CO_2 conversion to phenyl isocyanates by uranium(VI) bis(imido) complexes

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CO_2 conversion to phenyl isocyanates by uranium(VI) bis(imido) complexes

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Uranium(VI) *trans*-bis(imido) complexes [U(κ^4-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})(NPh)(NPh^R)] react with CO_2 to eliminate phenyl isocyanates and afford uranium(VI) *trans*-[O=U=NR]$^{2+}$ complexes, including [U((κ^4-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})(NPh)(O)] that was crystallographically characterized. DFT studies indicate that the reaction proceeds by endergonic formation of a cycloaddition intermediate; the secondary reaction to form a dioxo uranyl complex is kinetically hindered.

Uranium complexes have emerged as attractive candidates for activation of the very stable C=O bonds of carbon dioxide,[1,2,3] which must occur during CO_2 functionalization. U(III) with appropriate supporting ligands can effectively reduce carbon dioxide, giving rise to various products that include an end-on-bound $CO_2^{\bullet-}$ U(IV) complex,[4] uranium oxo species,[5,6] carbon monoxide,[5,6] carbonates,[7,8] oxalates,[9] and isocyanate.[10] It was also demonstrated that U(IV) complexes with suitable ancillary ligands and functionalities can facilitate CO_2 insertion into U-E bonds (E = C, N, O, S).[11,12,13,14] Meyer and co-workers showed that U(V) terminal oxo complexes [{(^{R}ArO)$_3$tacn}U=O] are formed upon treatment of U(V) mono-imidos with CO_2, probably *via* [2+2] cycloaddition with elimination of isocyanates.[13,15] Similar CO_2 transformations have been observed with high oxidation state early transition metals, such as titanium imido complexes.[16,17,18,19] Activation of CO_2 by hexavalent uranium imido complexes has not yet been achieved, and in general CO_2 activation by U(VI) complexes is rare.[20] In such a rare case, the terminal nitride [U(Tren^{TIPS})(N)] reacted with CO_2 to yield a U(VI) oxo-cyanate complex by bond metathesis and cleavage of a C=O bond, with rapid decomposition of the product to [U^V(Tren^{TIPS})(O)].[20]

Several structurally characterized uranium(VI) imido complexes have recently been reported,[21,22,23] but reactivity studies of the U=NR bonds remain scarce,[24] particularly for U(VI) *trans*-bis(imido) complexes. Such *trans*-[RN=U=NR]$^{2+}$ systems notably are isoelectronic with thermodynamically stable uranyl, {O=U=O}$^{2+}$, but exhibit greater bond covalency.[25] It has been proposed that the inverse *trans*-influence (ITI)[26] of the two uranium-nitrogen multiple bonds stabilizes and reduces reactivity of the {RN=U=NR}$^{2+}$ moiety. Accordingly, Boncella and co-workers showed that treating [U(=N^{t}Bu)$_2$I$_2$(OPPh$_3$)$_2$] with PhN=C=O does not result in a uranium oxo complex but rather an imido transfer takes place to form [U(=N^{t}Bu)(=NPh)I$_2$(OPPh$_3$)$_2$].[27] We here demonstrate that U(VI) *trans*-bis(imido) complexes supported by a bis(phenolate) cyclam ligand react with CO_2 to produce stable *trans*-[O=U=NR]$^{2+}$ with elimination of-aryl isocyanate.

Based on previous results for azobenzene activation with U(III) complex [U(κ^6-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})I] (**1**), with formation of [U(κ^4-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})(NPh)$_2$] (**2**),[28] the initial focus studies was on the synthesis of the new U(VI) bis(imido) [U(κ^4-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})(NPh)(NTol)] (**3**), with a goal of assessing reactivity with CO_2. The reaction of 4-methylazobenzene (TolNNPh) with 2 equiv. of U(III) complex **1** in toluene at room temperature resulted in four-electron cleavage of the N=N double bond, affording the soluble bis(imido) [U(κ^4-({(^{tBu2}ArO)$_2$Me$_2$-cyclam})(NPh)(NTol)] (**3**) and the insoluble U(IV) compound [U(κ^6-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})I][I], in a 1:1 ratio (Scheme 1).

Quality single crystals for X-ray diffraction were obtained by slow evaporation of a *n*-hexane/thf solution for two weeks. Refinement of the XRD data confirmed the expected U(VI) complex, with the phenyl imido and *p*-methyl phenyl imido ligands in a *trans* arrangement (N5-U1-N6 = 173.7(4)°) with an overall distorted octahedral geometry (Fig. S2 in SI). Structural parameters of **3**, including short U-N$_{imido}$ distances of 1.909(6) and 1.911(7) Å, are similar to those in the

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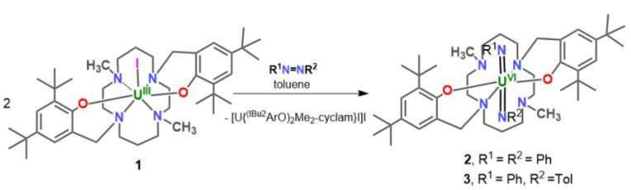
Electronic Supplementary Information (ESI) available: Computational and experimental details, NMR spectra, and detailed X-ray. CCDC 1954718-1954719. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x symmetric bis(imido) complex **2** (1.895(2) and 1.907(2) Å)[28] (structural parameters are in SI, Table S2).



Scheme 1. Synthesis of uranium(VI) bis(imido) complexes **2** and **3**.

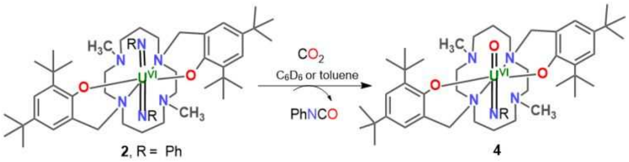
The ^1H NMR spectrum of **3** is characteristic of a diamagnetic compound, consistent with the asymmetric structure identified in the solid state. ^1H and ^{13}C NMR (see Figs. S3 and S4 in SI) revealed two sets of resonances for the phenolate arms of $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ and two distinct sets of resonances for the phenyl imido and *p*-methyl phenyl imido ligands.

Frozen brown solutions of **2** and **3** in benzene-d_6 were exposed to an excess of CO_2 (ca. 30 equiv.). Upon warming to room temperature, the colour of the solutions changed slowly from brown to dark cherry red. Following the reaction by ^1H NMR revealed that bis(imido) U(VI) complex **2** was completely consumed within 7 hours, with ingrowth of new *ortho*, *meta*, and *para* phenyl proton resonances at 5.19, 6.90 and 5.75 ppm, and aromatic resonances between 6.86 and 6.58 ppm, consistent with formation of a new uranium phenyl imido complex and elimination of phenyl isocyanate (Figs. S6 and S7 in SI).

The ^1H NMR spectrum of the new complex exhibited integrated intensities for the $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ and phenyl imido protons of 1:1, and revealed loss of the C_2 symmetry of the bis(phenolate) cyclam ligand. The benzylic protons gave rise to two AB systems with J_{AB} coupling of 12.1 and 12.3 Hz, and the four ^tBu phenolate substituents appeared as 4 singlets, indicating that the two phenolate arms of $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ have different chemical environments. In addition, two resonances for the NCH_3 protons were observed at 2.01 and 1.99 ppm and the phenyl imido protons showed only one set of resonances, which indicates free rotation about the N-C_{ipso} bond. The ^{13}C NMR data (Figs. S8 - S10 in SI) corroborated the ^1H NMR results, consistent with formation of U(VI) oxo imido complex $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(O)]$ (**4**).

An NMR tube-scale reaction of $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(NTol)]$ (**3**) with CO_2 showed that the bis(imido) complex is quantitatively converted to a mixture of mono-oxo imido $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(O)]$ (**4**) and $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NTol)(O)]$ (**5**), in approximately 1:1 ratio, along with the corresponding aryl isocyanates (Figs. S13 and S14 in SI). Although most ^1H NMR resonances of the two uranium compounds overlap, it was possible to differentiate resonances that match the phenyl imido ligand of **4** from those of the methyl phenyl imido ligand of **5** (see Fig. S14 in SI). Two of the ^tBu phenolate resonances of **5** are at 2.08 and 1.86 ppm, with the other two centered at 1.57 ppm and overlapping with a ^tBu resonance of **4**. ^{13}C NMR spectroscopy confirmed formation of the two U(VI) mono-oxo imido complexes, with the appearance of two pairs of carbon resonances for the C-O phenolates of $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ (**4**: 166.75 and 166.56 ppm; **5**: 166.81 and 166.69 ppm).

The reaction of $[U\{^{tBu2}ArO)_2Me_2\text{-cyclam}\}(NPh)_2]$ (**2**) with an excess of CO_2 in toluene resulted in a dark cherry red solid after evaporation of the solvent. ^1H NMR of the crude solid was consistent with formation of **4** and a minor side product, perhaps from dimerization of phenyl isocyanate.[29] Recrystallization of the crude solid from hexane provided single crystals; X-ray diffraction confirmed the molecular structure as oxo imido complex $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(O)(NPh)]$ (**4**) (Fig. 1).



Scheme 2. Synthesis of uranium(VI) oxo-imido complex **4**.

Like complexes **2** and **3**, **4** exhibits an octahedral geometry about the uranium center, with the $\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ ligand adopting a κ^4-N_2O_2 coordination mode, and the oxo and phenyl imido are *trans*-oriented. The geometric parameters of the $\{RN{=}U{=}O\}^{2+}$ core (U1-O3 1.787(3) Å, U1-N5 1.879(3) Å, O3-U1-N5, 176.4(1)°) are comparable to those of previously reported $[U({=}NPh^{iPr2})(O)Cl_2(tppo)_2]$ (U-O 1.778(2), U-N 1.847(3)),[30] while the U-O(aryloxide) and U-N(cyclam) bond distances are similar to those of **2** and **3**.

Crystallographically characterized *trans*-$[O{=}U{=}NR]^{2+}$ compounds are scarce, mostly prepared by oxygen atom transfer to U(IV) monoimido complexes or reductive cleavage of nitrite by a U(V) imido complex.[30,31,32] Treatment of U(VI) *trans*-bis(imido) $[U({=}N^tBu)_2I_2(THF)_2]$ with water reagent $B(C_6F_5)_3.H_2O$ also led to formation of a uranyl-like complex, $[U(O)({=}N^tBu)I_2(THF)_2]$.[33]

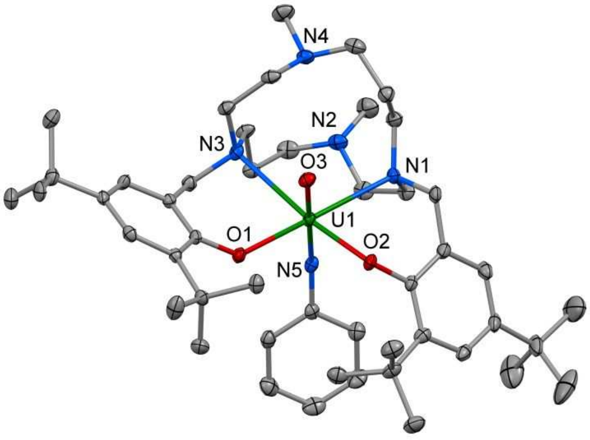


Figure 1. Molecular structure of $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(O)]$ (**4**) with 50 % probability thermal ellipsoids.

We have shown here the first activation of CO_2 by a U(VI) imido complex, specifically a *trans*-bis(imido), with formation of a terminal uranium oxo bond. Selective formation of *trans*-$[O{=}U^{VI}{=}NR]^{2+}$ complexes **4** and **5** by multiple bond metathesis is presumably driven by a thermodynamic preference for U=O bond formation with release of aryl isocyanate. Complex $[U(\kappa^4\text{-}\{^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(O)]$ (**4**) did not exhibit reactivity upon CO_2 exposure in benzene-d_6, possibly reflecting enhanced stability of complex **4** due to a greater inverse trans influence upon U=O bond formation.[26]

To elucidate mechanistic aspects of the observed reactivity, the ADF program[34] was used with the rev-PBE-D3 density functional[35,36,37] to compute the CO_2 cycloaddition/isocyanate extrusion reaction pathway (see SI for Computational Details). The starting reference state A (energy ≡ 0) is the two reactants infinitely separated (Figure 2). Van der Waals interaction between the reactants yields association complex B, which is followed by transition state, TS_B at 103.3 kJ mol^{-1} above A. The CO_2 insertion into a uranium imido site yields intermediate C at 59.5 kJ mol^{-1} above A. Cycloaddition via TS_B is a donor-acceptor process, as revealed by the frontier orbital in Figure 3. A second transition state (TS_C) corresponds to cleavage of isocyanate intermediate C and leads to formation of the uranium imido mono-oxo complex **4** and phenyl isocyanate (D). TS_C presents a substantial barrier of 116 kJ mol^{-1} above A and 140 kJ mol^{-1} above B, consistent with the observed slow kinetics at 25°C. The free energy of 26.2 kJ mol^{-1} to dissociate complex **4** (steps D-E) is mostly due to the electronic contribution (ΔE = +31.2 kJ mol^{-1}). The interaction in D is presumably dominated by dispersion bonding between the uranium complex and phenyl isocyanate.

Formation of the oxo-imido complex **4** in D is a thermodynamic minimum, which evidently hampers subsequent addition of a second CO_2. The reaction profile for addition of CO_2 to **4** is shown in Figure 4. Two aspects clearly differ from the profile in Fig. 2: formation of metallacycle intermediate H is more endothermic than for C ($\Delta\Delta G^o$ = +24.9 kJ mol^{-1}); and both transition states TS_G and TS_H are higher energy compared with TS_B and TS_C. In particular, rate determining transition state TS_H is 8.7 kJ mol^{-1} higher energy than TS_C. Notably, the exergonicity of step I (-53.4 kJ mol^{-1}) is not as favourable as for step D in Fig. 2 (-81.5 kJ mol^{-1}). Overall, it is apparent that CO_2 addition to complex **4** is both thermodynamically and kinetically hindered vis-à-vis CO_2 addition to bis(imido) complex **2**, consistent with observation of only the first process.

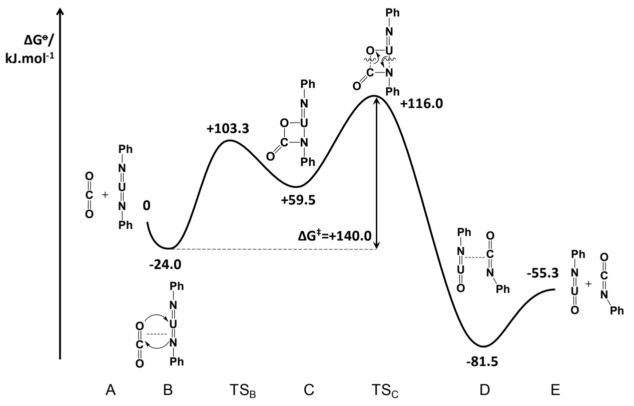


Figure 2. Free energy profile for the reaction of $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})(NPh)_2]$ (**2**) with CO_2.

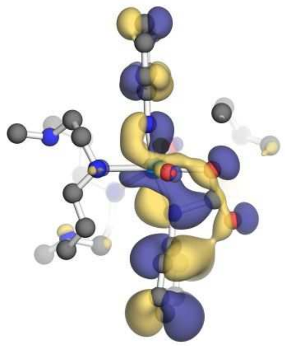


Figure 3. A clipped detail of the HOMO-5 of TS_B showing the U(5f)→O and N→C donor-acceptor interactions with the incoming CO_2 molecule establishing new bonds.

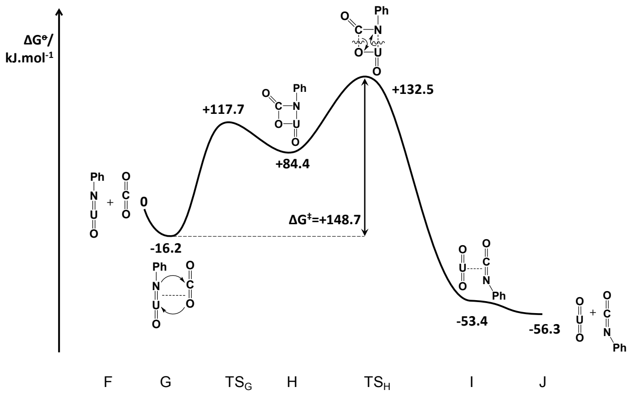


Figure 4. Free energy profile for the reaction of $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\}(NPh)(O)]$ (**4**) with CO_2.

^1H NMR spectra were collected during reaction of **2** with CO_2 under pseudo-first-order conditions of a large CO_2 excess at constant concentration. A plot of the ln(molar fraction) of reagent as a function of time yields a pseudo-first-order rate. The rate was obtained for different temperatures such that using the Arrhenius equation and plotting ln k_{obs} versus $1/T$ provided a reaction activation energy E_a = 102±12 kJ mol^{-1} (see SI for details). This E_a is somewhat smaller than the computed value of 140 kJ mol^{-1} in Fig. 2, which presumably reflects limitations of the computational and/or experimental methodologies (e.g. sample homogeneity during NMR acquisition). The effect of the higher pressure used in the experiments should be insignificant.

In conclusion, U(VI) *trans*-bis(imido) complexes supported by a bis(phenolate) cyclam ligand react with excess CO_2 to afford the *trans*-$[O=U=NAr]^{2+}$ species $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})(NAr)(O)]$. DFT computational studies suggest that the reaction proceeds via endergonic formation of a [2+2] cycloaddition intermediate, with subsequent extrusion of phenyl isocyanate and formation of the U(VI) oxo-imido computed to be exergonic. These reactions are unprecedented examples of activation and cleavage of CO_2 mediated by uranium(VI) imido complexes.

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A data set collection of computational results is available in the ioChem-BD repository[38] and can be accessed via https://doi.org/10.19061/iochem-bd-6-21.

Conflicts of interest

There are no conflicts to declare.

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The U(VI) *trans*-bis(imido) complexes $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)(NPh^R)]$ react with CO_2 to afford stable U(VI) *trans*-$[O{=}U{=}NR]^{2+}$ complexes with elimination of phenyl isocyanates. These are unprecedented examples of activation and cleavage of CO_2 mediated by U(VI) imido complexes.