CO₂ conversion to isocyanate via multiple N–Si bond cleavage at a bulky uranium(III) complex†

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Herein we show that the reaction of CO₂ with the sterically saturated uranium(III) tetrasislylamido complex [K(18c6)][U(N(SiMe₃)₂)₄] leads to CO₂ insertion into the U–N bond affording the stable U(IV) isocyanate complex [K(18c6)][U(N(SiMe₃)₂)₃(NCO)₂]ₙ that was crystallographically characterized. DFT studies indicate that the reaction involves the [2+2] cyclo-addition of a double bond of O==CO to the U–N(SiMe₃)₂ bond and proceeds to the final product through multiple silyl migration steps.

The reactivity of uranium(III) with small molecules such as CO₂, CO or N₂ has been attracting increasing interest in recent years due to the ability of uranium to promote unusual transformations.1,2 Bulky amides have been successfully used in uranium chemistry, as innocent ancillary ligands, as alternatives to the ubiquitous cyclopentadienyl systems.3 In particular the simple neutral [U(N(SiMe₃)₂)₃]₄ complex has provided a versatile precursor and has demonstrated interesting reactivity5 including arene reduction and functionalization,6 CO activation,7 and nitride formation.8 In contrast, the ability of the U–N bonds to undergo insertion reactions has been much less explored compared to U–Cσ-bonds.15 Only a few examples of insertion of CO₂ into U(III)–NR₂ and U(IV)–NR₂ bonds leading to the formation of U(N₂)11 and U(IV) carbamates12 have been reported.16 Examples of the insertion of CO₂ into metal-silylamide bonds have been reported13 for main group, d-block and f-block metals12 but are much rarer than the insertion of CO₂ into N-alkylamide bonds. In particular, [U¹⁹⁵(N(SiMe₃)₂)₃] was reported to react with CO₂ to give O==C==NSiMe₃ and a second product identified as the tetravalent uranium silanolate [U(OSiMe₃)₄].12a

The reaction of the sterically saturated uranium(III) tetrasislylamido complex [K(18c6)][U(N(SiMe₃)₂)₄] with CO₂ leads to CO₂ insertion into the U–N bond affording the stable U(IV) isocyanate complex [K(18c6)][U(N(SiMe₃)₂)₃(NCO)₂]ₙ that was crystallographically characterized. DFT studies indicate that the reaction involves the [2+2] cyclo-addition of a double bond of O==CO to the U–N(SiMe₃)₂ bond and proceeds to the final product through multiple silyl migration steps.

The graphene of the complex [K(18c6)][U(N(SiMe₃)₂)₃(NCO)₂]ₙ shows the presence of a 1D coordination polymer (Fig. 1). The uranium environment is trigonal bipyramidal with three silylamido ligands at equatorial

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positions and two NCO\textsuperscript{-} anions at apical positions. A K(18c6) cation bridges two NCO ligands from two distinct uranium complexes. The U1–N\textsubscript{amide} bond distances fall in the range of what was observed in the U(IV) silylamido species. Notably the structure of 2 is closely related to the isoelectronic azide species [Na(TTHF)\textsubscript{2}]\textsuperscript{+}[U(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3}N\textsubscript{3}\textsuperscript{-}] reported by Hayton and coworkers\textsuperscript{2e} featuring similar geometry and uranium-ligand bond distances. The three atoms X–C–X′ units are disordered across the mirror plane of the P2\textsubscript{1}/m space group and refine equally well when N or O or a mixture of both are used at the X and X′ positions. Thus, the X-ray data do not allow us to discriminate between a cyanoate (coordination through O) and an isocyanate (coordination through N) ligand. Similar disorder issues were observed in the [(Me\textsubscript{2}Al(μ-OSiMe\textsubscript{3})\textsubscript{3}Mg(THF)\textsubscript{2}(μ-OCN)]\textsubscript{2} complex\textsuperscript{1c} and in the dimeric U(IV) complex [U(μ-Cl\textsubscript{2}C\textsubscript{8}H\textsubscript{6}SiPr\textsubscript{3}-1,4)]\textsubscript{2} (μ-Cp\textsuperscript{+})(NCO)]\textsubscript{2}.\textsuperscript{15} However, in most previously reported U(IV) complexes the NCO ligand is N-bound\textsuperscript{16} and DFT calculations are in agreement with an N-bound coordination (see below and ref. 13). Therefore the structure was refined with N-bound OCN ligands (Fig. 1). The two U–N\textsubscript{NCO} bond distances at 2.337(3) and 2.338(4) Å are in the range of those found in the few uranium isocyanate complexes reported (2.338(3)\textsuperscript{13} 2.389(6)\textsuperscript{16b} and 2.336(5) Å\textsuperscript{19}).

The absorption band at 2201 cm\textsuperscript{-1} in the IR spectrum of 2 was assigned to the asymmetric stretching mode ν\textsubscript{NCO}. This value is similar to those found in the few terminal\textsuperscript{18} or bridging\textsuperscript{15} U(IV) and U(III) isocyanate complexes reported (2199–2122 cm\textsuperscript{-1}).

All the spectroscopic and analytical data (see ESI\textsuperscript{1}) support the assignment of the three atoms in 2 as NCO ligands. Notably the quaternary carbon (after reaction with \textsuperscript{13}CO\textsubscript{2}) resonance at δ = 492.4 ppm in the \textsuperscript{13}C NMR spectrum, the microanalytical data, and the parent ion in the mass spectrum for the anion [U(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3}N\textsubscript{3}\textsuperscript{-}]\textsuperscript{+} (m/z = 802.4) are in agreement with the assigned formula.

\textsuperscript{1}H and \textsuperscript{13}C NMR studies of the reaction of 1 with \textsuperscript{13}CO\textsubscript{2} were performed. After addition of 1 equivalent of \textsuperscript{13}CO\textsubscript{2} the reaction leads to the slow disappearance of the \textsuperscript{1}H signals assigned to complex 1 with completion after 48 hours. The \textsuperscript{13}C NMR spectrum of the final reaction mixture shows the presence of a signal at 307 ppm that could be assigned to the quaternary carbon of a carbamate or an isocyanate intermediate. No evident color change was observed during the reaction. Additional \textsuperscript{13}C NMR signals are also observed in the 5.6–1.8 ppm region. Further addition of 1 equivalent of \textsuperscript{13}CO\textsubscript{2} leads to a slow color change of the reaction mixture from dark purple to light pink. \textsuperscript{13}C NMR monitoring of the reaction showed a slow evolution with time with the disappearance of the \textsuperscript{13}C NMR signal at 307 ppm and the appearance of the \textsuperscript{13}C NMR signal at 492.4 ppm assigned to the isocyanate complex 2. All the \textsuperscript{13}C NMR resonances in the 5.6–1.8 ppm region remained present in the final \textsuperscript{13}C NMR spectrum but with increased intensity. In particular, two signals at 0.07 ppm in the \textsuperscript{1}H NMR spectrum and at 1.84 ppm in the \textsuperscript{13}C NMR spectrum were assigned to the hexamethylisiloxane (SiMe\textsubscript{3})\textsubscript{2}O by-product. Signals for SiMe\textsubscript{2}NCO were not observed. The \textsuperscript{1}H NMR spectrum of the final reaction mixture showed the resonances assigned to complex 2 and additional broad shifted resonances assigned to unidentified U(IV) products. Mass spectrometry studies showed the presence of [U\textsubscript{2}O(SiMe\textsubscript{3})\textsubscript{8}]\textsuperscript{+} and [U\textsubscript{2}N(CO)(OSiMe\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} species (see ESI\textsuperscript{1}).

In order to shed light on the mechanistic aspects of this peculiar reactivity outcome, DFT investigations using the B3PW91 functional were performed. The system of choice is the full anionic system [U(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{4}]\textsuperscript{−}, where the counter-cation is not taken into account.\textsuperscript{15} The anionic [U(IV)–CO\textsubscript{2}] intermediate Int1 is formed from the electronic reduction of CO\textsubscript{2} that occurs at the coordination to the initial U(IV) complex (so-called coordination-induced reduction).\textsuperscript{20} The first step of the mechanism involves the [2+2] cyclo-addition of a double bond from the O=CO\textsuperscript{−} radical anion to the U–N(SiMe\textsubscript{3})\textsubscript{2} bond, as it is shown in Fig. 2. The activation barrier for this process is found to be relatively small (14.8 kcal mol\textsuperscript{−1}). In particular, in the transition state the amide group that is involved in the insertion step is considerably far from the uranium center, at a non-bonding distance (d\textsubscript{U–N} = 3.63 Å). The nature of this late-transition state is most probably due to the directionality of the occupied molecular orbital of the nitrogen with respect to the electrophilic carbon of the carbon dioxide molecule. Moreover, the steric hindrance of the ligand environment may also play an important role in the non-bonding situation between the nitrogen and the uranium, providing a logical explanation for the outcome of this step. In particular, the IRC calculation did not converge into

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**Fig. 1** Solid-state molecular structure of [K(18c6)][U(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{3}N\textsubscript{3}\textsuperscript{-}], 2 crystallized from THF/hexane. Hydrogen atoms and disorder are omitted for clarity. Uranium (green), potassium (purple), silicon (yellow), nitrogen (blue), oxygen (red) and carbon (grey) atoms are represented with 30% probability ellipsoids. Selected bond distances [Å] and angles [deg]: U1–N1 = 2.2679(2), U1–N2 = 2.2696(2), U1–O/N42 = 2.3358(1). U1–O/N41 = 2.3370(1), X42–C42–X′42 = 171.6(1), X41–C41–X′41 = 175.5(1).

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**Fig. 2** Part of the energy profile that leads to the formation of the isocyanate complex 2.
an O,N-bound carbamate intermediate, but instead into an O,O-bound one (Int2), with a subsequent significant drop in enthalpy energy (43.0 kcal mol\(^{-1}\) with respect to the CO\(_2\) reduced adduct).

From the ligated diaionic O,O-bound carbamate the reaction can proceed through a sequence of two successive silyl migration steps (Fig. 2 and 3).

More specifically, the first step refers to the migration of the trimethylsilyl group from the nitrogen atom to one oxygen of the carbamate group, surmounting a moderate activation energy barrier of 14.4 kcal mol\(^{-1}\). From the ensuing intermediate, Int3, rotation around the Osiloxide–C bond of the silyl group is required for the Si atom to approach the coordinated oxygen atom, for the second migration to occur. This isomerization is an almost thermo-neutral process, with enthalpy energy difference of only 4.3 kcal mol\(^{-1}\) in favor of Int3. The following migration of the silyl group is more energy demanding than the previous one, with an accessible activation energy barrier of 26.9 kcal mol\(^{-1}\) in terms of \(\Delta H^\ddagger\).

In the following intermediate, Int5, a kind of cyanate fragment has been formed, now developing an \(\eta^2\)-N,O-type coordination with the uranium atom. This fragment can easily expel a siloxane molecule, which is observed experimentally, through an almost barrierless energy micro-step, \(\text{via TS}^\ddagger_{5-6}\). The resulting intermediate, Int6, is formally described as an OCN\(^2-\) complex of U(vi). At this point, one can envision two different potential paths, the first corresponding to the isomerization of the cyanate group to give a terminal bonded isocyanate complex or to the nucleophilic attack by a second CO\(_2\) molecule on the carbon atom of the OCN\(^2-\) moiety (Fig. 4). The first possibility results in an important stabilization energy of 21.4 kcal mol\(^{-1}\) with respect to the \(\eta^1\)-bound one. Then a putative free NCO radical (originating from a second uranium complex) can coordinate the vacant coordination site of Int7, on the axial position, \(\text{trans}\) to the other isocyanate, of the trigonal bipyramidal. Even though both correspond to highly exothermic processes (more than 100 kcal mol\(^{-1}\) stabilization energy), the N-bound intermediate, Int8, is more stable than the O-bound one, (see Int8’ in the ES†), by almost 10 kcal mol\(^{-1}\). This observation suggests that most probably the two OCN groups in the X-ray structure of complex 2 are bound to the uranium through their nitrogen atoms while the oxygen atoms bind the potassium atoms of the K(18c6) cation.

Besides, since the experimental reactivity is found to be influenced by the number of CO\(_2\) equivalents reacted with U(III), a second CO\(_2\) molecule can undergo a nucleophilic attack at the carbon of the \(\eta^2\)-cyanate group in intermediate Int6 (Fig. 4). This will result in the formation of an oxalate-like complex, Int9. Such reactivity is reminiscent of the oxalate formation in U(m) chemistry.\(^{21}\) Two molecules of Int9 can then disproportionate in order to give the bis-cyanate product Int8 and a CO\(_2\)\(^2-\) complex (Int10). Also in this route, an important stabilization energy is found (almost 130 kcal mol\(^{-1}\)). Attempts to compute a reaction pathway involving the insertion of CO\(_2\) into a U(m) species were not successful but showed that such a pathway is higher in energy.

In conclusion the bulky uranium(m) tetrasilylamido complex [K(18c6)][U(N(SiMe\(_3\))\(_2\))]\(_4\) reacts with CO\(_2\) to afford a rare example of a U(vi) isocyanate complex. DFT computational studies suggest that the reaction proceeds through carbon dioxide reduction followed by the [2+2] cyclo-addition of the carbonyl double bond of the reduced carbon dioxide to the U–N(SiMe\(_3\))\(_2\) bond and multiple silyl migration. The reactivity of this bulky “ate” complex differs from that reported for the neutral analogue [U(N(SiMe\(_3\))\(_2\))]\(_4\)^2\(^+\) highlighting the importance of the coordination environment for controlling the CO\(_2\) conversion at the uranium center.

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Notes and references


