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Facile CO Cleavage by a Multimetallic CsU₂ Nitride Complex

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Abstract: Uranium nitrides are important materials with potential application as fuel 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. Here we find that a complex containing a nitride bridging two uranium centres and a cesium cation readily cleaves the C≡O bond (one of the strongest bonds in nature) under ambient conditions. The product formed has a [CsU₂(μ-CN)(μ-O)] core indicating that the three cations cooperate to cleave CO. Moreover, the addition of MeOTf to the nitride complex leads to an exceptional valence disproportionation of the CsU^{IV}-N-U^{IV} core to yield CsU^{III}(OTf) and MeN=U^V fragments. The important role multimetallic cooperativity in both reactions is illustrated by the computed reaction mechanisms.

Uranium nitrides are of great interest because of the potential applications 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 C1 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 the Fischer-Tropsch hydrocarbon production from CO and H₂ is the cleavage of the CO triple bond, which is the strongest bond in chemistry (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 of

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 affording cyanate which in some case is spontaneously extruded.^[5d] Reductive carbonylation of monometallic U(V) and U(VI) nitrides by CO affording the isocyanate ligand has also been recently reported.^[5e] However 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 homologations effected by uranium(III) systems, yielding delatate,^[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 identified.

We recently demonstrated the unusually high nucleophilic character of the nitride-bridged di-uranium complex Cs{[U(OSi(OtBu)₃)₃]₂(μ-N)}, (**1**)^[2d, 12], that reacts in ambient conditions with CO₂ and CS₂ leading to N-C bond formation yielding cyanate and thiocyanate and unprecedented dicarbamate species.

Here we show that the unusually high nucleophilic character of **1**, and the multimetallic cooperativity of the CsU₂ core, lead to complete cleavage of the CO triple bond, yielding a cyanide. The cyanide ligand in **1** is easily transferred to electrophiles such as MeOTf and Me₃SiI, yielding organic nitriles. We also demonstrate that the direct methylation of the nitride complex **1** leads to disproportionation of the uranium cation, a completely unprecedented reactivity in nitride chemistry.

The addition of stoichiometric or excess amounts of CO or ¹³CO (1 equivalent) to the diuranium(IV) complex Cs{[U(OSi(OtBu)₃)₃]₂(μ-N)}, **1** in toluene at room temperature leads to an immediate colour change of the solution from brown to light blue. The proton NMR spectrum carried out at 25 °C immediately after the reaction shows 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(OtBu)₃)₃]₂(μ-CN)(μ-O)}, **2**, were isolated in 60% yield

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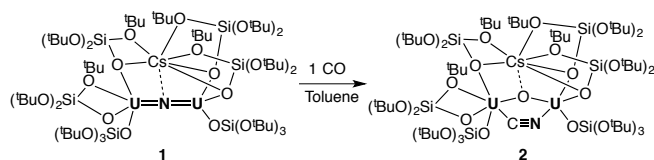
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at -40°C . Proton NMR studies showed that complex **2** is stable in toluene at room temperature for several hours. The ^{13}C NMR spectrum of complex **2** shows the presence of a signal at 866 ppm that is assigned to the ^{13}CN ligand. Traces of decomposition, evident from a new NMR peak assigned to the $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4]$ complex, appeared only after three days, probably as a result of ligand scrambling. The solid-state structure of **2** shows the presence of a diuranium(IV) complex where two $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]$ fragments are bridged by one oxo ligand and one cyanide group. This 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 (2.609(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]



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

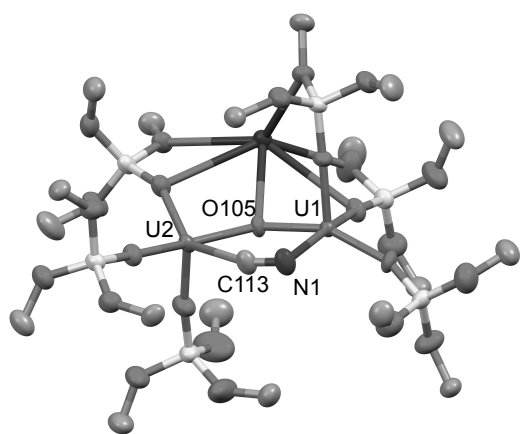
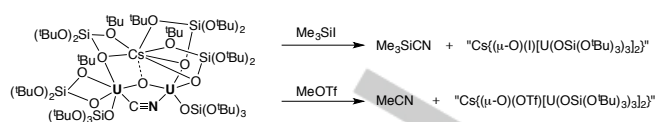


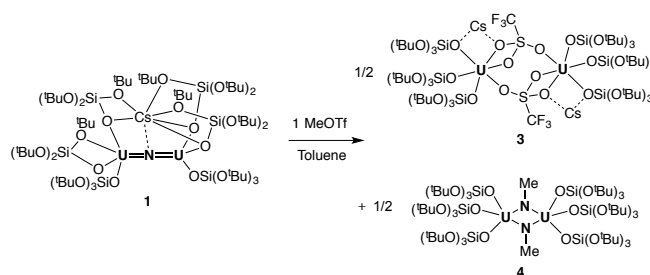
Figure 1. Molecular structure of $\text{Cs}\{[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-CN})(\mu\text{-O})\}$, **2**. Thermal ellipsoids depicted at 50% probability. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances (Å): U1-O105 2.124(4), U1-N1 2.576(6), 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 leading to the reductive carbonylation of U(V) and U(VI) affording $\text{U}^{\text{III}}\text{-OCN}$ and $\text{U}^{\text{IV}}\text{-OCN}$ complexes respectively.^[5e] Such remarkable difference in reactivity shows the importance of multimetallic cooperativity in CO scission. In order to confirm the presence of a cyanide ligand in complex **2** and to investigate the possibility of transferring the cyanide ligand to organic substrates, complex **2** was reacted with Me_3SiI and with MeOTf (Scheme 2).



Scheme 2. Reactions of **2** with the electrophiles MeOTf and Me_3SiI to afford MeCN and Me_3SiCN products.

The reaction of $\text{Cs}\{[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-}^{13}\text{CN})(\mu\text{-O})\}$ with one equivalent of Me_3SiI at room temperature in benzene leads to an immediate colour change, affording a white suspension. The ^{13}C NMR spectrum of the reaction mixture shows the disappearance of the peak assigned to the uranium-bound ^{13}CN and the appearance of a new signal at 126.3 ppm that is assigned to the cyanide group of the $\text{Me}_3\text{Si}^{13}\text{CN}$.^[14] After the addition of Me_3SiI , 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 is assigned to an intermediate oxo iodide species $\text{Cs}\{[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-O})(\text{I})\}$. This species decomposes rapidly and after 48 hours only a peak assigned to $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4]$ is observed. The formation of a stable $\mu\text{-oxo}$ iodide complex and $\text{Me}_3\text{Si}^{13}\text{CN}$ was observed from the reaction of the dihafnium oxo cyanide complex, $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Hf}(\text{NCO})](\mu\text{-O})[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Hf}(\text{CN})]$, with Me_3SiI .^[14] The formation of $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4]$ from the intermediate iodide is the result of ligand scrambling. Ligand scrambling leading to the formation of bis(oxo) complexes and unidentified products has previously been reported for the diuranium(IV) oxo- and cyanate-bridged complex $\text{Cs}\{[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3]_2(\mu\text{-NCO})(\mu\text{-O})\}$.^[12] The reaction of **2** with MeOTf proceeds more slowly and after 24 hours at room temperature a large amount of starting material is still present. The ^1H NMR spectrum in d_8 -toluene after 24 hours shows the presence of the signal assigned to $[\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4]$ and a broad signal at 0.63 ppm assigned to $\text{CH}_3^{13}\text{CN}$. The formation of $\text{CH}_3^{13}\text{CN}$ 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_3SiI) to complex **1** results in the conversion of CO into organic nitrile compounds.



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

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For comparison, we also investigated the reactivity of the nitride complex **1** with MeOTf.

The reaction of **1** with one equivalent of MeOTf at room temperature resulted in a slow (24 hours) colour change of the solution from brown to green, affording a mixture of complexes **3** and **4** (Scheme 3). Storing the solution at -40° resulted in the isolation of light blue crystals of the bis(imido) complex $[\{U^V(OSi(OtBu)_3)_3\}_2(\mu-NMe)_2]$, **4**. Attempts to isolate the two products in a pure form from this reaction were not successful. The reaction is faster when **1** is reacted with two equivalents of MeOTf, but the same mixture of complexes **3** and **4** is obtained, as indicated by the proton NMR spectrum. However, in this case storing the reaction mixture at -40° for 24 hours resulted in the isolation of green-blue crystals of the complex $Cs_2\{[U(OSi(OtBu)_3)_3]_2(\mu-OTf)_2\} \cdot 2(C_7H_8)$, **3.2(C₇H₈)** in 60% yield. The crystallization of complex **3** is probably favoured by the presence of an excess of MeOTf in the solution. Subsequent cooling of the mother liquor afforded a few crystals of complex **4**. Due to its low stability, the isolation of complex **4** in sufficient amounts for further characterization was not possible. The low stability of the U^V imido complex **4** is consistent with the observed instability of the previously reported “[$U^V(OSi(OtBu)_3)_3(NR)$]” (R=adamantly) intermediate that could not be isolated because it rapidly disproportionate to afford $[U^{IV}(OSi(OtBu)_3)_4]$ and $[U^{VI}_2(NR)_4(OSi(OtBu)_3)_4]$.^[2d]

The solid-state structure of **3** (Figure 2) consists of a diuranium(III) complex where two $[U(OSi(OtBu)_3)_3]$ fragments are bridged by two triflate anions, each one binding the two uranium centres and a cesium cation in a $\mu_3:\kappa^2(O,O):\eta^1-O$ fashion. The mean $U-O_{\text{siloxide}}$ bond length is similar (2.165(3) Å) to the $U-O_{\text{siloxide}}$ distance found in the $U(IV)$ complex **1** ($U-O_{\text{avg}}$ 2.19(3) Å) and in the diuranium(III) tris(siloxide) complex $[U(OSi(OtBu)_3)_3]_2(\mu-OSi(OtBu)_3)_2$ (2.193(4) Å).^[15] The U-U distance is longer (5.636 Å) than that found in the $[U(OSi(OtBu)_3)_3]_2(\mu-OSi(OtBu)_3)_2$ complex (3.9862(2) Å.)

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** where two $[U(OSi(OtBu)_3)_3]$ fragments are bridged by two methylimido ligands. The mean $U-O_{\text{siloxide}}$ bond length (2.110(5) Å) is slightly shorter than that found in the $U(V)$ terminal imido complex $[K(18c6)][U(NSiMe_3)(OSi(OtBu)_3)_4]$ ($U1-O_{\text{avg}}$ 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 (2.319(6) Å in **4a** and 2.309(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 centre, leading to the transformation of two $U(IV)$ cations into a $U(V)$ and a $U(III)$ complex. This is exceptional reactivity since $U(IV)$ complexes are generally much more stable than their $U(III)$ and $U(V)$ analogues, which are usually more prone to disproportionation reactions.^[18] For instance, the diuranium(IV) imido-bridged complex, $[(MeC_5H)_4U_2(\mu-NPh)_2]$, was obtained from the comproportionation

reaction of the imido complex $(MeC_5H)_3U^V NPh$ with the tris-(cyclopentadienyl) complex $[(MeC_5H_5)_3U^{III}]$.^[19] The reactivity of complex **1** could be explained by the presence of asymmetric bonding in the $U^{IV}-N-U^{IV}$ core that may be formulated as a mixed valent U^V-N-U^{III} complex, but this formulation is not supported by both the optimized geometry and the metrical parameters in complex **1** (See SI).^[2d]

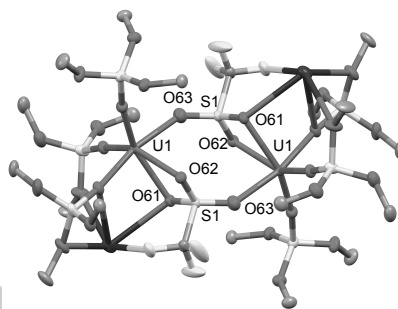


Figure 2. Thermal ellipsoid drawing of $Cs_2\{[U(OSi(OtBu)_3)_3]_2(\mu-OTf)_2\}$ **3**; probability 50%. Hydrogen atoms, methyl groups and interstitial solvent molecules were omitted for clarity. Selected bond distances (Å): U1-O61 2.537(3), U1-O62 2.479(3), U1-O63 2.323(3), S1-O61 1.504(3), S1-O62 1.492(3),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

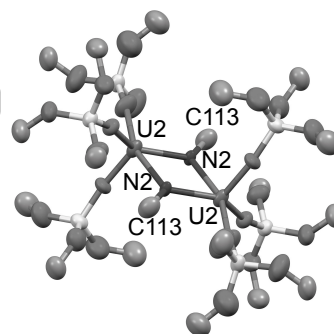


Figure 3. Thermal ellipsoid drawing for $[U(OSi(OtBu)_3)_3]_2(\mu-NMe)_2$, **4a** (only one complex is displayed); probability 50%. Hydrogen atoms and methyl groups were omitted for clarity. Selected bond distances (Å): U1-N1 2.324(6), U1-N1#1 2.314(6), N1-C53 1.429(13), U2-U2 3.8735(5). A = -x+1, -y+2, -z+1.

The unique reactivity of complex **1** towards CO and MeOTf substrates, was further explored by examining plausible reaction pathways with calculations at the DFT level of theory (see SI for computational details).^[20]

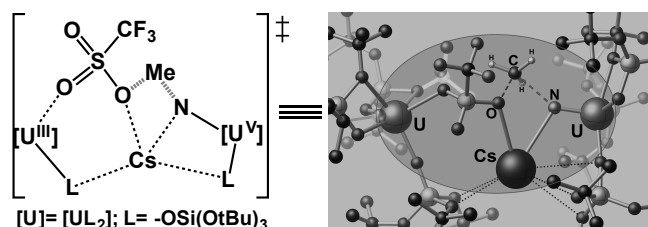


Figure 4. 2D and 3D-representation of the DFT computed **ts-BC**.

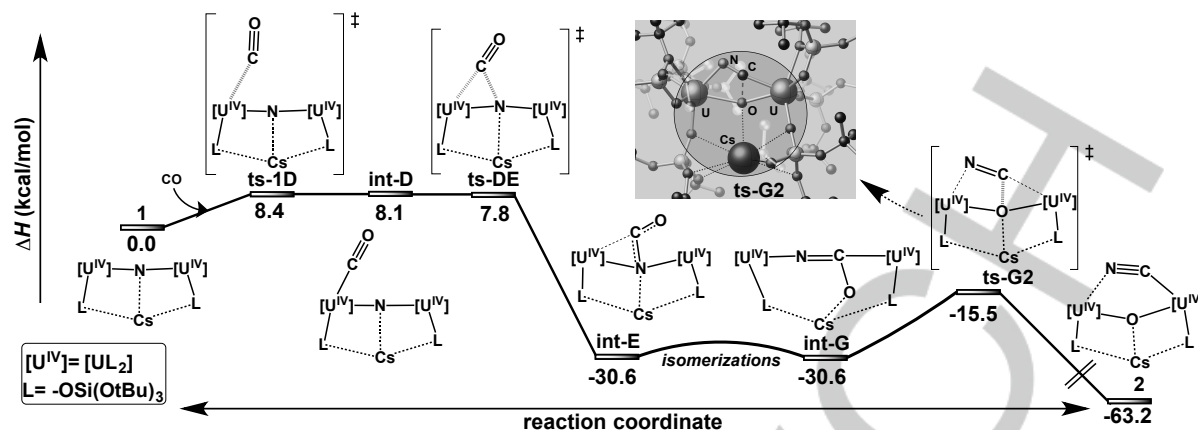


Figure 5. DFT computed enthalpy profile for the reaction of CO with complex **1** to afford complex **2** at room temperature (the values are given in kcal.mol⁻¹). In the inset a 3D representation of the active core of the **ts-G2** is given.

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 (Figure S21 in SI) the first step involves the coordination of the MeOTf to complex **1** yielding a mixed-valent intermediate (**int-B**) that is enthalpically more stable compared to the charge-delocalized one (**int-A**). Interestingly, no direct methyl-transfer TS from MeOTf to the nitride (in an outer-sphere-type mechanism) could be located, as every attempt leads to either **int-A** or **int-B**. The Cs⁺ plays a crucial role in holding the fragments together in the 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) where the methyl group is transferred from the triflate moiety to terminal nitride. This reaction can be better described as a methyl transfer from oxygen to nitrogen at the Cs atom rather than at the uranium centre, as illustrated nicely in Figure 4. Eventually, the uranium atoms act solely as Lewis acid centres to activate the nitride and methyl triflate ligands.

This leads to the formation of complex **int-C**, which is a mixed-valence bimetallic complex involving two fragments (a U(III) sulfonate (Cs) and a U(V) imido) that further dimerizes to yield the two homoleptic U(III) and U(V) experimental complexes, **3** and **4** respectively.

The 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 di-hafnium complex to yield a μ -oxo/ μ -cyanido species 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 centre with an activation barrier of 8.6 kcal/mol, yielding an unstable CO adduct (endothermic formation of 8.1 kcal/mol). Subsequently, the CO molecule undergoes a barrierless migratory insertion onto the U-nitride bond. The insertion yields **int-E**, that is a $\eta^2(\text{C,N}):\kappa^2(\text{O,N})$ bimetallic complex. The **int-E** then undergoes an isomerization process assisted by the Cs cation to yield the isoenergetic but reactive isomer **int-G** (see SI for the full

isomerization part). The geometry of complex **int-G** is quite interesting as the cyanate ligand exhibits a $\eta^1\text{-N}$ coordination with one uranium centre and $\eta^2(\text{C,O})$ with the other uranium (η^1, η^2 is a classical coordination for bimetallic uranium complexes of triatomic molecules such as CO₂^[15]). From **int-G**, an easy 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.

The high nucleophilic reactivity of the nitride ligand in the heterodimetallic **1** leads to the first example of complete cleavage of CO by a nitride complex under ambient conditions. The CO cleavage affords 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 leading to N-C bond formation and release of organic molecules such as CH₃CN or CH₃SiCN. An exceptional outcome is also observed for the reaction of the U(IV) with the electrophilic MeOTf leading to the unprecedented valence disproportionation of U(IV) to U(III) and U(V) with concomitant formation of a U(V) imido complex. The 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 that might provide new routes to the use of the easily available CO substrate in the synthesis of valuable chemicals.

Acknowledgements

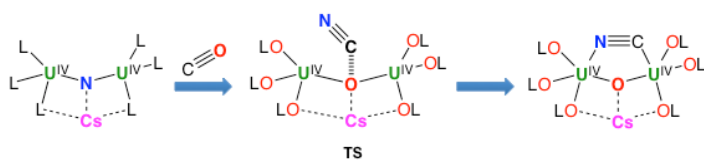
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Keywords: uranium • nitrides • carbon monoxide cleavage • uranium disproportionation • cooperativity

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Facile CO Cleavage by a Multimetallic
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