Remodeling of N-Heterocyclic Iminato Ligand Frameworks for the Facile Synthesis of Isoureas from Alcohols and Carbodiimides Promoted by Organoactinide (Th, U) Complexes

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ABSTRACT: A new class of actinide complexes [(L)An(N[SiMe3]2)3] (An = Th or U) (Th1–Th3 and U1–U3) supported by highly nucleophilic seven-membered N-heterocyclic iminato ligands were synthesized and fully characterized by single-crystal X-ray diffraction. These complexes were successfully exploited as powerful catalysts for the addition of alcohols to carbodiimides to yield the corresponding desirable isourea products at room temperature with short reaction times and excellent yields. Thorough stoichiometric, thermodynamic, and kinetic studies were carried out, allowing us to propose a plausible mechanism for the catalytic reaction.

INTRODUCTION

Isoureas, the isomeric analogues of urea, are being vastly exploited as a component of fertilizers as it is an easily accessible source of nitrogen to stimulate the growth of crops.1−3 Besides agriculture, these compounds are also equally important as anti-inflammatory drugs in the pharma industry, a raw material for the manufacture of plastics, surfactants, chemical fire extinguishers, and, last but not least, biocatalysts.4−12 Apparently, to compensate for the skyrocketing demand, many new synthetic methodologies are being designed to synthesize isoureas using ureas, carbodiimides, chloroformamidines, cyanamides, organic cyanates, or isocyanates, as starting materials.5,13 The straightforward synthesis of isoureas via the addition of an alcohol to a carbodiimide (RN=C=NR′) has drawn great attention for being atom-efficient and utilizing easily available starting materials. For being less electrophilic, the reactions of carbodiimides with alcohols require either very high thermal energy or Lewis acid catalyst activation. Although transition metal, copper (CuCl, CuCl2, and Cu4O) and zinc (ZnCl2), salts have fairly conducted the reaction, this method is restricted by limited catalytic species, narrow substrate scope, and longer reaction time.14−21 The continuing search for improved catalytic systems has led Cantat et al. to investigate the catalytic efficacies of the alkali metal (Na and K) salts of 1,5,7-triazabicyclo[4,4,0]dec-5-ene, which have turned out to be a good example of transition metal-free catalysts to promote the formation of isoureas by the addition of alcohols to carbodiimides.22 Zhao and Yao have also successfully employed rare earth metal amides for the same reaction.23−25

Over the last few years, our group has been attempting to design different actinide (Th, U)-based catalytic systems for the addition of alcohols to carbodiimides with high turnover frequencies under mild conditions. Our initial attempt with mono-(imidazolin-2-imino)thorium (IV) or -uranium (IV) complexes (II in Scheme 1b) was unexpectedly futile even though these complexes have demonstrated high activities in the catalytic insertions of carbodiimides into E=H (NH, PH, SH, ≡CH, etc.) moieties.25 In 2016, for the first time, the actinide complexes U[N(SiMe3)2]3 and [(Me3Si)2N]2An-[k(N,N)-(Me3Si)(CH2)2N(SiMe3)] (An = Th or U, 1 mol %) (I in Scheme 1a) were reported to catalyze the intermolecular addition of alcohol to aryl/alkyl-substituted carbodiimides with moderate to excellent yields at elevated temperature (75 °C).26 Inevitably, the high oxophilicity of the actinides, which results from the strong An–O bond strength (Th–O = 208.0 kcal/mol and U–O = 181.0 kcal/mol), renders the catalytic transformations with oxygen-containing substrates very challenging.27−29 According to the mechanistic studies, in the above-mentioned case, the catalytic cycle has been initiated via the formation of the alkoxo active species [An]−OR and completed with the regeneration of an alike moiety [An]−OR′. Hence, this almost thermoneutral process is assumed to be the driving force for the reaction, where no energy is being paid for breaking the strong An–OR bond.

However, for being highly basic and nucleophilic in nature, N-heterocyclic iminato ligands were employed to decrease the
high oxophilicity of the actinide metal centers, which eventually should have accentuated the catalytic effectiveness of complexes (II) in comparison to (I) or U[N(SiMe₃)₂]₂]. Despite this, the reactivity of the two aforementioned systems (I and II) has operated in a contradictory way. Hence, we have speculated the reason proposing that the presence of a bulky N-substituted wingtip (dipp = 2,6-diisopropylphenyl) of the imidazolin-2-iminato ligand might have restrained the expected active species, monoimidazolin-2-iminato)thorium (IV) trialkoxides, from attacking the carbodiimide, consequently leading to no activity. To prove the merit of this assumption, we strategized to modify the architectures of the N-heterocyclic iminato ligands further and therefore make the ligand framework further less sterically encumbered around the backbone. A recrystallization from a toluene and hexane mixture at −35 °C has afforded the target actinide complexes [(L)AnN₃″] [An = U or Th; N₃″ = N(SiMe₃)₂] in high yields. Compounds Th₁/U₁⁻¹² and Th₂ are known earlier and the additional complexes are new for the present studies. The molecular structures of compounds U₂, Th₂, and U₃ were established by X-ray crystallography (Figure 2a–c) and compared with the previously reported complexes (Th₁, U₁⁻¹, and Th₂) for detailed crystallographic data and selected bond lengths and angles, see the Supporting Information.

X-ray analysis reveals that all three new complexes are isostructural (Figure 2a–c), displaying pseudo-tetrahedral geometries around the central metal ions, surrounded by one N-heterocyclic iminato ligand and three silylated amide moieties. N1−C1 ipso bond distances of 1.292(12), 1.305(11), and 1.271(5) Å are observed for the complexes U₂, Th₂, and U₃, respectively. The An−N₁ bond distances [2.140(9) (U₂), 2.129(7) (Th₂), and 2.204(3) (U₃)] are shorter than the An−N₁ₐₚₐₚ₁ bond distances in the respective complexes [0.15 Å on average shorter, see the Supporting Information]. Moreover, the An−N₁(C₁) angles [165.6(8)° (U₂), 165.6(7)° (Th₂), and 164.5(3)° (U₃)] are close to linearity. These parameters are indicative of the substantial π donation from the ligand to the metal, confirming a high bond order for the Th−N₁/U−N₁ bonds. It is important to point out that we
should expect the Th complexes to have an M–N bond length slightly longer as compared to the corresponding uranium complex. However, by comparing complexes Th-3 and U-3, the opposite is observed, indicating the effective repulsion among the iminato ligand and the two electrons in the uranium f-orbitals. Furthermore, no interaction has been observed between the methoxy group and the uranium metal center in the solid state of the complex U-2. Instead, the methoxy group is bent away from the metal, providing less steric clashes around the metal center; a behavior that has been observed previously in the complex Th-2.

**Catalytic Addition of Alcohols to Carbodiimide**

**Scope.** Initially, we have investigated the catalytic efficiencies of all six complexes (1 mol %) in the intermolecular addition of methanol (MeOH) to 1,3-di-p-tolycarbodiimide (DTC), at room temperature. Our initial findings have shown that all six complexes are capable of catalyzing the addition of MeOH to DTC, exhibiting comparable activities (>99%, 0.5 h) (entries 1–6, Table 1), whereas no reaction has been observed in the absence of actinide complexes (entry 7, Table 1). Encouraged by this observation, we continued our studies with other carbodiimides by varying the steric and electronic properties of carbon, which in turn suppresses the addition of the alkoxo moiety.

The delicate interplay of the acidity, steric bulkiness, and functional group tolerance of alcohols by the actinide complexes has been systematically investigated using DTC as the additional substrate with Th-1/U-1 catalysts. When studying both of the catalysts (Th-1/U-1), the reaction of the 2-methyl-substituted carbodiimide with MeOH required a little longer reaction time (1 h) to obtain a full conversion as compared to DTC (entries 8–9, Table 1), which is attributed as a steric encumbrance imparted by the ortho-substituted methyl groups. Likewise, bulky mesityl (Mes)-substituted carbodiimide afforded only 64 and 29% conversions after 24 h using Th-1 and U-1, respectively (entries 10–11, Table 1).

Unfortunately, the highly sterically encumbered Dipp-substituted carbodiimide has shown no activity using both catalysts (entries 12–13, Table 1). The carbodiimide in which the phenyl rings are substituted with electron-donating methoxy groups at the para position has exhibited excellent activity (>99%, 1 h), employing both catalysts (entries 14–15, Table 1).

Both Th-1 and U-1 have demonstrated low to moderate activity using aliphatic-substituted carbodiimides, such as diisopropylcarbodiimide (DIC) (Th-1: 47% and U-1: 37%) and dicyclohexylcarbodiimide (DCC) (Th-1: 25% and U-1: 16%), with MeOH after 24 h at an elevated temperature of 75 °C (entries 16–19, Table 1). At room temperature, both the catalysts have remained inactive in the reaction of DIC or DCC with MeOH. The electron-pushing ability of aliphatic groups on the carbodiimide results in decreased electrophilicity of carbon, which in turn suppresses the addition of the alkoxo moiety.

The delicate interplay of the acidity, steric bulkiness, and functional group tolerance of alcohols by the actinide complexes has been systematically investigated using DTC as the additional substrate with Th-1/U-1 catalysts (1 mol %), at room temperature. All the results are summarized in Table 2. We have described previously that the reaction of methanol and DTC has afforded the corresponding isourea product in >99% conversion only within 0.5 h. Due to the increase in the chain length from methanol to ethanol and 1-propanol, the reactions have required 1–2 h to achieve full conversions (entries a,b, Table 2). The sterically hindered 2-propanol has taken a longer reaction time (6 h) to afford full conversion (entry c, Table 2). Interestingly, both catalysts have shown moderate activity [Th-1: 71% and U-1: 45%] in the case of cyclic cyclohexanol (entry d, Table 2). The increase in steric encumbrance of the alcohol (tBuOH) has resulted in the

Table 1. Optimization Table

| entry | cat. | R in R≡C=N=C≡N−R | time [h] | conv. [%] |
|-------|------|-------------------|-----------|-----------|
| 1     | Th-1 | 4-methoxyphenyl   | 0.5       | >99       |
| 2     | U-1  |                   | 0.5       | >99       |
| 3     | Th-2 |                   | 0.5       | >99       |
| 4     | U-2  |                   | 0.5       | >99       |
| 5     | Th-3 |                   | 0.5       | >99       |
| 6     | U-3  |                   | 0.5       | >90       |
| 7     |      |                   | 24        |           |
| 8     | Th-1 | 2-methylphenyl    | 1         | >99       |
| 9     | U-1  |                   | 1         | >99       |
| 10    | Th-1 | Mes               | 24        | 64        |
| 11    | U-1  |                   | 24        | 29        |
| 12    | Th-1 | Dipp              | 24        |           |
| 13    | U-1  |                   | 24        |           |
| 14    | Th-1 | 4-methoxyphenyl   | 1         | >99       |
| 15    | U-1  |                   | 1         | >99       |
| 16    | Th-1 | isopropyl         | 24        | 47        |
| 17    | U-1  |                   | 24        | 37        |
| 18    | Th-1 | cyclohexyl        | 24        | 25        |
| 19    | U-1  |                   | 24        | 16        |

*Reaction conditions: actinide precatalysts (2 μmol), carbodiimide (0.20 mmol), alcohol (0.20 mmol), 550 μL of C_{6}D_{6} and room temperature. Conversion determined by 1H NMR spectroscopy of the crude reaction mixture versus 1,3,5-trimethoxybenzene as the internal standard. °C.*
slowdown of the reaction rate significantly, affording 58% (Th-1) and 67% (U-1) of the corresponding isourea after 24 h (entry e, Table 2).

Benzyl alcohol has been smoothly inserted into DTC using both catalysts, achieving full completion after 1 h (entry f, Table 2). The high Lewis acidity of thorium and uranium usually favors the binding of electronegative heteroatoms (O, S, and N) attached to the substrate, which eventually diminishes the catalytic activity of the actinide complexes. However, our catalysts [Th-1 and U-1] are found to efficiently catalyze the aforementioned reaction also using heteroaromatic alcohols such as 2-furanmethanol, 2-thiophenemethanol, and 2-pyridinemethanol, providing >99% conversion within 2 h (entries g–i, Table 2). The presence of highly nucleophilic seven-membered N-heterocyclic iminato ligand diminishes the electrophilicity of the actinide metal center, in this sense, allowing high activities even in the presence of electronnegative coordinating groups.

The substrate scope has been further extended by employing several substituted phenols where the catalyst Th-1 has been found more compatible than U-1. Using phenol, the reaction has become slower as compared to the unhindered aliphatic alcohols in the case of both the catalysts [Th-1 and U-1]. Both electron-donating and electro-withdrawing substituents on the aromatic ring of phenol have shown roughly similar reaction rates providing 90–99% conversion after 8–10 h (entries j–m, Table 2). However, the U-1 catalyst has been found to be more dependent on the acidity of the phenol derivatives. A gradual increase in the conversion has been observed with the change in pK_a values of the para-substituted phenol derivatives 4-(F)-phenol (30%, 24 h), phenol (53%, 24 h), and 4-(tBu)-phenol (71%, 24 h) (entries j–l, Table 2). In the case of p(OMe)-phenol an odd drop in the reactivity was observed (56%, 24 h) compared to 4-(tBu)-phenol (entry m, Table 2).

The consequence of the steric hindrance has been observed by employing a bulky tert-butyl group on the ortho position of phenol, resulting in merely 39% (Th-1) and 36% (U-1) conversions after 24 h (entry o, Table 2). However, the substitution of sterically demanding groups at the meta position does not affect the reaction rate (entry p, Table 2).

In addition, the regioselectivity of the product formation has been investigated by reacting methanol and some unsymmetrical carbodiimides with two different groups: a sterically demanding Mes or Dipp and a relatively smaller phenyl group. The reaction reaches completion after 1 h, providing two products in both cases (entries 1−2, Table 3). It could be noted that hydrogen (H) from the alcohol is selectively transferred to the nitrogen atom bearing the smaller

| R in Ph−N=C−N−R | conv. [%] | products ratio (A:B) |
|------------------|---------|----------------------|
| 1 Mes            | >99     | 2:5                  |
| 2 Dipp           | >99     | 1:10                 |

*Reaction conditions: actinide precatalsysts (2 μmol), carbodiimide (0.20 mmol), alcohol (0.20 mmol), 550 μL of C_6D_6, and room temperature. Conversion determined by 1H NMR spectroscopy of the crude reaction mixture versus 1,3,5-trimethoxybenzene as the internal standard.
substituent, directed by the less sterically encumbered Ph group.

This high regioselectivity is likely to be the result of a highly ordered transition state (Scheme 3), in which the orientation of the isourea moiety is determined by steric interactions.

Once the carbodiimide reacts with the alcohol, a second alcohol molecule will induce the protonolysis of the product. The incoming alcohol will preferably engage in an orientation with the larger R group pointing away from the reaction center. Accordingly, the transition state (a) should be favored over transition state (b) in Scheme 3, giving rise to the product selectively.

**Mechanistic Studies.** In order to gain an insight into the reaction mechanism, kinetic measurements were performed for the catalytic addition of isopropanol (iPrOH) to DTC catalyzed by the complex Th-1. The rate law has been determined by initial rate analysis at various catalyst and substrates concentrations, exhibiting a first-order dependence on the catalyst and DTC and an inverse first-order dependence on iPrOH (eq 1) (Figures S45–S50 in the Supporting Information). For the full kinetic equation treatment, please see the Supporting Information.

\[
\frac{dp}{d\tau} = [\text{Th-1}]_0 [\text{DTC}]_0 [\text{iPrOH}]^{-1}
\]  
(1)

Moreover, the activation parameters for the addition of iPrOH to DTC catalyzed by the complex Th-1 have been determined from the Eyring and Arrhenius plots, displaying a moderate activation barrier \((E_a)\) of 16.4(0.5) kcal/mol. Enthalpy \((\Delta H^\circ)\) and entropy \((\Delta S^\circ)\) of activation are 15.8(0.5) kcal/mol and -26(2) eu, respectively, indicating a highly ordered transition state during the rate-determining step (RDS) (Figures S52–S53). Deuterium-labeling studies using iPrOD, DTC, and complex Th-1 revealed a KIE value of \(K_H/K_D = 0.99\), indicating that protonolysis is a fast step compared to the insertion of the metal-alkoxo moiety into the carbodiimide (Figure S54).

Next, a great number of stoichiometric experiments have been conducted using the pre-catalyst (Th-1), iPrOH, and DTC to get an insight into the activation pathways of the complex. First, no reaction is observed between complex Th-1 and DTC alone. In contrast, the reaction between 8 equiv of iPrOH and Th-1 has exhibited the protonolysis of all the \([-\text{HN(SiMe}_3]_2\) moieties from the metal center, which is indicated by the appearance of a new signal at 0.10 ppm in the \(^1H\) NMR spectrum, assigned to \(-\text{CH}_3\) groups of hexamethyldisilazane [HN(SiMe\(_3)\] (Figure S57). Moreover, the excess alcohol molecules attached to the metal center are accountable for the inverse first-order in iPrOH. In order to verify the number of iPrOH molecules bound irreversibly to the metal center, the excess alcohol and free HN(SiMe\(_3)\] have been completely removed, by evaporation resulting in the \([(L^1\text{H})\rightarrow \text{Th(OiPr)}_4]\) species. From \(^1H\) NMR, it is confirmed that four \(-\text{OPr}\) groups are surrounding the metal sphere, corroborated by the signal at 1.50 ppm and the broad septet at 4.65 of the \(-\text{OCH(CH}_3)\] moiety (Figure S58) and supported by MS analysis. Moreover, a new singlet appeared at 6.14 ppm as a result of ligand protonation (\(-\text{NH}\) moiety) (Figure S58). Additionally, the parent signal at 4.49 ppm for the \((\text{Me}_2)C-H\) proton of the complex Th-1 is now absent (Figure S55). Instead, two different broad signals at 4.85 and 3.50 ppm with the same intensity have appeared (Figure S58). This phenomenon indicates that the \((\text{Me}_2)C-H\) proton is now experiencing two different electronic environments rising from the geometrical change caused by the ligand protonation, which suggests that the ligand still remains coordinated to the metal center. In an additional experiment, the complex Th-1 has been treated with 8 equiv of iPrOH followed by the addition of 4 equiv of DTC at room temperature, resulting in the formation of 4 equiv of the isourea product and \([(L^1\text{H})\rightarrow\]
Th(OPr)₄₃ (Figure S59). Coordination of a protonated mono(benzimidazolin-2-imino) ligand to a Hf metal center, also supported by the solid-state crystal structure, was reported by our group. However, in spite of our repeated efforts, we did not achieve good X-ray quality single crystals.

In order to confirm the absence of a free ligand via the −N−H moiety, we have performed Fourier transform infrared (FT-IR) studies (Figures S62–S65). We have investigated the FT-IR spectrum of (a) Th-I, (b) Th-I + PrOH (4 equiv), and (c) Th-I + PrOD (4 equiv). We have observed a signal at 3329 cm⁻¹ that could be presumed as the signal for −N−H. However, the corresponding N−D stretching is absent in the spectra arguable because of a bridging hydrogen bond between the N−H−OR moieties as was observed for a similar hafnium complex. In addition, in all the protonolysis experiments, the signal at 2970 cm⁻¹ of the free ligand was absent, indicating that even at large alcohol excess the ligand is still attached to the complex. The fact that our catalyst Th-I has a higher efficiency than complex I also strongly substantiates the significant role of the ancillary ligand in the reaction.

Based on the kinetics studies, the thermodynamic parameters, and stoichiometric studies, a plausible mechanism is presented in Scheme 4. The first step of the proposed mechanism is the rapid protonolysis of the starting actinide precatalyst Th-I by the alcohol with the displacement of three molecules of hexamethyldisilazine and protonation of the ligand producing the active catalyst [A]. Subsequently, the insertion of carbodiimide (DTC) into the thorium−alkoxide bond produces intermediate [B] as the RDS. A fast protolytic cleavage by the alcohol with the intermediate [B] releases isourea and regenerates the active species [A] catalyst. The inhibiting effect of the alcohol, observed in the kinetic studies, is expected for the formation of the resting state [C] of the catalyst, in the reaction mixture, in the presence of excess alcohol. In addition, the presence of the ligand improves the solubility of the complex and suppresses the oligomerization of the actinide−alkoxide species even in a high ratio of coordinated alcohols.

### CONCLUSIONS

In this work, Th(IV) and U(IV) complexes bearing a new class of seven-membered N-heterocyclic iminato ligands were synthesized. The catalytic efficiencies of the resulting actinide complexes toward the addition of alcohols to carbodiimide have been studied. All the complexes have demonstrated high activity, yielding the corresponding isoureas in high conversion, with good functional group tolerance under mild reaction conditions (1 mol% and room temperature). Kinetic analysis and isotope labeling studies have allowed us to propose a plausible mechanism, suggesting an insertion of a carbodiimide into an actinide−alkoxide moiety as the RDS.

### EXPERIMENTAL SECTION

**General Procedures and Materials.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or J-Young Teflon valve-sealed NMR tubes on a dual-manifold Schlenk line interfaced to a high vacuum (10⁻⁵ Torr) line or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1–2 ppm of O₂). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 A molecular sieve column. Hydrocarbon solvents, benzene-d₆ (Cambridge Isotopes), were distilled under vacuum from the Na/K alloy and degassed by three freeze–pump–thaw cycles prior to use. 1,3-diisopropyl carbodiimide (DIC) (Sigma-Aldrich) was dried by vacuum transfer. DTC (Sigma-Aldrich) and 1,3-di-cyclohexyl carbodiimide (DCC) were dried overnight on a high vacuum line (5–10 torr) and stored in a glovebox before use. Other carbodiimides, including 1,3-di-(2,4,6-trimethylphenyl)-carbodiimide, 1,3-di-(2,6-diisopropylphenyl) carbodiimide, 1,3-di-p-methoxyphenyl carbodiimide, 1,3-di-o-tolyl carbodiimide, N'-[2,6-diisopropylphenyl]-N'-phenyl carbodiimide, and N-(2,4,6-trimethylphenyl)-N'-phenyl carbodiimide, were synthesized according to previous reports. Liquid alcohols were distilled from CaH₂ before their use and stored over 4 Å molecular sieves; solid alcohols (Sigma-Aldrich) were dried overnight on a high vacuum line (5–10 torr). The actinide complex precursors, [(Me₃Si)₂N]₂An[κ²-[(N,C)CH₂Si(CH₃)₂N(SiMe₃)] (An = Th or U) and thorium and uranium metallacycles, were prepared according to the published procedures. N'-isopropyl-[1,1'-biphenyl]-2,2'-diamine and ligands LH and L₂H and actinide complexes Th-I, U-I, and Th-II were synthesized according to our previous reports and NMR spectra were recorded on Bruker ADVANCE 300 and 500 and Bruker ADVANCE III 400 and 600 spectrometers for crude reaction mixtures. Chemical shifts for ¹H and ¹³C NMR are referenced to internal protosilanol and reported relative to tetramethylsilane. J-values are reported for ¹H NMR coupling constants in the unit of Hertz (Hz). MS experiments were performed at 200 °C (source temperature) on a Maxis Impact (Bruker) mass spectrometer with an APCI solid probe method. The single-crystal material was immersed in perfluoropolyalkylether and was quickly fished out with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen. Data collection was performed using monochromatic Mo Kα radiation using ϕ and ω scans to cover the Ewald sphere. Accurate cell parameters were obtained with the amount of indicated reflections. The structure was solved by SHELXS-97 direct methods and refined using the SHELXL-97 program package. The atoms were refined anisotropically. Hydrogen atoms were included using the riding model. The crystallographic figures have been generated using Diamond 3 software. CCDC-1996442 (U-2), 1996443 (Th-3), and 1996444 (U-3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis of N²-Benzyl-N²'-isopropyl-[1,1'-biphenyl]-2,2'-diamicine.** A mixture of benzaldehyde (0.45 mL, 4.42 mmol) and N²'-isopropyl-[1,1'-biphenyl]-2,2'-diamine (a) (1 g, 4.42 mmol) in ethanol (50 mL) was refluxed for 24 h. Next, the solvent was removed, and the intermediate imine product was redissolved in MeOH (30 mL). The reaction mixture was then cooled to 0 °C and NaBH₄ (0.37 g, 9.72 mmol) was added slowly. The mixture was allowed to reach room temperature and stirred for 12 h. 2 M aqueous NaOH solution (50 mL) was added, and the aqueous and organic layers separated. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, and the solvent was removed under reduced pressure. The product was purified by column chromatography (neutral Al₂O₃) using hexane and ethyl acetate as the eluant (85:15). Yield: 1.18 g (85%). ¹H NMR...
Synthesis of [L\textsuperscript{3}H\textsubscript{2}BBr]. A solution of cyanogen bromide (0.46 g, 4.34 mmol) in toluene (50 mL) was added dropwise to a stirred solution of N\textsubscript{2}-benzyl-N\textsuperscript{2}-isopropyl-\textsl{[1,1\textsuperscript{'}}-biphenyl\textsuperscript{2,2\textsuperscript{'}}]-diamine (0.92 g, 2.91 mmol) in toluene at 110 °C. After complete addition, the mixture was stirred at 110 °C for 12 h. The reaction mixture was allowed to come to room temperature. The volume of toluene was reduced to about 5 mL by using a rotary evaporator and 100 mL of diethyl ether was added to obtain a solid precipitate. Next, the precipitate was filtrated and washed with diethyl ether (3 × 30 mL) and dried in a vacuum, to afford a white solid. Yield: 1.10 g (90%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 294 K): δ 9.57 (br, 2H, −NH\textsubscript{2}), 7.66 (d, J = 8.0 Hz, 1H, Ar\textsuperscript{7}), 7.54–7.48 (m, 4H, ArH), 7.44–7.39 (m, 2H, ArH), 7.35–7.32 (m, 1H, ArH), 7.06–7.02 (m, 1H, ArH), 6.96 (t, J = 4.0 Hz, 2H, ArH), 6.75 (d, J = 8.0 Hz, 2H, ArH), 5.54 (d, J = 16.0 Hz, 1H, −CH\textsubscript{2}−Br), 5.17 (d, J = 16.0 Hz, 1H, −CH\textsubscript{2}−Br), 4.70 (septet, J = 8.0 Hz, 1H, −CH(\textsuperscript{3})\textsubscript{2}), 1.51 (d, J = 8.0 Hz, 3H, −CH(\textsuperscript{4})\textsubscript{3}), 0.86 (d, J = 8.0 Hz, 3H, −CH(\textsuperscript{3})\textsubscript{2}), 0.44 (s, 54H, −N(SiMe\textsubscript{3})\textsubscript{2}). 13C NMR (100 MHz, CDCl\textsubscript{3}, 294 K): δ 165.2, 142.2, 138.9, 136.6, 134.9, 133.9, 129.4, 128.9, 128.6, 128.5, 128.2, 127.9, 127.7, 127.5, 127.4, 124.5, 58.7, 43.9, 21.8 ppm. ESI-MS: m/z, 342.19 [M + H\textsuperscript{+}].

Synthesis of L\textsuperscript{4}H. Aqueous KOH (0.25 g, 4.44 mmol) was added to the diethyl ether (50 mL) suspension of L\textsuperscript{3}H\textsubscript{2}BBr (1 g, 2.22 mmol), and the mixture was vigorously stirred for 30 min at room temperature. Using a separatory funnel, the ether layer was separated and washed with distilled water (3 × 20 mL). The ether layer was dried over anhydrous MgSO\textsubscript{4} and the solvent was removed under reduced pressure. Yield: 0.72 g (95%). 1H NMR (400 MHz, CDCl\textsubscript{3}, 294 K): δ 7.38 (t, J = 7.5 Hz, 2H, Ar\textsuperscript{7}), 7.34–7.26 (m, 2H, ArH), 7.23 (m, 2H, ArH), 7.15 (m, 2H, ArH), 7.09 (m, 2H, ArH), 6.98 (m, 8H, ArH), 6.79 (m, 2H, ArH), 5.01 (d, J = 15.4 Hz, 1H, −CH\textsubscript{2}−Br), 4.63 (d, J = 15.4 Hz, 1H, −CH\textsubscript{2}−Br), 3.99 (br, 1H, −CH(\textsuperscript{3})\textsubscript{2}), 1.27 (d, J = 6.5 Hz, 3H, −CH(\textsuperscript{4})\textsubscript{3}), 0.86 (d, J = 6.5 Hz, 3H, −CH(\textsuperscript{4})\textsubscript{3}), 0.44 (s, 54H, −N(SiMe\textsubscript{3})\textsubscript{2}). 13C NMR (100 MHz, CDCl\textsubscript{3}, 294 K): δ 166.90, 144.58, 142.18, 138.06, 137.49, 135.15, 128.40, 128.22, 128.10, 127.78, 127.55, 127.12, 126.59, 125.94, 125.27, 124.84, 121.49, 52.62, 50.53, 23.63, 21.79. ESI-MS: m/z, 342.20 [M + H\textsuperscript{+}].

Synthesis of the Complex U-2 ([L\textsuperscript{4}H]U[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}). To a solution of uranium metalloccyly (0.10 g, 1.4 mmol) in 5 mL of toluene was added dropwise to a 5 mL of toluene solution of the ligand L\textsuperscript{4}H (51.7 mg, 1.4 mmol). The reaction mixture was stirred at room temperature for 12 h. After that, the solvent was removed under high vacuum. X-ray-quality crystals of U-2 were grown from the toluene/hexane mixture at 35 °C. Yield: 134 mg (88%). 1H NMR (500 MHz, CD\textsubscript{3}D\textsubscript{2}O): δ 25.30 (s, 1H, Ar\textsubscript{7}), 24.15 (s, 2H, ArH), 13.57 (s, 1H, ArH), 11.99 (t, J = 7.4 Hz, 1H, Ar\textsubscript{7}), 11.84 (d, J = 8.3 Hz, 1H, Ar\textsubscript{7}), 11.10 (d, J = 7.4 Hz, 1H, Ar\textsubscript{7}), 9.77 (t, J = 8.1 Hz, 1H, Ar\textsubscript{7}), 8.92 (dd, J = 8.1, 5.5 Hz, 1H, Ar\textsubscript{7}), 7.69 (s, 3H, Ar\textsubscript{7}), 6.63 (d, J = 5.5 Hz, 1H, Ar\textsubscript{7}), 0.15 (s, 3H, −OCH\textsubscript{3}), −8.06 (s, 3H, −CH(\textsuperscript{3})\textsubscript{2}), −8.79 (s, 3H, −CH(\textsuperscript{3})\textsubscript{2}), −9.44 (s, 54H, −N(TMS)). 13C NMR (126 MHz, CD\textsubscript{3}D\textsubscript{2}O): δ 169.89, 165.02, 159.24, 147.74, 146.33, 139.79, 139.15, 133.69, 132.06, 131.06, 129.32, 129.29, 128.56, 128.33, 125.69, 125.44, 121.78, 120.18, 59.42, 21.42, 14.30, 2.64. MS (APCI): m/z, 1088.5326 [M + H\textsuperscript{+}].
Seedling Growth.
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