Multi-electron Transfer by U(II) and Masked U(II) Complexes

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Abstract: Complexes of uranium in low oxidation state have shown the ability to activate non-reactive small molecules such as N_2. However, the multi-electron transfer required for such activation remains limited in uranium chemistry. Here, we review our recent research on the use of different strategies to overcome this issue, which has led to the isolation of a diuranium(III) bridging oxide complex that reacts as a U(II) synthon able to effect one-electron transfer per uranium center to *N*-heterocycles and multi-electron transfer to diphenylacetylene and azobenzene. We also showed that a closely related molecular U(II) complex effects the same reactions providing the first unambiguous example of a monouranium four-electron transfer.

Keywords: Electron transfer · Multimetallic complexes · Oxide · Redox-active ligands· Uranium

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1. Introduction

Small molecules such as N_2, CO and CO_2 are abundant on Earth and thus attractive starting materials to produce value-added compounds.[1,2] Low oxidation state uranium compounds have been shown to have unique properties, resulting in high reactivity towards these molecules.[3–5] In particular, U(II) and U(III) compounds are highly reducing, as required for the activation of unreactive small molecules, but they predominantly undergo single-electron transfer reactions, whereas small molecule transformation requires multiple electrons.

In order to overcome this, several strategies can be employed. Firstly, multimetallic complexes can be used to implement multi-electron transfer through cooperation of the different uranium ions. This strategy has been successfully applied by our group, resulting in diuranium(III) complexes, able to effect the four-electron reduction of N_2 by two cooperative U(III)/U(V) oxidations (Scheme 1a, **1–5**).[6–8] Nevertheless, multimetallic complexes in low oxidation states remain largely unexplored due to difficulties in devising rational syntheses.

Secondly, redox active ligands can be combined with uranium to store extra electrons, available for reactivity. Various redox-active ligands have been used, resulting in uranium-redox active ligand systems that are able to reduce compounds such as alkynes to metallacycles or azobenzene to bis-imido complexes (Scheme 1b, **6,7**), reactions that require two and four electrons, respectively.[9–12]

Finally, the electronic structure of uranium ions can be tuned by the ligands to enable monouranium multi-electron transfer. The +2 oxidation state was identified for the first time in molecular compounds in 2013[13] and since then only a limited number of U(II) complexes[14–19] have been reported. Furthermore, their reactivity remains practically unexplored, partially due to their high reactivity.[15,20] Notably, U(II) complexes can potentially transfer four electrons, but a first study of a U(II) complex indicated that while it is able to transfer two electrons, it is also prone to undergo competitive one-electron transfer (Scheme 1c, **8–10**).[15]

Here we review the recent advancements in our group to achieve multi-electron transfer by uranium using a combination of the strategies discussed above.[21,22] Inspired by previous results obtained in our group using $OSi(O^tBu)_3$ as supporting ligands in uranium chemistry,[6–8] a new diuranium(III) oxo-bridged complex was synthesized, supported by the more electron-donating $N(SiMe_3)_2$ ligands. The oxo linker was chosen, as it is usually inert and cleavage of the M-O-M bond has only very rarely been observed. Only one example of a reactive bridging oxide has been reported in uranium chemistry.[23] In transition metal chemistry, an Fe(III)-O-Fe(III) complex has been reported to form a Fe(IV)=O and a Fe(II) fragment, although only upon irradiation.[24,25]
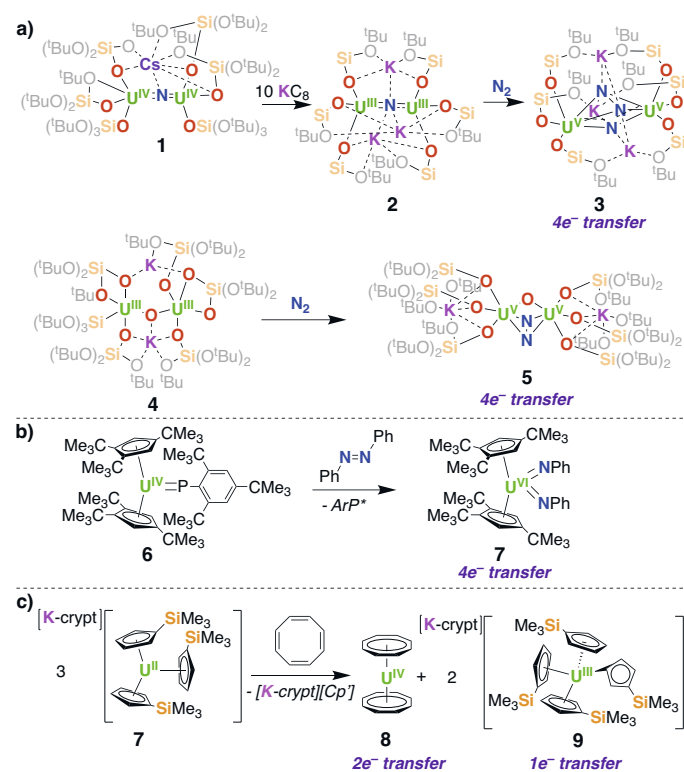
2. Linker Effect

In our group, we also reported the synthesis of the nitride-bridged diuranium(IV) complex $[NBu_4][\{((Me_3Si)_2N)_3U\}_2(\mu-N)]$ (**12**) from a reaction of $[U\{N(SiMe_3)_2\}_3]$,[26] (**11**) with 0.5 equivalents of NBu_4N_3 (Scheme 2a). However, due to the significantly increased electron-donating ability of the $N(SiMe_3)_2$ ligands, reduction of the diuranium(IV) to afford the diuranium(III) nitride-bridged complex could not be achieved.

In contrast, reduction of the previously reported oxo-bridged complex $[\{((Me_3Si)_2N)_3U\}_2(\mu-O)]$,[27] (**13**) with 10 equivalents

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a)

1 → **2** → **3** 4e⁻ transfer

4 → **5** 4e⁻ transfer

b)

6 → **7** 4e⁻ transfer

c)

7 → **8** 2e⁻ transfer + **9** 1e⁻ transfer

Scheme 1. Examples of multi-electron transfer by a) cooperation between uranium centers in multimetallic complexes,[6,7] b) cooperation between a uranium center and a redox-active ligand,[11] and c) a single uranium center.[15]

of KC_8 in the presence of cryptand at –80 °C resulted in the formation of the diuranium(III) complex $[K(2.2.2\text{-cryptand})]_2$ $[\{((Me_3Si)_2N)_3U\}_2(\mu\text{-O})]$ (**14**) (Scheme 2b). This complex can be isolated as purple crystals in 70% yield by diffusion of hexane into the THF solution. The molecular structure of **14** (Fig. 1a) as determined by X-ray crystallography consists of a dianionic oxo-bridged diuranium(III) complex and two K(2.2.2-cryptand) counterions. The metrical parameters in the structure of **14** are similar to those of the parent complex **13**, except for a longer average U–N_{amide} bond length, which increased from 2.29(1) to 2.430(5) Å, consistent with the increase in ionic radius upon reduction of U(IV) to U(III) (ionic radii in octahedral environment: U(III): 1.025 Å; U(IV): 0.89 Å).[28]

Complex **14** was expected to be highly reducing due to the presence of the more electron-donating $N(SiMe_3)_2$ ligands, compared to the $OSi(O^tBu)_3$ analogue, and therefore a good candidate to react with small molecules. Surprisingly, its reactivity is significantly

lower than the siloxide complex **4**, showing no reactivity with N_2, CO or H_2. The reaction of **14** with CO_2 yielded a few crystals of the U(III) complex $[K(2.2.2\text{-cryptand})][U\{N(SiMe_3)_2\}_3\{OSiMe_3\}]$, which is likely formed due to ligand scrambling.[29]
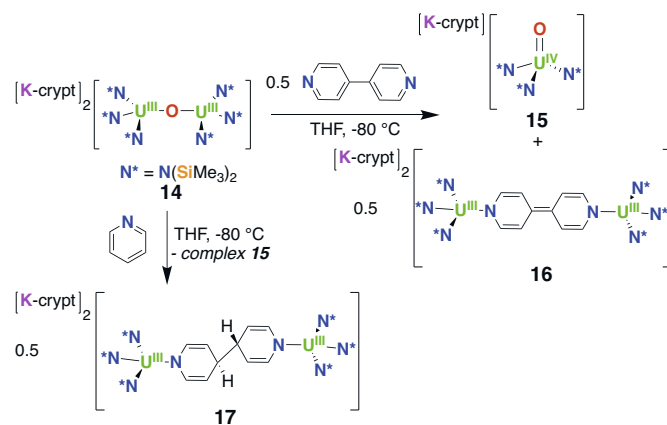
The lack of reactivity observed for this diuranium(III) complex parallels the decreased nucleophilic reactivity of the amide supported nitride-bridged diuranium(IV) complex **12** compared to the siloxide analogue **1**. Such differences were explained in terms of an increased covalent interaction between the uranium center and the amide ligands that results in a decreased electron density at the bridging nitride. Electronic effects could also play a role in the observed absence of interaction of the amide diuranium(III) complex, but steric effects leading to a decreased accessibility of the uranium center cannot be ruled out. In order to assess if steric effects were dominant we investigated the reactivity of these complexes with other bulkier but more coordinating substrates.
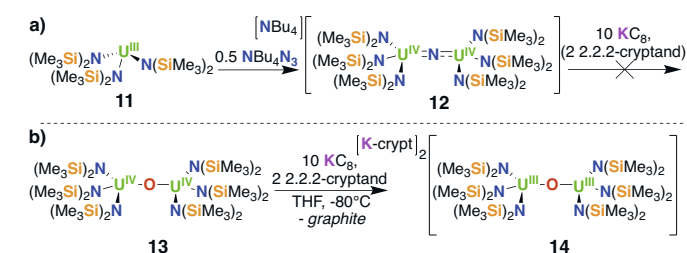
3. One-electron Transfer Reactions

Complex **14** showed extraordinary reactivity with N-heterocycles, during which the usually inert U–O is easily cleaved. Indeed, the reaction with 4,4'-bipyridine (4,4'-bpy) and pyridine (pyr) resulted in the release of a U(II) synthon and the U(IV) terminal oxo side product, $[K(2.2.2\text{-cryptand})][U(O)$ $\{N(SiMe_3)_2\}_3]$ (**15**). Two U(II) synthons react cooperatively with the substrate to transfer two electrons. This led to the isolation of diuranium(III) complexes bridged by two-electron reduced ligands.

Upon addition of 4,4'-bpy to a purple solution of complex **14** in THF-d_8 at –80 °C, the color changed immediately to dark brown. Diffusion of hexane into a concentrated THF solution afforded a mixture of pink and brown crystals characterized as complex **15** and the 4,4'-bpy-bridged diuranium(III) complex, $[K(2.2.2\text{-cryptand})]_2[\{((Me_3Si)_2N)_3U\}_2(\mu\text{-4,4'-bpy})]$ (**16**, Scheme 3). This is the first example of reduction of 4,4'-bpy by uranium, although Meyer and colleagues did report the one-electron reduction of 2,2'-bipyridine by a U(III) complex,[30] which is harder to reduce ($E_{1/2}$ in DMF vs. Ag/AgCl: 4,4'-bpy: –1.91 V –2.47 V, 2,2'-bpy: –2.19V and –2.76 V).[31] Complex **16** cannot be obtained clean from this reaction, since complex **15** has similar solubility. Nevertheless, it can be obtained in 68% yield through an alternative method involving reduction of the diuranium(IV) analogue of **16**, $[\{((Me_3Si)_2N)_3U\}_2(\mu\text{-4,4'-bpy})]$ (**18**) which can be synthesized by reacting $[U\{N(SiMe_3)_2\}_3]$ with 4,4'-bpy (Scheme 5, below).

Pyridine reduction reactions are significantly more rare than bpy ones due to its high reduction potential ($E_{1/2}$ in DMF vs. Ag/

a)

11 → [NBu₄] **12** → (10 KC_8, (2 2.2.2-cryptand)) ✗

b)

13 → (10 KC_8, 2 2.2.2-cryptand, THF, -80°C, - graphite) **14**

Scheme 2. Synthesis of $[K(2.2.2\text{-cryptand})]_2[\{((Me_3Si)_2N)_3U\}(\mu\text{-O})]$ (**11**) by reduction of $[\{((Me_3Si)_2N)_3U\}(\mu\text{-O})]$ (**10**) with excess KC_8 in the presence of 2.2.2-cryptand.

14 → (0.5 4,4'-bpy, THF, -80 °C) **15** + **16**

14 → (pyridine, THF, -80 °C, - complex **15**) **17**

N* = N(SiMe₃)₂

Scheme 3. Reactivity of $[K(2.2.2\text{-cryptand})]_2[\{((Me_3Si)_2N)_3U\}(\mu\text{-O})]$ (**14**) with 4,4'-bipyridine and pyridine to yield $[K(2.2.2\text{-cryptand})]_2$ $[\{((Me_3Si)_2N)_3U\}(\mu\text{-4,4'-bpy})]$ (**16**) and $[K(2.2.2\text{-cryptand})]_2[\{((Me_3Si)_2N)_3U\}$ $(\mu\text{-(pyr)}_2)]$ (**17**) with the side product $[K(2.2.2\text{-cryptand})]_2[U(O)\{N(SiMe_3)_2\}_3]$ (**15**).
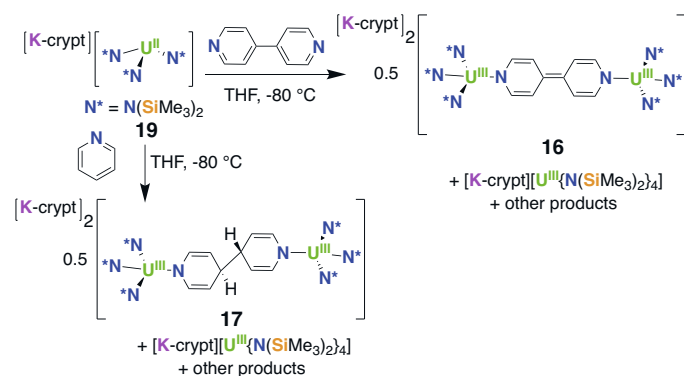
Scheme 4. Reactivity of [K(2.2.2-cryptand)]₂[U{N(SiMe₃)₂}₃] (**19**) with 4,4'-bipyridine and pyridine to yield [K(2.2.2-cryptand)]₂[{((Me₃Si)₂N)₃U}(μ-4,4'-bpy)] (**16**) and [K(2.2.2-cryptand)]₂[{((Me₃Si)₂N)₃U}(μ-(pyr)₂)] (**17**) along with [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₄] and other side products.

Scheme 5. Reactivity of [{((Me₃Si)₂N)₃U}(μ-4,4'-bpy)] (**18**) with 2 equivalents of $^{13}CO_2$ to yield $^{13}CO^{2-}$ quantitatively, while releasing 4,4'-bipyridine.

AgCl = –2.76 V).[31] Only a few examples have been reported in the literature of complexes able to reductively couple pyridine: Ln(II), Sc-arene, Th(III) and Fe(II).[32–36] Remarkably, complex **14** is the first example of pyridine reduction by uranium.

Upon addition of pyridine to a purple solution of complex **1** in THF-d₈ at –80 °C, the color remained purple, but ^1H NMR signals of complex **15** were immediately observed in the ^1H NMR spectrum, along with a new set of signals. Diffusion of hexane into a concentrated THF solution afforded a mixture of pink and purple crystals, characterized as complex **15** and [K(2.2.2-cryptand)]₂[{((Me₃Si)₂N)₃U}₂(μ-pyr)₂] (**17**, Scheme 3). Washing the mixture with toluene allowed the removal of **15** and clean isolation of **17** in 35% yield.

The molecular structures of **16** (Fig. 1b) and **17** (Fig. 1c) show dianionic diuranium(III) complexes, in which each uranium center is bound by three N(SiMe₃)₂ ligands and they are linked by the 4,4-bpy ligand or two reductively coupled pyridine molecules, respectively. The average U–N_amide bond lengths (**16**: 2.387(11) Å; **17**: 2.385(5) Å) are similar to that of complex **14**, corroborating the assignment as the U(III) oxidation state. Furthermore, 4,4'-bpy is a redox-active ligand and the C–C_interring bond length is indicative of the degree of reduction. In **16**, the C–C_interring bond length of 1.393(8) Å is typical for two-electron reduced 4,4'-bpy[36,37] and is significantly shorter than the values reported for actinide complexes containing neutral 4,4'-bpy.[38] In contrast, the C–C_interring bond length in **17** is considerably longer at 1.570(17) Å, in line with a single bond. This bond length is comparable to those in previously reported pyridine complexes (1.559(4) Å to 1.563(6) Å).[32–36]

The U(II) complex corresponding to the U(II) synthon released by **14**, [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₃] (**19**) was previously reported by Evans and colleagues.[18] To further support the release of a U(II) synthon associated with the reactivity of **14**, the reduction of bipyridine and pyridine by complex **19** were studied. Indeed, the formation of the same products
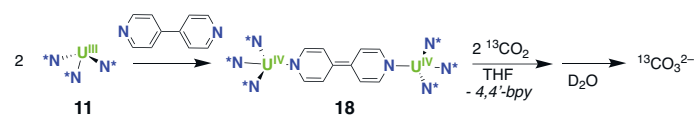
was observed in the ^1H NMR spectra, but the scrambling product [K(2.2.2-cryptand)][U{N(SiMe₃)₂}₄] and other unidentified products were also observed, in particular if the *in situ* solution of complex **19** was not reacted immediately (Scheme 4). These results clearly demonstrate that complex **14** indeed behaves as a U(II) synthon, but its reactivity is considerably more controlled and cleaner compared to the actual U(II) complex **19**, highlighting the importance of such synthons.

In the previous reactions, one electron is transferred per uranium center, either by a U(II) complex or a U(II) synthon, and two of these fragments cooperate to reduce the substrate by two electrons in total. Furthermore, the products of these reactions store multiple electrons, which can potentially be transferred to other substrates. We probed this possibility with complex **18** in a reaction with CO_2. The diuranium(IV) analogue of **16** was chosen to confirm that the electrons transferred in the reaction are released by the ligand and do not come from the uranium, as U(III) complexes[39,40] have been reported to reduce CO_2 to afford carbonate using the electrons of the uranium center, while a U(IV) complex[41] was only able to reduce CO_2 using the electrons stored in a redox-active ligand. The addition of two equivalents of $^{13}CO_2$ to [{((Me₃Si)₂N)₃U}₂(μ-4,4'-bpy)], followed by quenching in D_2O (pD = 13) showed complete conversion to $^{13}CO_2$ in the quantitative $^{13}C\{^1H\}$ NMR spectrum, indicating the successful transfer of the two electrons stored in 4,4'-bpy (Scheme 5).

4. Multi-electron Transfer Reactions

Furthermore, we investigated whether other substrates, requiring the transfer of two electrons, could trigger the release of the U(II) synthon from complex **14** and thus whether multi-electron transfer was possible. This also inspired us to further study the reactivity of the isolated U(II) complex **19**.

The addition of diphenylacetylene to complex **14** at –80 °C in THF resulted in a color change from purple to brown. The metallocyclopropene complex [K(2.2.2-cryptand)][U(η²-C₂Ph₂){N(SiMe₃)₂}₃] (**20**) could be isolated in 25% yield after washing with toluene to remove complex **15** (Scheme 6). The low yield is caused by the partial solubility of **5** in toluene and the conversion of the reaction is >65% as determined by ^1H NMR (with TMS₂O as internal standard). The reactivity of complex **1** as a U(II) synthon was again confirmed by the reaction of *in situ* formed com-

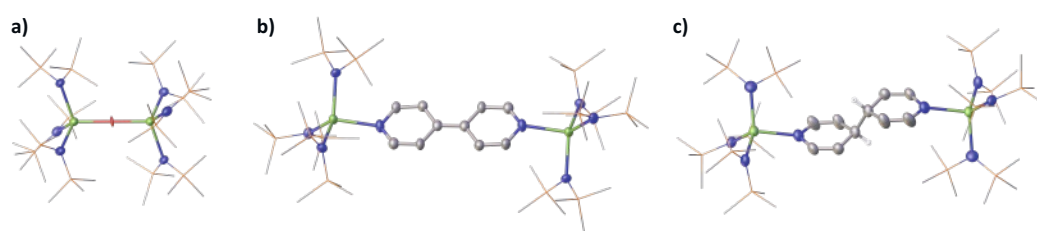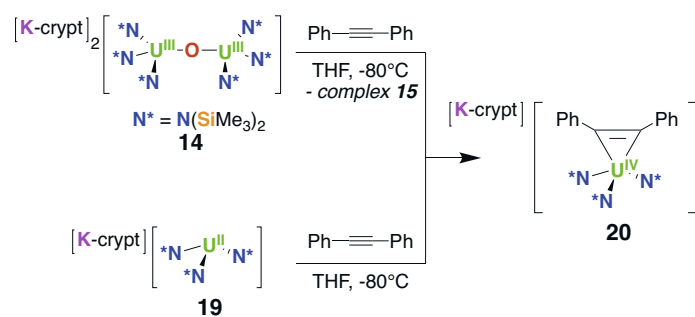**Fig. 1.** Molecular structures of a) [K(2.2.2-cryptand)]₂ [{((Me₃Si)₂N)₃U}(μ-O)] (**14**), b) [K(2.2.2-cryptand)]₂ [{((Me₃Si)₂N)₃U}(μ-4,4'-bpy)] (**16**), and c) [K(2.2.2-cryptand)]₂ [{((Me₃Si)₂N)₃U}(μ-(pyr)₂)] (**17**). Thermal ellipsoids depicted at 50% probability. Hydrogen atoms, except for the bridging carbon hydrogens in **3**, and the [K(2.2.2-cryptand)]⁺ counterions were omitted for clarity.
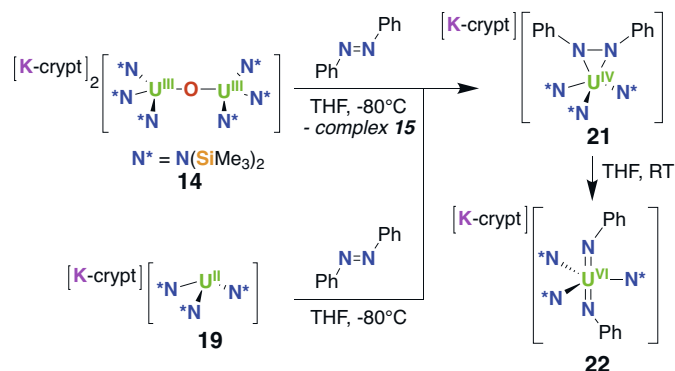
Scheme 6. Reactivity of [K(2.2.2-cryptand)]$_2$[{((Me$_3$Si)$_2$N)$_3$U}(μ-O)] (**14**) and [K(2.2.2-cryptand)]$_2$[U{N(SiMe$_3$)$_2$}$_3$] (**19**) with diphenylacetylene to yield [K(2.2.2-cryptand)][U(η^2-C$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$] (**20**).

plex **19** with diphenylacetylene. This is only the fourth example of a metallocyclopropenyl complex. Previous examples were obtained either by the use of an external reducing agent[42] or by complexes displaying similar U(II) synthon reactivity reported by Marks[43] and Walter.[11,12] The former is released *via* a similar disproportionation reaction of U(III) to U(IV) and U(II), while the latter is released by releasing a PMes* ligand.

The molecular structure of **20** (Fig. 2a) shows the presence of an anionic uranium complex, supported by three N(SiMe$_3$)$_2$ ligands and a bidentate PhCCPh ligand. The C–C bond length of 1.342(5) Å is elongated compared to the free ligand (1.192(5) Å),[44] indicating two-electron reduction to a double bond. Furthermore, all metrical parameters of **20**, such as the U–C bond lengths (2.345(3) and 2.352(3) Å) and the C-U-C angle (33.22(11)°) are consistent with the previously reported metallocyclopropenyl uranium complexes (U–C = 2.303(3) to 2.350(9) Å and C-U-C = 33.3(3)°, 33.7(1)°) and confirm the assignment of **20** as a U(IV) complex containing the two-electron reduced diphenylacetylene ligand.

Since U(II) can potentially transfer four electrons, we also studied the reactivity of both complexes **14** and **19** with azobenzene, a possible four-electron oxidant. The addition of a red solution of azobenzene in THF at –80 °C to purple crystals of **14** immediately caused a color change to red/brown. Furthermore, the ^{1}H NMR spectrum at –80 °C showed the signals corresponding to complex **15**. At –40 °C and at 0 °C a new set of signals was observed in the ^{1}H NMR spectrum. Upon increasing the temperature to 25 °C the color changed to yellow/brown and these signals immediately start to decrease, while simultaneously another new set of signals grows in. The conversion is complete after 2 h. Crystallization at low temperature yielded crystals of the two-electron reduction product [K(2.2.2-cryptand)][U(N$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$] (**21**) while crystallization of the room temperature reaction mixture afforded crystals of the four-electron reduction, bis-imido product [K(2.2.2-cryptand)][U(NPh)$_2${N(SiMe$_3$)$_2$}$_3$] (**22**, Scheme 7). This shows that the reduction occurs in two consecutive two-electron steps. Complex **19** again showed the same reactivity.

In the molecular structure of complex **21** (Fig. 2b) the uranium center is supported by three N(SiMe$_3$)$_2$ ligands and one bidentate

Scheme 7. Reactivity of [K(2.2.2-cryptand)]$_2$[{((Me$_3$Si)$_2$N)$_3$U}(μ-O)] (**14**) and [K(2.2.2-cryptand)]$_2$[U{N(SiMe$_3$)$_2$}$_3$] (**19**) with azobenzene to yield [K(2.2.2-cryptand)][U(N$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$] (**21**) at –80 °C, which transforms into [K(2.2.2-cryptand)][U(NPh)$_2${N(SiMe$_3$)$_2$}$_3$] (**22**) at room temperature.

PhNNPh ligand. The structure is similar to complex **20** with a comparable averge U–N$_{amide}$ bond length of 2.34(2) Å, but with a hydrazido instead of a cyclopropenyl bidentate ligand. The N–N bond length of 1.43(2) Å is considerably longer than in free azobenzene (1.251 Å). Furthermore, it is longer than in the one-electron reduced azobenzene U(IV) complex [((SiMe$_2$NPh)$_3$-tacn)U(η$_2$-N^{2}Ph$_2$)] (1.353(4) Å)[45] and close to the only other reported U(IV) hydrazido complex, Tp*$_2$U(η^2-N$_2$Ph$_2$) (Tp = hydrotris(3,5-dimethyl pyrazolyl)borate) (1.440(3) Å),[46] consistent with a two-electron reduction. The latter did not show any further reduction to the bis-imido complex.

The molecular structure of complex **22** (Fig. 2c) shows the presence of a uranium complex supported by three N(SiMe$_3$)$_2$ ligands and two NPh ligands in a trigonal bipyrimidal geometry. The uranyl analogue of this complex, [K(2.2.2-cryptand)][U(O)$_2${N(SiMe$_3$)$_2$}$_3$], was previously reported by Liddle and colleagues and the average U–N$_{amide}$ bond lengths are comparable (**22**: 2.34(2) Å; uranyl: 2.323(2) Å).[47] In addition, the U–N$_{imido}$ bond lengths of 1.929(8) and 1.935(8) Å fall within the range of previously reported bis-imido complexes (1.840(4) to 1.992(5) Å).[48–50]

These results show that both complexes **14** and **19** are able to transfer up to four electrons by effecting two consecutive two-electron transfer processes to azobenzene. Notably, the reaction with complex **19** is the first example of unambiguous monouranium four-electron transfer.

5. Conclusion

In conclusion, our recent work[21,22] demonstrated that in diuranium(III) oxo-bridged complexes, the ligands have a large influence on the reactivity. With the N(SiMe$_3$)$_2$ ligand, the U(III)-O-U(III) did not show any reactivity with N$_2$ in contrast to the four-electron reduction of N$_2$ reported for the analogous siloxide complex. However, the U–O bond in the amide U(III)-O-U(III) complex showed an increased lability in the presence of more coordinating substrates, resulting in the release of a U(II) synthon upon suitable substrate binding, which can effect multi-electron transfer. The released U(II) synthon and isolated U(II) can both co-
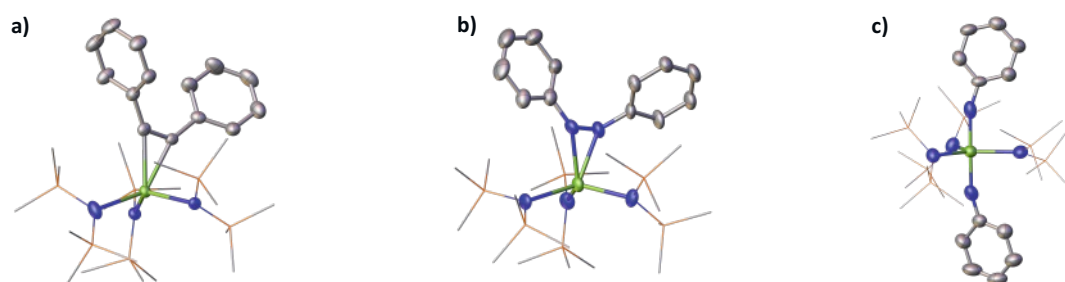

Fig. 2. Molecular structures of a) [K(2.2.2-cryptand)][U(η^2-C$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$] (**20**), b) K(2.2.2-cryptand)][U(N$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$] (**21**), and c) [K(2.2.2-cryptand)][U(NPh)$_2${N(SiMe$_3$)$_2$}$_3$] (**22**). Thermal ellipsoids depicted at 50% probability. Hydrogen atoms and the [K(2.2.2-cryptand)]$^+$ counterions were omitted for clarity.

operatively effect the two-electron reduction of N-heterocycles by transferring one electron per uranium. However, we also showed that both the released U(II) synthon and the isolated U(II) complex are able to transfer multiple electrons per metal center to unsaturated molecules, such as diphenylacetylene and azobenzene. This allowed us to demonstrate for the first time the unambiguous mon-uranium four-electron transfer to a substrate. These results indicate that while single-electron transfer processes are dominant in uranium chemistry, the coordination environment can be tuned to enable both cooperative and independent multi-electron transfer. This understanding is essential in the design of new complexes that are highly reactive towards small molecules.

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