

CO₂ conversion to phenyl isocyanates by uranium(vi) bis(imido) complexes†‡

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ABSTRACT:

Uranium(vi) *trans*-bis(imido) complexes [U(κ⁴-{(tBu₂ArO)₂Me₂-cyclam})-(NPh)(NPh^R)] react with CO₂ to eliminate phenyl isocyanates and afford uranium(vi) *trans*-[O=U=NR]²⁺ complexes, including [U(κ⁴-{(tBu₂ArO)₂Me₂-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 both thermodynamically and kinetically hindered.

Uranium complexes have emerged as attractive candidates for activation of the very stable C=O bonds of carbon dioxide,^{1–3} which must occur during CO₂ functionalization. U(III) with appropriate supporting ligands can effectively reduce carbon dioxide, giving rise to various products that include an end-on-bound CO₂^{•-} 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 CO₂ insertion into U–E bonds (E = C, N, O, S).^{11–14} Meyer and co-workers showed that U(V) terminal oxo complexes [(^RArO)₃tacn}U=O] are formed upon treatment of U(V) mono-imidos with CO₂, probably *via* [2+2] cycloaddition with elimination of isocyanates.^{13,15} Similar CO₂ transformations have been observed with high oxidation state early transition metals, such as titanium imido complexes.^{16–19}

Activation of CO₂ by hexavalent uranium imido complexes has not yet been achieved, and in general CO₂ activation by U(VI) complexes is rare.²⁰ In such a rare case, the terminal nitride [U(Tren^{TIPS})(N)] reacted with CO₂ 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,^{21–23} 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^tBu)₂I₂(OPPh₃)₂] with PhN=C=O does not result in a uranium oxo complex but rather an imido transfer takes place to form [U(=N^tBu)(=NPh)I₂(OPPh₃)₂].²⁷ We here demonstrate that U(VI) *trans*-bis(imido) complexes supported by a bis(phenolate) cyclam ligand react with CO₂ 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(κ⁶-{(tBu₂ArO)₂Me₂-cyclam})I] (**1**), with formation of [U(κ⁴-{(tBu₂ArO)₂Me₂-cyclam})-(NPh)₂] (**2**),²⁸ the initial focus studies was on the synthesis of the new U(VI) bis(imido) [U(κ⁴-{(tBu₂ArO)₂Me₂-cyclam})-(NPh)(NTol)] (**3**), with a goal of assessing reactivity with CO₂. 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(κ⁴-{(tBu₂ArO)₂Me₂-cyclam})-(NPh)(NTol)] (**3**) and the insoluble U(IV) compound [U(κ⁶-{(tBu₂ArO)₂Me₂-cyclam})I]₂[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

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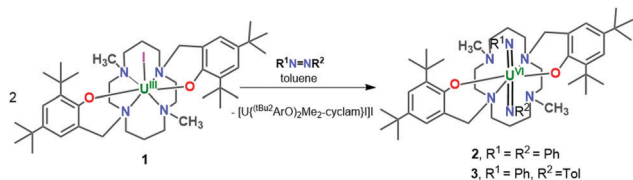
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† A data set collection of computational results is available in the ioChem-BD repository³⁸ and can be accessed *via* <https://doi.org/10.19061/iochem-bd-6-21>.

‡ Electronic supplementary information (ESI) available: Computational and experimental details, NMR spectra, and detailed X-ray data. CCDC 1954718 and 1954719. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc07411b



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

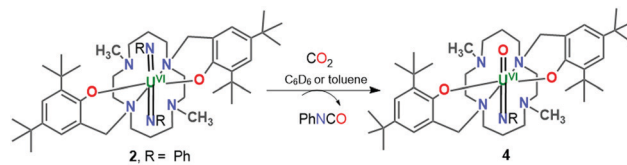
overall distorted octahedral geometry (Fig. S2 in ESI[†]). Structural parameters of **3**, including short U–N_{imido} distances of 1.909(6) and 1.911(7) Å, are similar to those in the symmetric bis(imido) complex **2** (1.895(2) and 1.907(2) Å)²⁸ (structural parameters are in ESI[†] Table S2).

The ¹H NMR spectrum of **3** is characteristic of a diamagnetic compound, consistent with the asymmetric structure identified in the solid state. ¹H and ¹³C NMR (see Fig. S3 and S4 in ESI[†]) revealed two sets of resonances for the phenolate arms of $\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\}^{2-}$ 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 CO₂ (*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 (Fig. S6 and S7 in ESI[†]).

The ¹H NMR spectrum of the new complex exhibited integrated intensities for the $\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\}^{2-}$ and phenyl imido protons of 1 : 1, and revealed loss of the C₂ 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 $\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\}^{2-}$ have different chemical environments. In addition, two resonances for the NCH₃ 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 ¹³C NMR data (Fig. S8–S10 in ESI[†]) corroborated the ¹H NMR results, consistent with formation of U(vi) oxo imido complex $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NPh)}\text{(O)}]$ (**4**).

An NMR tube-scale reaction of $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NPh)}\text{(NTol)}]$ (**3**) with CO₂ showed that the bis(imido) complex is quantitatively converted to a mixture of mono-oxo imido $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NPh)}\text{(O)}]$ (**4**) and $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NTol)}\text{(O)}]$ (**5**), in approximately 1 : 1 ratio, along with the corresponding aryl isocyanates (Fig. S13 and S14 in ESI[†]). 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 ESI[†]). Two of the ^tBu phenolate resonances of **5** are at 2.08 and 1.86 ppm, with the other



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

two centered at 1.57 ppm and overlapping with a ^tBu resonance of **4**. ¹³C 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 $\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\}^{2-}$ (**4**: 166.75 and 166.56 ppm; **5**: 166.81 and 166.69 ppm).

The reaction of $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NPh)}_2]$ (**2**) with an excess of CO₂ in toluene resulted in a dark cherry red solid after evaporation of the solvent (Scheme 2). 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 $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(O)}\text{(NPh)}]$ (**4**) (Fig. 1).

Like complexes **2** and **3**, **4** exhibits an octahedral geometry about the uranium center, with the $\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\}^{2-}$ ligand adopting a $\kappa^4\text{-N}_2\text{O}_2$ coordination mode, and the oxo and phenyl imido are *trans*-oriented. The geometric parameters of the $\{\text{RN}=\text{U}=\text{O}\}^{2+}$ 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 $[\text{U}(\text{O}=\text{NPh}^{\text{IPr}_2})(\text{O})\text{Cl}_2(\text{tppo})_2]$ (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*- $[\text{O}=\text{U}=\text{NR}]^{2+}$ 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.^{30–32} Treatment of U(vi) *trans*-bis(imido) $[\text{U}(\text{O}=\text{N}^t\text{Bu})_2\text{I}_2(\text{THF})_2]$ with water reagent B(C₆F₅)₃·H₂O also led to formation of a uranyl-like complex, $[\text{U}(\text{O})(\text{O}=\text{N}^t\text{Bu})_2(\text{THF})_2]$.³³

We have shown here the first activation of CO₂ by a U(vi) imido complex, specifically a *trans*-bis(imido), with formation

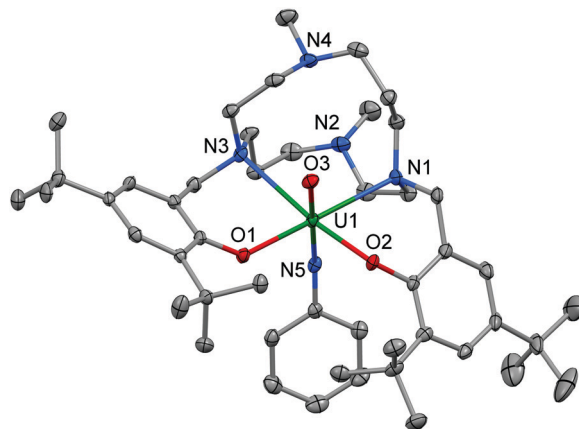


Fig. 1 Molecular structure of $[\text{U}(\kappa^4\text{-}\{({}^t\text{Bu}_2\text{ArO})_2\text{Me}_2\text{-cyclam}\})\text{(NPh)}\text{(O)}]$ (**4**) with 50% probability thermal ellipsoids.

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(κ^4 -{(tBu₂ArO)₂Me₂-cyclam})(NPh)(O)] (**4**) did not exhibit reactivity upon CO₂ 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 program³⁴ was used with the rev-PBE-D3 density functional^{35–37} to compute the CO₂ cycloaddition/isocyanate extrusion reaction pathway (see ESI† for Computational details). The starting reference state A (energy ≡ 0) is the two reactants infinitely separated (Fig. 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 CO₂ 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 Fig. 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

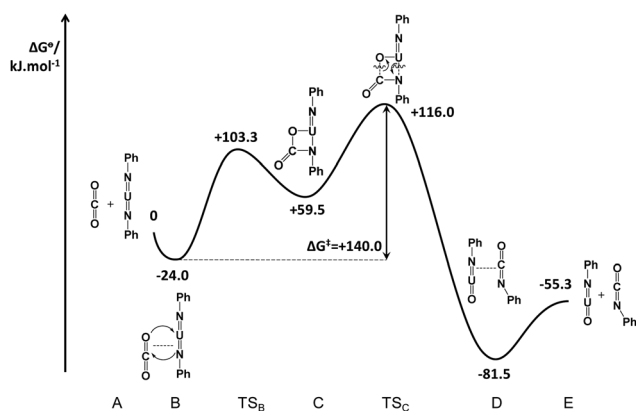


Fig. 2 Free energy profile for the reaction of [U(κ^4 -{(tBu₂ArO)₂Me₂-cyclam})(NPh)₂] (**2**) with CO₂.

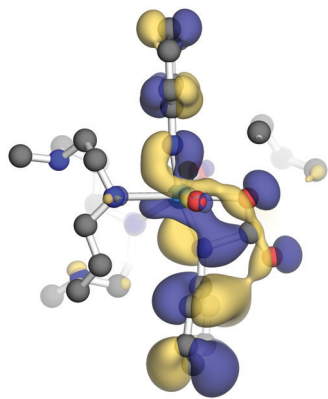


Fig. 3 A clipped detail of the HOMO–5 of TS_B showing the U(5f) → O and N → C donor–acceptor interactions with the incoming CO₂ molecule establishing new bonds.

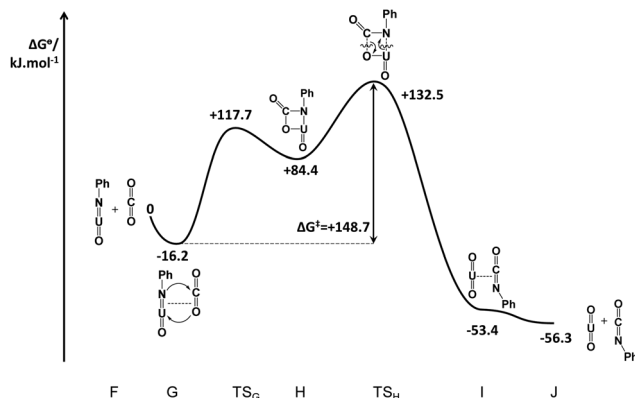


Fig. 4 Free energy profile for the reaction of [U(κ^4 -{(tBu₂ArO)₂Me₂-cyclam})(NPh)(O)] (**4**) with CO₂.

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 ($\Delta E = +31.2$ 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 CO₂. The reaction profile for addition of CO₂ to **4** is shown in Fig. 4. Two aspects clearly differ from the profile in Fig. 2: formation of metallacycle intermediate H is more endergonic than for C ($\Delta\Delta G^\circ = +24.9$ 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 CO₂ addition to complex **4** is both thermodynamically and kinetically hindered *vis-à-vis* CO₂ addition to bis(imido) complex **2**, consistent with observation of only the first process.

¹H NMR spectra were collected during reaction of **2** with CO₂ under pseudo-first-order conditions of a large CO₂ 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 ESI† 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 CO₂ to afford the *trans*-[O=U=NR]²⁺ species [U(κ^4 -{(tBu₂ArO)₂Me₂-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 CO₂ mediated by uranium(vi) imido complexes.

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Conflicts of interest

There are no conflicts to declare.

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