CO Cleavage

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Facile CO Cleavage by a Multimetallic CsU_2 Nitride Complex

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Abstract: *Uranium nitrides are important materials with potential for application as fuels for nuclear power generation, and as highly active catalysts. Molecular nitride compounds could provide important insight into the nature of the uranium–nitride bond, but currently little is known about their reactivity. In this study, we found that a complex containing a nitride bridging two uranium centers and a cesium cation readily cleaved the C≡O bond (one of the strongest bonds in nature) under ambient conditions. The product formed has a* $[CsU_2(\mu\text{-}CN)(\mu\text{-}O)]$ *core, thus indicating that the three cations cooperate to cleave CO. Moreover, the addition of MeOTf to the nitride complex led to an exceptional valence disproportionation of the* $CsU^{IV}\text{–}N\text{–}U^{IV}$ *core to yield* $CsU^{III}(OTf)$ *and* $[MeN{=}U^{V}]$ *fragments. The important role of multimetallic cooperativity in both reactions is illustrated by the computed reaction mechanisms.*

Uranium nitrides are of great interest because of their potential application in both stoichiometric and catalytic transformations and in materials science and engineering.[1] The recent discovery and characterization of stable mononuclear and dinuclear uranium nitride complexes[2] has now rendered the investigation of the reactivity of these species accessible.

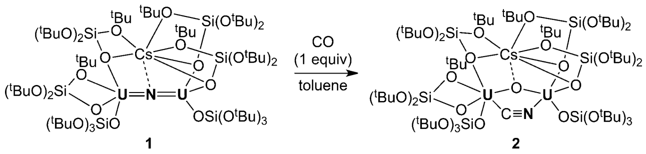
Carbon monoxide is an inexpensive and readily available C_1 feedstock used in industry for the production of a wide variety of chemicals, such as methanol, acetic acid, phosgene, and hydrocarbons.[3] A key step in Fischer–Tropsch hydrocarbon production from CO and H_2 is the cleavage of the CO triple bond, which is the strongest chemical bond (dissociation energy at 298 K: 1076 $kJ\,mol^{-1}$). This process requires the use of heterogeneous transition-metal catalysts at elevated temperatures.[4] The cleavage of the CO bond under mild conditions is an important fundamental challenge in the search for new routes for the production of functionalized organic molecules from CO.

The direct addition of CO to a metal nitride is a rare event observed only for highly nucleophilic nitride complexes of d-block transition metals, such as V, Fe, and Hf.[5] Notably, a few terminal monometallic nitrido complexes and only one example of nitride-bridged dimetallic complex[5f] effect nitrogen-atom transfer to CO to afford cyanate, which in some cases is spontaneously extruded.[5d] Reductive carbonylation of monometallic U^{V} and U^{VI} nitrides by CO to afford the isocyanate ligand has also been reported recently.[5e] However, the complete cleavage of CO by a nitride complex has not been reported so far.

Several examples of CO cleavage by metal complexes have been reported,[6] and these reactions often yield metal–carbide complexes and oxo clusters. The binding[7] and the reduction[8] of CO by uranium(III) complexes has been demonstrated. Several examples of CO reductive homologation effected by uranium(III) systems with the formation of deltate,[9] squarate,[9b,10] or ethynediolate dianions[9b,11] have also been identified. However, uranium compounds that effect the deoxygenation of CO have not yet been described.

We recently demonstrated the unusually high nucleophilic character of the nitride-bridged diuranium complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**),[2d,12] which reacted under ambient conditions with CO_2 and CS_2 to form a C–N bond and yield cyanate, thiocyanate, and unprecedented dicarbamate species. Herein we show that the unusually high nucleophilic character of **1**, and the multimetallic cooperativity of the CsU_2 core, lead to complete cleavage of the CO triple bond to yield a cyanide. The cyanide ligand in **1** is readily transferred to electrophiles, such as MeOTf and Me_3SiI, thus yielding organic nitriles. We also demonstrate that the direct methylation of the nitride complex **1** leads to disproportionation of the uranium cation: completely unprecedented reactivity in nitride chemistry.

The addition of stoichiometric or excess amounts of CO or ^{13}CO (1 equiv) to the diuranium(IV) complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$ (**1**) in toluene at room temperature led to an immediate color change of the solution from brown to light blue (Scheme 1). The proton NMR spectrum recorded at 25 °C immediately after the reaction showed the disappearance of the peak assigned to complex **1** and the appearance of a single new signal at −1.34 ppm. Blue crystals of the complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}CN)(\mu\text{-}O)\}]$ (**2**) were isolated in 60 % yield at −40 °C. Proton NMR studies showed that



Scheme 1. CO cleavage reaction effected by complex **1** under ambient conditions to afford the complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}CN)(\mu\text{-}O)\}]$ (**2**).

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complex **2** was stable in toluene at room temperature for several hours. The ^{13}C NMR spectrum of complex **2** showed the presence of a signal at 866 ppm, which was assigned to the ^{13}CN ligand. Traces of decomposition, evident from a new NMR peak assigned to the [U(OSi(O^{t}Bu)$_3$)$_4$] complex, appeared only after three days, probably as a result of ligand scrambling. The solid-state structure of **2** (Figure 1) shows the presence of a diuranium(IV) complex in which two [U(OSi(O^{t}Bu)$_3$)$_3$] fragments are bridged by one oxo ligand and one cyanide group. This structure indicates that the highly nucleophilic character of the bridging nitride promotes the ready cleavage and deoxygenation of carbon monoxide to afford a N≡C triple bond and a bridging oxo group. The resulting cyanide ligand adopts a bridging mode with U−C (2.610(7) Å) and U−N (2.576(6) Å) bond distances comparable to those reported for cyanide-bridged diuranium(IV) complexes (2.549(8)–2.583(2) Å).[13] The N−C bond distance (1.155(9) Å) compares well to that found in cyanide-bridged diuranium(IV) complexes (1.177(4) Å).[13b]

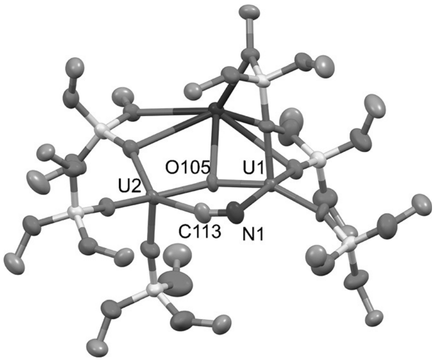
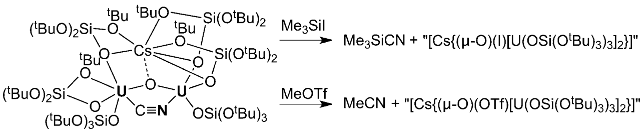


Figure 1. Molecular structure of [Cs{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-CN)(μ-O)}] (**2**). Thermal ellipsoids are depicted at 50% probability. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances [Å]: U1–O105 2.124(4), U1–N1 2.576(6), N1–C113 1.155(9), U2–O105 2.144(4), U2–C113 2.610(7).

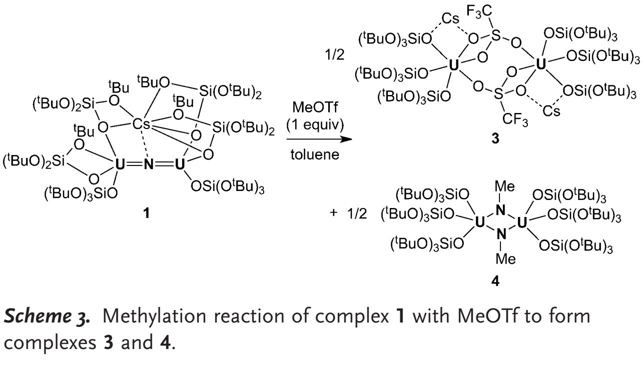
The outcome of the reaction of **1** with CO is very different from that recently reported for the reaction of mononuclear uranium nitride complexes with CO, which led to the reductive carbonylation of U^{V} and U^{VI}, thus affording U^{III}–OCN and U^{IV}–OCN complexes, respectively.[5e] This remarkable difference in reactivity shows the importance of multimetallic cooperativity in CO scission.

To confirm the presence of a cyanide ligand in complex **2** and to investigate the possibility of transferring the cyanide ligand to organic substrates, we treated complex **2** with Me$_3$SiI and with MeOTf (Scheme 2). The reaction of [Cs{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-^{13}CN)(μ-O)}] with Me$_3$SiI (1 equiv) at room temperature in benzene led to an immediate colour change and afforded a white suspension. The ^{13}C NMR spectrum of the reaction mixture showed the disappearance of the peak assigned to the uranium-bound ^{13}CN group and the appearance of a new signal at 126.3 ppm, which was assigned to the cyanide group of Me$_3$Si^{13}CN.[14] After the addition of Me$_3$SiI, proton NMR studies showed the immediate disappearance of the peak assigned to complex **2** and the appearance of only one new major signal at −1 ppm. This signal was assigned to an intermediate oxo iodide species "[Cs{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-O)(I)}]". This species decomposes rapidly and after 48 h only a peak assigned to [U(OSi(O^{t}Bu)$_3$)$_4$] was observed. The formation of a stable μ-oxo iodide complex and Me$_3$Si^{13}CN was observed in the reaction of the dihafnium oxo cyanide complex [{(η$_5$-C$_5$Me$_4$H)$_2$Hf(NCO)}(μ-O){(η$_5$-C$_5$Me$_4$H)$_2$Hf(CN)}] with Me$_3$SiI.[14] The formation of [U(OSi(O^{t}Bu)$_3$)$_4$] from the intermediate iodide is the result of ligand scrambling. Ligand scrambling leading to the formation of bis(oxo) complexes and unidentified products was previously observed for the diuranium(IV) oxo- and cyanate-bridged complex "[Cs{[U(OSi(O^{t}Bu)$_3$)$_3$]$_2$(μ-NCO)(μ-O)}]".[12] The reaction of **2** with MeOTf proceeded more slowly, and after 24 h at room temperature a large amount of starting material was still present. The ^{1}H NMR spectrum in [D$_8$]toluene after 24 h showed the presence of the signal assigned to [U(OSi(O^{t}Bu)$_3$)$_4$] and a broad signal at 0.63 ppm assigned to CH$_3$^{13}CN. The formation of CH$_3$^{13}CN was confirmed by the presence of a signal at 113 ppm in the ^{13}C NMR spectrum. The cyanide-alkylation reaction was complete after overnight heating at 55 °C. NMR studies did not show evidence of products arising from the alkylation of the bridging oxo ligand. Overall, the successive addition of CO and MeOTf (or Me$_3$SiI) to complex **1** resulted in the conversion of CO into organic nitrile compounds.



Scheme 2. Reactions of **2** with the electrophiles MeOTf and Me$_3$SiI to afford MeCN and Me$_3$SiCN. OTf = trifluoromethanesulfonate.

For comparison, we also investigated the reactivity of the nitride complex **1** with MeOTf. The reaction of **1** with MeOTf (1 equiv) at room temperature resulted in a slow (24 h) color change of the solution from brown to green and a mixture of complexes **3** and **4** (Scheme 3). Storage of the solution at −40 °C resulted in the isolation of light-blue crystals of the bis(imido) complex [{U^{V}(OSi(O^{t}Bu)$_3$)$_3$}$_2$(μ-NMe)$_2$], (**4**). Attempts to isolate the two products in pure form from this reaction were not successful. The reaction was faster when **1** was treated with 2 equivalents of MeOTf, but the same mixture of complexes **3** and **4** was obtained, as indicated by the proton NMR spectrum. However, in this case storage of



Scheme 3. Methylation reaction of complex **1** with MeOTf to form complexes **3** and **4**.

the reaction mixture at −40 °C for 24 h resulted in the isolation of green-blue crystals of the complex $[\mathrm{Cs_2}\{[\mathrm{U(OSi(O^tBu)_3)_3}]_2(\mu\text{-OTf})_2\}]\cdot 2(\mathrm{C_7H_8})$ (**3·2(C$_7$H$_8$)**) in 60 % yield. The crystallization of complex **3** is probably favored by the presence of excess MeOTf in the solution. Subsequent cooling of the mother liquor afforded a few crystals of complex **4**. Owing to its low stability, the isolation of complex **4** in sufficient amounts for further characterization was not possible. The low stability of the U$^{\mathrm{V}}$ imido complex **4** is consistent with the observed instability of previously reported "$[\mathrm{U^V(OSi(O^tBu)_3)_3}(\mathrm{NR})]$" (R = adamantyl) intermediate, which that could not be isolated because it rapidly disproportionated to afford $[\mathrm{U^{IV}(OSi(O^tBu)_3)_4}]$ and $[\mathrm{U^{VI}{}_2(NR)_4(OSi(O^tBu)_3)_4}]$.[2d]

The solid-state structure of **3** (Figure 2) consists of a diuranium(III) complex in which two $[\mathrm{U(OSi(O^tBu)_3)_3}]$ fragments are bridged by two triflate anions, each one binding the two uranium centres and a cesium cation in a μ_3:κ^2-(O,O):η^1-O fashion. The mean U−O$_{\mathrm{siloxide}}$ bond length is similar (2.165(3) Å) to the U−O$_{\mathrm{siloxide}}$ distance found in U$^{\mathrm{IV}}$ complex **1** (U−O$_{\mathrm{avg}}$: 2.19(3) Å) and in the diuranium(III) tris(siloxide) complex $[\{\mathrm{U(OSi(O^tBu)_3)_2}(\mu\text{-}\mathrm{OSi(O^tBu)_3})\}_2]$ (2.193(4) Å).[15] The U–U distance is longer (5.6356(1) Å) than that found in the $[\{\mathrm{U(OSi(O^tBu)_3)_2}(\mu\text{-}\mathrm{OSi(O^tBu)_3})\}_2]$ complex (3.9862(2) Å).

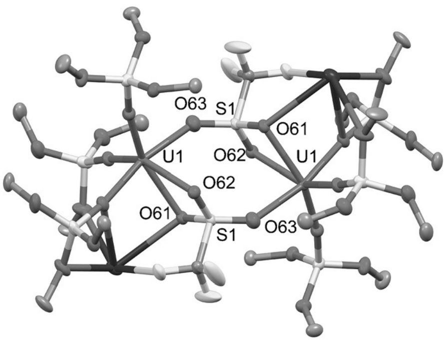


Figure 2. Thermal-ellipsoid drawing (50% probability) for $[\mathrm{Cs_2}\{[\mathrm{U(OSi(O^tBu)_3)_3}]_2(\mu\text{-OTf})_2\}]$ (**3**). Hydrogen atoms, methyl groups, and interstitial solvent molecules were omitted for clarity. Selected bond distances [Å]: U1–O61 2.537(3), U1–O62 2.479(3), U1–O63 2.323(3), S1–O61 1.504(3), S1–O62 1.492(3), S1–O63 1.462(3), U1–U1A 5.6356(1); *A* = −*x*+1,−*y*+2,−*z*+1.

The solid-state structure of **4** was determined by X-ray crystallography (Figure 3). The unit cell consists of two independent diuranium(V) complexes, **4a** and **4b**, in which two $[\mathrm{U(OSi(O^tBu)_3)_3}]$ fragments are bridged by two methylimido ligands. The mean U−O$_{\mathrm{siloxide}}$ bond length (2.110(5) Å) is slightly shorter than that found in the U$^{\mathrm{V}}$ terminal imido complex $[\mathrm{K(18c6)}][\mathrm{U(NSiMe_3)(OSi(O^tBu)_3)_4}]$ (U1–O$_{\mathrm{avg}}$: 2.16(2) Å).[2d] The average U–U distance in **4** is 3.8612(6) Å. The U–N distances in the two complexes are slightly different (2.309(6) Å in **4a** and 2.319(6) Å in **4b**). These values can be compared to those found in the rare examples of previously reported imido-bridged diuranium(V) complexes (2.387(5)–2.078(5) Å).[16] The formation of imide complexes from the alkylation of nucleophilic bridging nitrides has been reported[17] but did not lead to valence disproportionation. In contrast, the alkylation of **1** promotes the disproportionation of the metal center, thus leading to the transformation of two U$^{\mathrm{IV}}$ cations into a U$^{\mathrm{V}}$ and a U$^{\mathrm{III}}$ complex. This reactivity is exceptional, since U$^{\mathrm{IV}}$ complexes are generally much more stable than their U$^{\mathrm{III}}$ and U$^{\mathrm{V}}$ analogues, which are usually more prone to disproportionation reactions.[18] For example, the diuranium(IV) imido-bridged complex $[(\mathrm{MeC_5H})_4\mathrm{U_2}(\mu\text{-NPh})_2]$ was obtained from the comproportionation reaction of the imido complex $[(\mathrm{MeC_5H})_3\mathrm{U^VNPh}]$ with the tris(cyclopentadienyl) complex $[(\mathrm{MeC_5H_5})_3\mathrm{U^{III}}]$.[19] The reactivity of complex **1** can be explained by the presence of asymmetric bonding in the U$^{\mathrm{IV}}$–N–U$^{\mathrm{IV}}$ core, which may be formulated as a mixed-valence U$^{\mathrm{V}}$–N–U$^{\mathrm{III}}$ complex, but this formulation is not supported by either the optimized geometry or the metrical parameters in complex **1** (see the Supporting Information).[2d]

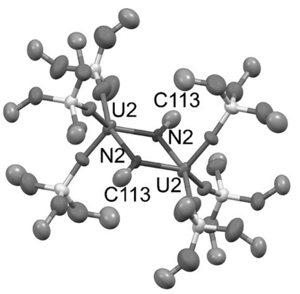


Figure 3. Thermal-ellipsoid drawing (50% probability) for $[\{\mathrm{U(OSi(O^tBu)_3)_3}\}_2(\mu\text{-NMe})_2]$ (**4a**; only one complex is displayed). Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances [Å]: U2–N2 2.309(6), U2–N2A 2.309(6), U2–U2A 3.8489(6), N2–C113 1.441(14); *A* = −*x*+1,−*y*+2,−*z*+1.

The unique reactivity of complex **1** towards CO and MeOTf was further explored by examining plausible reaction pathways through calculations at the DFT level of theory (see the Supporting Information for computational details).[20] Full systems without any simplifications or geometrical constraints were considered in the calculations.[21] In the computed profile for the reaction of **1** with MeOTf (see Figure S21 in the Supporting Information), the first step involves the coordination of MeOTf to complex **1** to yield a mixed-valence intermediate, **int-B**, which is enthalpically more stable than the charge-delocalized species, **int-A**. Interestingly, no transition state for direct methyl transfer from MeOTf to the nitride (in an outer-sphere-type mechanism) could be located, as every attempt led to either **int-A** or **int-B**. The Cs$^+$ ion plays a crucial role in holding the fragments together in the

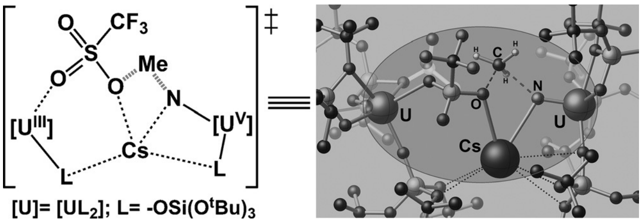


Figure 4. 2D and 3D representation of DFT-computed **ts-BC**.

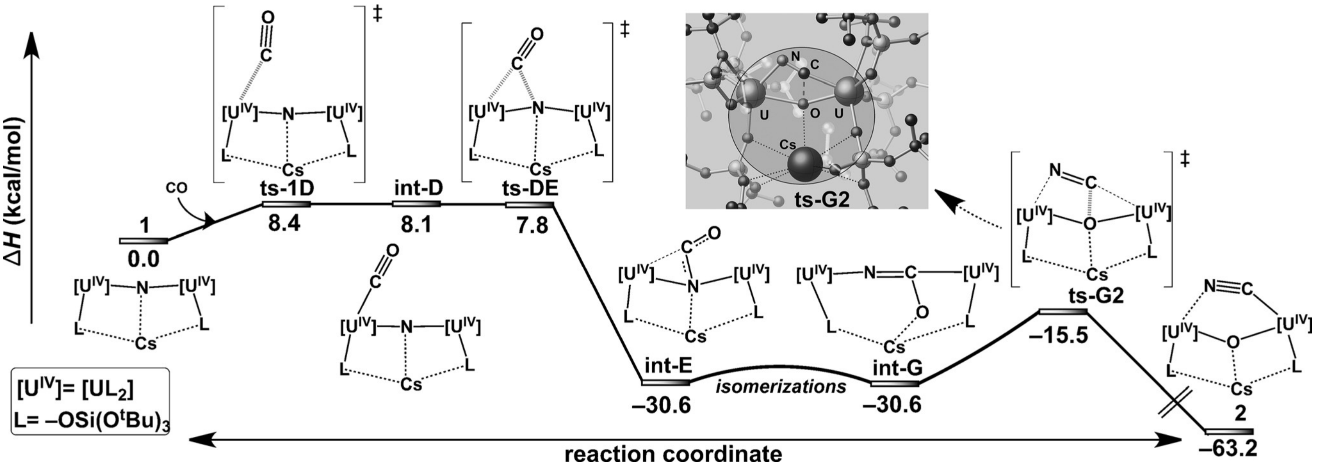


Figure 5. DFT-computed enthalpy profile for the reaction of CO with complex **1** to afford complex **2** at room temperature (the values are given in kcal mol^{-1}). The inset shows a 3D representation of the active core of **ts-G2**.

dinuclear mixed-valence complex, but also in stabilizing the anionic, monomeric formally U^V nitride molecular part. From **int-B**, the system can reach the transition state **ts-BC** (Figure 4), in which the methyl group is transferred from the triflate moiety to terminal nitride. This reaction can be better described as methyl transfer from the oxygen atom to the nitrogen atom at the Cs atom rather than at the uranium center (see Figure 4). The uranium atoms appear to act solely as Lewis acid centers to activate the nitride and methyl triflate ligands. This process leads to the formation of complex **int-C**, a mixed-valence bimetallic complex containing two fragments (a U^{III}–sulfonate–Cs moiety and a U^V imido moiety), that further dimerizes to yield the two homoleptic U^{III} and U^V experimental complexes, **3** and **4**, respectively.

A computational mechanistic investigation of the reaction between complex **1** and CO was also carried out (Figure 5). The closest, unique analogue of such exceptional reactivity is the high-temperature (110 °C) cleavage of CO by a diazenido dihafnium complex to yield a μ-oxo/μ-cyanido species in a reaction that proceeds through the formation of a stable oxamidide intermediate.[14] Computational and experimental studies suggest that this stable oxamidide species forms via an unstable nitride intermediate.[22] However, the uranium nitride reactivity appears to be significantly different (Figure 5). First the CO molecule binds one uranium center with an activation barrier of 8.4 kcal mol^{-1}, thus yielding an unstable CO adduct (endothermic formation by 8.1 kcal mol^{-1}). Subsequently, the CO molecule undergoes barrierless migratory insertion into the uranium–nitride bond. The insertion yields **int-E**, which is a η^2(C,N):κ^2(O,N) bimetallic complex. This intermediate **int-E** then undergoes an isomerization process assisted by the Cs cation to yield the isoenergetic but reactive isomer **int-G** (see the Supporting Information for the full isomerization mechanistic part). The geometry of complex **int-G** is quite interesting, as the cyanate ligand exhibits η^1-N coordination with one uranium center and η^2(C,O) coordination with the other uranium center (η^1,η^2 is a classical coordination mode for bimetallic uranium complexes of triatomic molecules, such as CO_2[15]). From **int-G**, ready elimination of a CN^- anion (i.e., full C–O bond scission from carbon monoxide) takes place with an activation barrier of 15.1 kcal mol^{-1}.

The high nucleophilic reactivity of the nitride ligand in the heterodimetallic complex **1** led to the first example of complete cleavage of CO by a nitride complex under ambient conditions. CO cleavage afforded a new complex, **2**, containing two U^{IV} cations bridged by an oxo and a cyanide group. This complex can transfer the cyanide group to electrophiles, thus leading to N–C bond formation and the release of organic molecules, such as CH_3CN or Me_3SiCN. An exceptional outcome was also observed for the reaction of the U^{IV} center with electrophilic MeOTf, which led to unprecedented valence disproportionation of U^{IV} to U^{III} and U^V with concomitant formation of a U^V imido complex. DFT studies support the presence of a multimetallic cooperative effect in the complete cleavage of CO and in the methyl transfer to the uranium-bound nitride. The results show novel reactivity of highly nucleophilic metal nitrides, which might provide new routes to the use of the readily available substrate CO in the synthesis of valuable chemicals.

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Keywords: carbon monoxide cleavage · cooperativity · nitrides · uranium · uranium disproportionation

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