although this product had been made in many ways in the past (e.g. Scheme 6) [150,153–155] and the sample had NMR spectra that matched the literature, the fact that it could be generated from one equivalent of $(C_5Me_5)_3U$ was suspect. Accordingly, further efforts were made to identify it and to avoid confusing it with a two electron reduction product containing $(PhNNPh)^{2-}$. The product was hydrolyzed and GC–MS was used to insure that the hydrolysis products contained $PhNH_2$ and not PhNHNHPh.

7.2. $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$

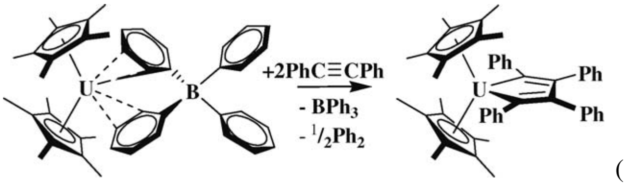
7.2.1. Two electron reduction

Examination of the reductive chemistry of the synthetic precursor to $(C_5Me_5)_3U$, namely $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$, revealed another case in which the combination of ligand and U^{3+} reduction generated a two electron reduction system. Although it was expected that $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ would function simply as a one electron U^{3+} reductant, it was found that the $(BPh_4)^{1-}$ ligand in this complex is not an innocent counter-anion. It can react according to the half reaction in Eq. (101) [152].

$$(BPh_4)^{1-} \rightarrow e^{1-} + BPh_3 + \tfrac{1}{2}Ph_2 \qquad (101)$$

Although thermochemical, photochemical, and electrochemical oxidations of $(BPh_4)^{1-}$ had been extensively studied [156–161], combining this type of reactivity with a metal-based reductant, such as U^{3+}, to effect a two electron reduction is unusual.

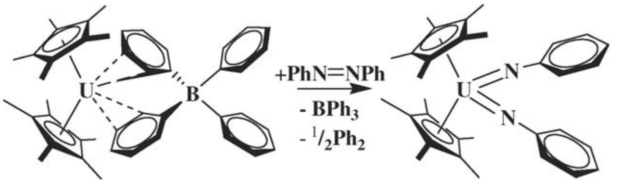
Hence, as shown in Eq. (102), $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ reduces PhC≡CPh to $(C_4Ph_4)^{2-}$ by a two electron process to make the same product, $(C_5Me_5)_2U(C_4Ph_4)$, shown above in Eqs. (6), (9) and (89). The formation of BPh_3 and Ph_2 indicates participation of the $(BPh_4)^{1-}$ ligand in the reduction.



(102)

7.2.2. Four electron reduction

$[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ reduces PhNNPh to $(C_5Me_5)_2U(NPh)_2$ in a four electron process, Eq. (103) [152]. This reaction is similar to Eq. (100), since ligand-based



(103)

redox chemistry is combined with a U^{3+} to U^{6+} transformation. However, in Eq. (103), the redox active ligand is $(BPh_4)^{1-}$ and again BPh_3 and Ph_2 were observed as byproducts. Because of the unexpected nature of this reaction and possibility of making $(PhNNPh)^{n-}$ products, the sample was analyzed by X-ray diffraction studies to confirm that the NN bond was completely cleaved in the $(C_5Me_5)_2U(NPh)_2$ product.

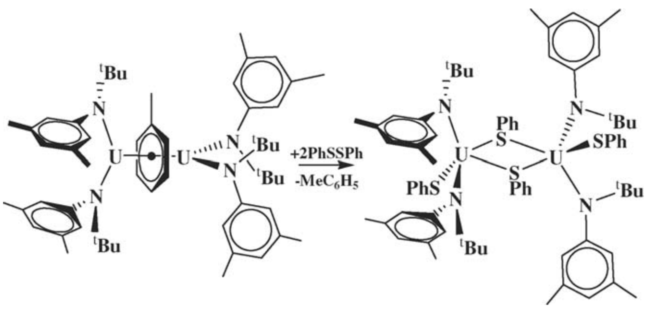
7.3. *Uranium arene complexes*

A relatively new class of highly reducing uranium complexes is comprised of compounds in which a ligand derived from an arene is sandwiched between two uranium centers ligated by two anionic ligands, $(X_2U)_2(C_6H_5R)$ (R = H, Me; X = $(NR_2)^{1-}$ [162], $(C_5Me_5)^{1-}$ [163]). The electron distribution in these complexes could be arranged in several ways. These complexes can be considered to be divalent uranium complexes of a neutral arene, trivalent complexes of an arene dianion, or tetravalent complexes of an arene tetraanion.

For reasons given in detail elsewhere [163], we favor the $U^{3+}/(C_6H_6)^{2-}$ description for the X = $(C_5Me_5)^{1-}$ complexes and include the reductive chemistry of this class in this U^{3+} review. Note that the arene ligands in these complexes differ substantially from those in the U^{3+} coordination complexes described in Section 5.23. The rings are not planar, the U-C(arene) bond distances are shorter by approximately 0.4 Å compared to the U^{3+} arene coordination complexes, and in the examples examined to date, the rings are not displaced by polar solvents or more electron donating arenes. Regardless of how the electrons are distributed, the reductive reactivity described below is unequivocal.

7.3.1. *$\{[(^tBuAr)_2N]_2U\}_2(C_6H_5Me)$, a four electron reductant*

The first example of a complex of this type was the bis(amido)uranium species, $\{[(^tBuAr)_2N]_2U\}_2(C_6H_5Me)$ [162]. This complex can effect the four electron reduction of two equivalents of PhSSPh to form $\{[(^tBuAr)_2N]_2(PhS)U\}_2(\mu\text{-}SPh)_2$, Eq. (104) [162]. This reaction can be viewed as a combination of two U^{3+} to U^{4+} reactions with a $(C_6H_6)^{2-}$ to C_6H_6 process according to Scheme 9.



(104)

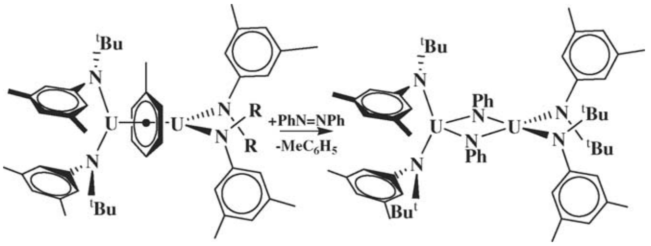
$$2PhS{-}SPh + 4e^{1-} \longrightarrow 4(PhS)^{1-}$$

$$2U^{3+} \longrightarrow 2e^{1-} + 2U^{4+}$$

$$(MeC_6H_5)^{2-} \longrightarrow 2e^{1-} + MeC_6H_5$$

Scheme 9.

Another four electron reduction observed for $\{[(^tBuAr)_2N]_2U\}_2(C_6H_5Me)$ is the reductive cleavage of the PhN=NPh to form the $(NPh)^{2-}$ bridged U^{4+} dimer, $\{[(^tBuAr)_2N]_2U\}_2(\mu\text{-}NPh)_2$, Eq. (105) [162]. In contrast to the reductions reported above in Eqs. (100) and (103) that form U^{6+} bis(imido) products, this reaction forms products in which the $(NPh)^{2-}$ ligands bridge two lower valent ions. As discussed in Section 6, this is an option for $(NPh)^{2-}$ and $(O)^{2-}$ ligands.



(105)

7.3.2. *$[(C_5Me_5)_2U]_2(C_6H_6)$*

A second type of $[X_2U]_2(C_6H_5R)$ complex has been isolated in which the X groups are pentamethylcyclopentadienyl rings, i.e. $[(C_5Me_5)_2U]_2(C_6H_6)$ [163]. This complex differs from $\{[(^tBuAr)_2N]_2U\}_2(C_6H_5Me)$ in that it has unusually long metal ligand distances. The U-C(C_5Me_5) distances are similar to those observed in the long bond organometallic complexes, i.e. $(C_5Me_5)_3U$ [143], $(C_5Me_5)_3UX$ (X = F [101], Cl [101], Me [164]), and $(C_5Me_5)_3UL$ (L = CO [144], N_2 [145]). These distances suggested that $[(C_5Me_5)_2U]_2(C_6H_6)$ might also display sterically induced reduction chemistry.

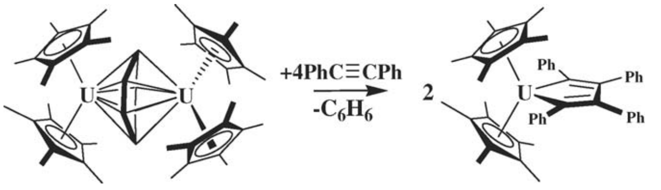
7.3.2.1. *Four electron reduction.* Like $\{[(^tBuAr)_2N]_2U\}_2(C_6H_5Me)$, the $[(C_5Me_5)_2U]_2(C_6H_6)$ complex can react as a four electron reductant by combining two U^{3+}/U^{4+} processes with reduction by $(C_6H_6)^{2-}$. This is demonstrated by the reductive coupling of four equivalents of PhC≡CPh to form two $(Ph_4C_4)^{2-}$ dianions and free C_6H_6, Eq. (106) [152]. The half reactions are shown in Scheme 10.

$$4PhC{\equiv}CPh + 4e^{1-} \longrightarrow 2(C_4Ph_4)^{2-}$$

$$2U^{3+} \longrightarrow 2e^{1-} + 2U^{4+}$$

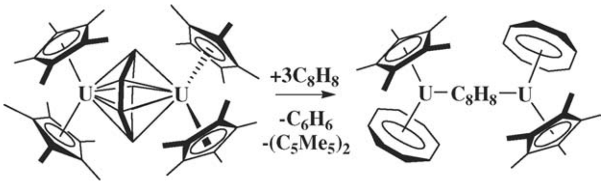
$$(C_6H_6)^{2-} \longrightarrow 2e^{1-} + C_6H_6$$

Scheme 10.



(106)

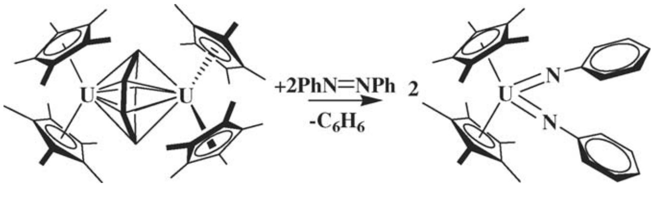
7.3.2.2. Six electron reduction. $[(C_5Me_5)_2U]_2(C_6H_6)$ can also display six electron reduction chemistry. This occurs in its reduction of 1,3,5,7-C_8H_8. One equivalent of this complex reacts with three equivalents of 1,3,5,7-C_8H_8 to generate the previously characterized $[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)$ [93] along with C_6H_6 and $(C_5Me_5)_2$, Eq. (107) [163].



(107)

The six electron conversion of three C_8H_8 substrates to three $(C_8H_8)^{2-}$ ligands can be explained by the half reactions in Scheme 11. Hence, three different types of reductive processes combine in this case: U^{3+}/U^{4+}, $(C_6H_6)^{2-}/C_6H_6$, and sterically induced reduction involving $(C_5Me_5)^{1-}/C_5Me_5$. Eq. (107) is significant in that it represents the first identified example of sterically induced reduction occurring in a bis-(C_5Me_5) complex rather than a tris-(C_5Me_5) complex.

7.3.2.3. Eight electron reduction. When the $(C_6H_6)^{2-}/(C_6H_6)$ couple is combined with a U^{3+}/U^{6+} reaction, the bimetallic $[(C_5Me_5)_2U]_2(C_6H_6)$ can function as an eight electron reductant. This occurs in the cleavage of PhN=NPh to make the U^{6+} imido complex described above in Eqs. (84), (100) and (103) [152]. Hence, one equivalent of $[(C_5Me_5)_2U]_2(C_6H_6)$ reduces two equivalents of PhN=Ph to form two equivalents of $(C_5Me_5)_2U(NPh)_2$ Eq. (108). The relevant half reactions are shown in Scheme 12. This reaction contrasts with Eq. (105) above in which $(NPh)^{2-}$ ligands are also made, but the product contains tetravalent uranium ions and a $[U(\mu\text{-}NPh)_2U]^{4+}$ structure [162].



(108)

$$3C_8H_8 + 6e^{1-} \longrightarrow 3(C_8H_8)^{2-}$$

$$2U^{3+} \longrightarrow 2e^{1-} + 2U^{4+}$$
$$(C_6H_6)^{2-} \longrightarrow 2e^{1-} + C_6H_6$$
$$2(C_5Me_5)^{1-} \longrightarrow 2e^{1-} + (C_5Me_5)_2$$

Scheme 11.

$$2PhN{=}NPh + 8e^{1-} \longrightarrow 4(NPh)^{2-}$$
$$(C_6H_6)^{2-} \longrightarrow 2e^{1-} + C_6H_6$$
$$2U^{3+} \longrightarrow 6e^{1-} + 2U^{6+}$$

Scheme 12.

8. Summary

This review shows that molecular complexes of U^{3+} can act as 1, 2, 3, 4, 6 and 8 electron reductants depending on the particular complex employed and the substrate. These reactions formally involve three types of U^{3+} redox couples, U^{3+}/U^{4+}, U^{3+}/U^{5+}, and U^{3+}/U^{6+} in combination with a variety of ligand-based processes. These include reduction by $(C_6H_6)^{2-}$ and $(BPh_4)^{1-}$ anions as well as sterically induced reduction via the $(C_5Me_5)^{1-}/C_5Me_5$ redox couple.

The results summarized here suggest several areas for future growth. For example, not all of these ligand-based reductions have been combined with the metal redox couples. Similarly, some of the processes combining two U^{3+}/U^{4+} couples with ligand redistribution to mimic the presence of a U^{2+} center, e.g. Eqs. (10), (12) and (85) have not been applied broadly to the other U^{3+}-based redox systems. The various combinations of a uranium redox couple and a ligand-based process have also not been combined with the use of external reductants such as the Na/Hg used in Eqs. (11) and (18) and Schemes 2, 4 and 6. Yet another area for future exploration is the nature of these U^{3+} reductions at higher temperatures—for example, at the 100 °C level used for the oxidative elimination of hydrogen in Eq. (16). Overall, there seem to be many options to expand U^{3+} reduction beyond the individual examples summarized here. We look forward to the continuation of new developments in this area.

Acknowledgment

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