Inorganic Chemistry
Article
pubs.acs.org/IC

Uranium(III) Redox Chemistry Assisted by a Hemilabile Bis(phenolate) Cyclam Ligand: Uranium−Nitrogen Multiple Bond Formation Comprising a *trans*-$\{RN{=}U(VI){=}NR\}^{2+}$ Complex

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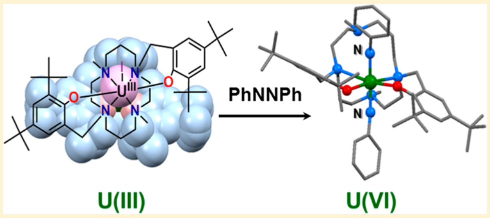
Ⓢ *Supporting Information*



ABSTRACT: A new monoiodide U(III) complex anchored on a hexadentate dianionic 1,4,8,11-tetraazacyclotetradecane-based bis(phenolate) ligand, $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]$ (**1**), was synthesized from the reaction of $[UI_3(THF)_4]$ (THF = tetrahydrofuran) and the respective potassium salt $K_2(^{tBu2}ArO)_2Me_2$-cyclam and structurally characterized. Reactivity of **1** toward one-, two-, and four-electron oxidants was studied to explore the reductive chemistry of this new U(III) complex. Complex **1** reacts with one-electron oxidizers, such as iodine and $TlBPh_4$, to form the seven-coordinate cationic uranium(IV) complexes $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I][X]$ (X = I (**2-I**), BPh_4 (**2-BPh$_4$**)). The new uranium(III) complex reacts with inorganic azides to yield the pseudohalide uranium(IV) complex $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)_2]$ (**4**) and the nitride-bridged diuranium(IV/IV) complex $[(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)U(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})]$ (**5**). Two equivalents of $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]$ (**1**) effect the four-electron reduction of 1 equiv of PhN=NPh to form the bis(imido) complex $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)_2]$ (**6**) and the U(IV) species **2-I**. Moreover, the hemilability of the hexadentate ancillary ligand $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ allows to perform the reductive cleavage of azobenzene with an unprecedented formation of a *trans*-bis(imido) complex. The complexes were characterized by NMR spectroscopy, and all the new uranium complexes were structurally authenticated by single-crystal X-ray diffraction.

■ INTRODUCTION

Controlling the metal coordination environment and reactivity through variation of the supporting ligand is a common theme in coordination and organometallic chemistry, including in uranium(III) chemistry.[1] Trivalent uranium complexes capable of performing one or more electron reactions at a single metal center are important for accessing high uranium oxidation states and in establishing the utility of these complexes for organic transformations and for the activation and functionalization of small molecules.[1−4] Moreover, in the last three decades trivalent uranium complexes have been used as precursors to access uranium-ligand multiple bond complexes,[5,6] comprising terminal mono(imido),[7−18] bis(imido),[19−27] nitride,[24,28−33] and even tris(imido)[34,35] uranium complexes, in which the metal varies in oxidation state from +4 to +6. One of the interests in these uranium species arises from the need for a better understanding of the nature of uranium-ligand bonding, especially in regard to the extent of 5f and 6d orbitals participation in bonding in the different oxidation states, which is also relevant to understand the chemical behavior of uranium in the nuclear fuel cycle and the environment.

The geometry, stability, and reactivity of the uranium(III) compounds are strongly affected by the choice of the charge, steric, and electronic properties of the ancillary ligands. A remarkable result was the isolation of the first terminal U≡N triple bond complex from the two-electron oxidation of a U(III) complex anchored on a sterically demanding trianionic triamidoamine ligand.[32]

We are interested in stabilizing U(III) cations with dianionic bis(phenolate) derivative ligands; however until now, salt metathesis reactions of uranium triiodide with potassium salts of bis(phenolate) derivatives only led to the isolation of uranium(IV) complexes, and the synthesis of stable uranium(III) complexes was not successful.[36,37]

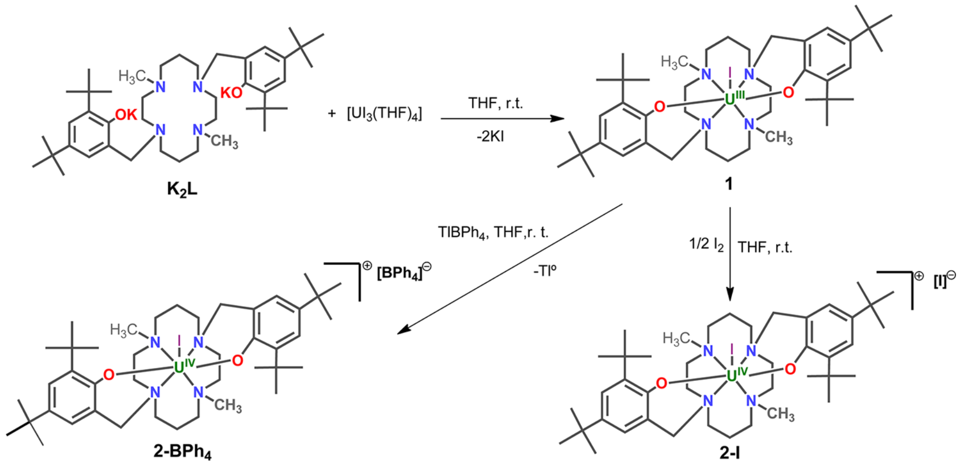
Recently, we demonstrated that the bulky and hemilabile dianionic tetraazamacrocyclic-based bis(phenolate) ligand $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ is adequate for the stabilization of yttrium(III) and lanthanide(III) complexes.[38] The flexibility displayed by the tetraamine macrocyclic frame leads to distinct bonding modes depending on the size of the rare earth metal ion. The ligand coordinated to the smaller Y(III) and Ln(III) cations in a κ^5 mode through the two O phenolate atoms and three N atoms of the amine macrocycle core, or in a κ^6 bonding mode, through the six donor atoms $O_2N_2N'_2$ of the chelate, to the larger Ln(III) metal ions.

Because of the chelating properties and hemilabile behavior of this new dianionic $\{O_2N_2N'_2\}^{2-}$ ligand with trivalent metals, we set out to explore its ability for stabilization of highly reactive trivalent uranium complexes that allow access to high-valent uranium complexes and uranium−nitrogen multiple

Received: July 10, 2015
Published: September 10, 2015

DOI: 10.1021/acs.inorgchem.5b01547
Inorg. Chem. 2015, 54, 9115−9126

Scheme 1. Synthesis of the Bis(phenolate) cyclam U(III) and U(IV) Complexes 1, 2-I, and 2-BPh$_4$



bond compounds, through electron-transfer processes. Herein, we describe the synthesis and structural characterization of a new U(III) complex and its use as an excellent precursor for the synthesis of neutral and cationic U(IV) complexes, as well for the synthesis of the first *trans*-bis(imido) U(VI) complex through the azobenzene reduction route and the structural characterization of a rare neutral nitride-bridged diuranium(IV/IV) complex.

■ RESULTS AND DISCUSSION

Bis(phenolate) cyclam U(III/IV) Iodide Complexes. The reaction of [UI$_3$(THF)$_4$] with 1 equiv of the dipotassium salt of the bis(phenolate) cyclam K$_2$(^{tBu2}ArO)$_2$Me$_2$-cyclam (K$_2$L) in tetrahydrofuran (THF) at room temperature after workup gave [U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}I] (**1**) as a violet solid in 79% yield (Scheme 1). In contrast with the previous studies of the acyclic diamine bis(phenolate) ligands R$_2$-salan^{2-} with [UI$_3$(THF)$_4$],[32] the dianionic macrocycle derivative allowed to isolate a trivalent uranium complex. The monoiodide uranium(III) compound **1** is soluble in THF and pyridine, presents a limited solubility in aromatic solvents (toluene and benzene), and is insoluble in *n*-hexane.

The ^{1}H NMR of **1** recorded in THF-d_8 shows 34 paramagnetically shifted and broadened resonances, ranging from 90.23 to −66.04 ppm (Figure S1 in the Supporting Information). Four relatively sharp signals at 8.50, 7.64, 6.48, and −8.33 ppm are assigned to the four *tert*-butyl groups of the phenolate arms of the ligand, and two resonances for the methyl NCH$_3$ protons of the ligand are observed at −49.44 and −66.07 ppm. The remaining 28 paramagnetically shifted and broadened resonances integrate to 1H each, corresponding to the aromatic protons, to the diastereotopic benzylic protons, and to the 20 methylenic protons of the tetraazamacrocycle core, for which the assignment remains equivocal. The NMR pattern is indicative of the presence of a C_1 symmetric compound in solution.

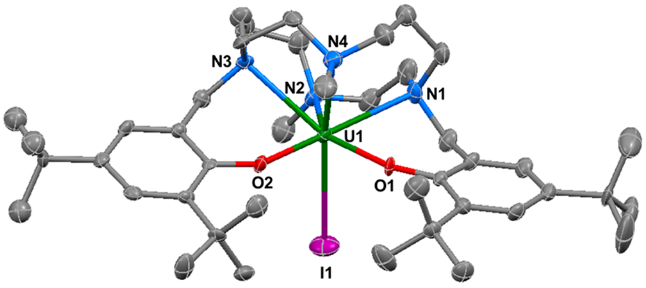


Figure 1. Solid-state molecular structure of [U(κ^6-{(^{tBu2}ArO)$_2$Me$_2$-cyclam})I] (**1**) in 1.2C$_6$D$_6$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 1 and 2-I

complex	**1**	**2-I**
U−O	2.263(3); 2.223(4)	2.109(2); 2.141(2)
U−N$_{benzyl}$	2.733(5); 2.794(5)	2.642(2); 2.624(3)
U−N$_{CH3}$	2.809(5); 2.721(5)	2.672(3); 2.829(3)
U−I	3.2089(5)	3.0854(3)
O−U−O	97.03(13)	94.16(8)
N$_{benzyl}$−U−N$_{benzyl}$	111.58(14)	112.78(8)
N$_{CH3}$−U−N$_{CH3}$	113.88(15)	114.04(8)
I−U−N$_{CH3(trans)}$	161.36(11)	164.63(6)
I−U−O	86.92(10); 85.48(9)	83.51(6); 82.08(6)

In addition to being characterized by ^{1}H NMR spectroscopy, compound [U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}I] (**1**) was characterized by single-crystal X-ray crystallography, and the asymmetric structure observed in the solid state is likely to be maintained in solution. Complex **1** crystallized as dark crystals from a saturated benzene-d_6 solution, in the monoclinic centrosymmetric space group $P2_1/c$, as a mononuclear U(III) complex with two benzene molecules in the lattice. The molecular structure of **1** (Figure 1 and Table 1) shows that the dianionic (^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-} ligand acts as a hexadentate chelator and gives rise to a N$_4$O$_2$ donor set. An additional iodine atom completes the seventh coordination position of the coordination polyhedron, which is best described as a distorted monocapped trigonal prism, as observed for lanthanum(III) and samarium(III) bis(phenolate) cyclam complexes [Ln{(^{tBu2}ArO)$_2$Me$_2$-cyclam}Cl].[38] The four nitrogen atoms of the tetraazamacrocycle core are nearly coplanar, with the uranium metal center sitting 1.521 Å above the average plane, and define one of the rectangular faces. The phenolate oxygen O1 is capping the quadrangular face formed by two amine nitrogens, one phenolate oxygen, and the iodine atom. The dihedral angle between the two triangular faces of the trigonal prism (N1, N2, I1; N3, N4, O2) is 6.22°. The phenolate groups are bound in a

DOI: 10.1021/acs.inorgchem.5b01547
Inorg. Chem. 2015, 54, 9115−9126

cis fashion with an O1−U−O2 angle of 97.03(13)° and with a dihedral angle between the two phenolate rings of 15.6(3)°. The two coordinating anionic phenolate oxygen atoms of the ancillary ligand and the iodide ion compensate the formal +3 charge of the uranium ion. The U−O bond distances for the phenolate groups in **1** of 2.223(4) and 2.263(3) Å are similar to those found in the trivalent complex $[U\{(^{tBu}ArO_3)tacn\}(NCCH_3)]$ (av. 2.26 Å).[8] The U−N bond distances range from 2.721(5) to 2.809(5) Å (av. 2.76(5) Å) with the longer U−N distance corresponding to the smallest of the I−U−N angles (84.5(1)°). These distances are slightly longer than the U−N(amine) distances observed in $[\{(^{tBu}ArO_3)tacn\}U(NCCH_3)]$ (av. 2.70 Å).[8] The U−I bond length (3.2089(5) Å) is in the upper range of the U(III)−I distances reported in the literature (3.0851(3)−3.2944(7) Å)[39−58] and is comparable with the U−I bond distances reported for $[U(Tp^{Me2})_2I]$ (3.2196(8),[44] 3.2121(2),[45] and 3.1936(4)[45] Å).

We first looked at the propensity of **1** to react with one-electron oxidants and to access stable U(IV) species. Treatment of a dark-violet solution of $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}I]$ (**1**) in THF with 0.5 equiv of elemental iodine resulted in a color change to green-yellow. The U(IV) cationic complex $[UI\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}]I$ (**2-I**; Scheme 1) was isolated from the reaction mixture as a green-yellow solid by centrifugation. After it recrystallized in acetonitrile, **2-I** was obtained in 67% yield. Treatment of **1** with 1 equiv of $TlBPh_4$ in THF also resulted in one-electron oxidation of the metal, with the formation of the cationic U(IV) species $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}I][BPh_4]$ (**2-BPh₄**) in good yield (Scheme 1). The coordination of six strong donor atoms makes the uranium(III) complex more reactive and contrasts with the reaction of $TlBPh_4$ with monoiodide U(III) complexes anchored on softer donor chelate ligands, in which the abstraction or replacement of the iodide atom occurs without oxidation of the metal center.[59−61] The formation of **2-BPh₄** points out the enhanced reactivity of **1**.

Compounds **2-I** and **2-BPh₄** are insoluble in benzene, toluene, and *n*-hexane, slightly soluble in THF, and soluble in the polar solvents acetonitrile and dichloromethane.

Compounds **2-I** and **2-BPh₄** were characterized by elemental analysis and ^1H NMR, and their structures were confirmed by single-crystal X-ray diffraction analysis. Green crystals of **2-I** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of **2-I** in acetonitrile, and $\mathbf{2\text{-}I}\cdot CH_3CN$ crystallized in the triclinic space group $P\bar{1}$. The refinement of the data revealed a solvent-free seven-coordinated mono(iodide) uranium(IV) cationic complex in a distorted capped trigonal prismatic geometry. The molecular structure and selected geometrical parameters of **2-I** are presented in Figure 2 and Table 1, respectively.

Like **1**, one of the quadrangular faces of the distorted monocapped trigonal prism is defined by the four nitrogen amines of the macrocycle, nearly coplanar, and with the uranium metal center sitting 1.472 Å above the average plane. The face defined by N2, N3, I1, and O1 is capped by the other phenolate oxygen atom O2. The dihedral angle between the two triangular faces of the trigonal prism (N3, N4, I1; N1, N2, O1) is smaller than in **1** (3.1°). The phenolate groups are bonding to the metal in a similar way to that in **1**, with an O1−U-2 angle of 94.2(1)° and with a dihedral angle between the two phenolate rings of 17.9(1)°.

Compound **2-BPh₄** was also analyzed by X-ray diffraction, although the poor quality of the crystals only allowed confirming unambiguously the molecular structure as the monocationic complex $[U\{(^{tBu2}OAr)_2Me_2\text{-cyclam}\}I][BPh_4]$ (Figure S2 in the Supporting Information).

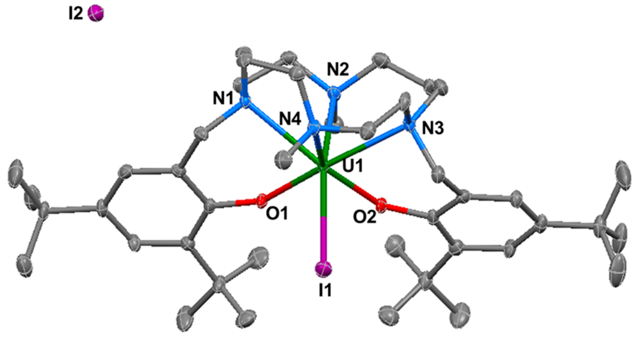


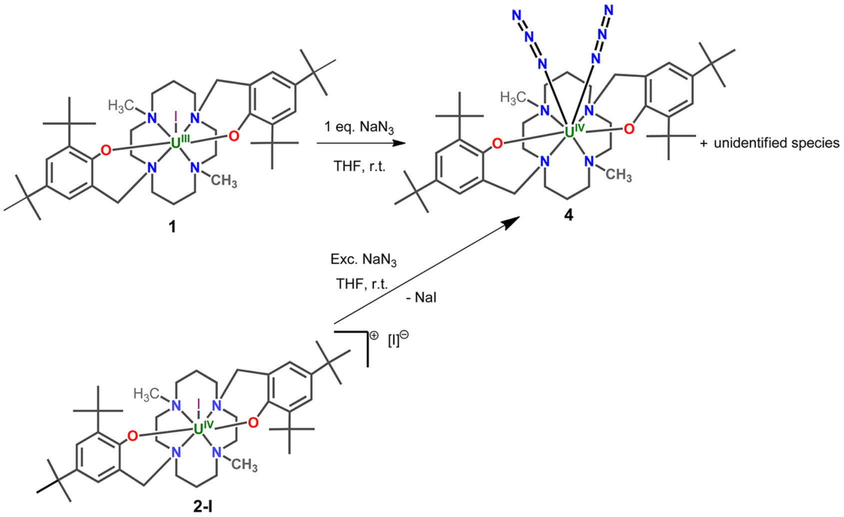
Figure 2. Solid-state molecular structure of $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]I$ (**2-I**) in $\mathbf{2\text{-}I}\cdot CH_3CN$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and cocrystallized solvent molecule are omitted for clarity.

In **2-I** the U−O bond distances of 2.109(2) and 2.141(2) Å are smaller than those observed for the U(III) precursor, as expected for a decrease of ca. 0.14 Å in ionic radii for U(IV),[62] and are within the values reported for other U(IV) bis(phenolate) derivatives.[36] The U−I bond length of 3.0854(3) Å is 0.12 Å smaller than in the neutral uranium(III) precursor **1** and can be compared with those observed in other tetravalent uranium iodide compounds.[14,36,63−65] The U−N distances are asymmetric, ranging from 2.624(3) to 2.829(3) Å, with the uranium distance to the nitrogen atom closer to the iodine atom, corresponding to the smallest of the I−U−N angles (80.5(1)°), being much longer than the other three U−N distances. The mean value of these three U−N distances (2.65(2) Å) is 0.11 Å smaller than the mean U−N value in **1** (2.76(5) Å), again in accord with the difference in ionic radii of U(III) and U(IV).

As expected, the ^1H NMR spectra of **2-I** and **2-BPh₄** are similar and present paramagnetic chemical shifts for the $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligand. However, the ^1H NMR chemical shifts and patterns are different in acetonitrile-d_3 and dichloromethane-d_2. The spectrum of **2-I** in dichloromethane-d_2 (Figure S3 in Supporting Information) at room temperature, 23 °C, displays 34 resonances ranging from 113.76 to −61.30 ppm, with four resonances at 10.03, 7.86, 1.25, and −10.60 ppm assignable to the *tert*-butyl protons of the two phenolate moieties, and two resonances at −39.42 and −61.30 ppm assignable to the two methyl NCH_3 protons of the macrocycle core. This reveals the presence of two non-equivalent phenolate arms of the complex in solution in agreement with the asymmetric solid-state structure for the cation $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}I]^+$.

In acetonitrile-d_3 solutions of **2-I** and **2-BPh₄**, the C_2 symmetry of the dianionic ligand $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ is restored (Figures S4 and S5 in Supporting Information), and the ^1H NMR spectra display 17 proton resonances that range from 173.9 to −88 ppm. The observation of one set of resonances for the aryloxide arms and the NCH_3 groups are indicative that the mutually *trans* substituents of the tetraazamacrocycle core are magnetically equivalent in solution. Two resonances can be identified at 9.93 and −8.71 ppm for **2-I**, assigned to the ^tBu groups, and one resonance at −13.79 ppm assigned to the two NCH_3 groups. In agreement with a C_2 symmetric compound, the spectra display additional 14 sharp

Scheme 2. Synthesis of the Uranium(IV) Bis(azide) Complex 4



resonances, integrating to two protons each, which are assigned to the aromatic and benzylic protons and to the methylenic protons of the macrocyclic ligand backbone. In the case of **2-BPh$_4$**, three additional signals are observed in the diamagnetic zone (7.11, 6.92, and 6.79 ppm), assigned to the aromatic protons of one $[BPh_4]^-$ anion. The C_2 symmetry observed in acetonitrile solution contrasts with the asymmetric molecular structure determined in the solid state. Following the ^1H NMR of **2-I** in dichloromethane-d_2 and acetonitrile-d_3 during two weeks, no evidence of decomposition was observed. The differences in the NMR spectra in these solvents strongly suggest that the U(IV) monocation species were converted into new compounds in acetonitrile. In view of the high polarity of acetonitrile and the high lability of the iodide, the most plausible hypothesis is the formation of dicationic species in acetonitrile solutions with coordination of solvent molecules.

In fact, the addition of 2 equiv of $TlBPh_4$ to **2-I** in acetonitrile led to the precipitation of the yellow TlI and to a green solution, which after slow evaporation resulted in a microcrystalline yellow-green solid identified by NMR and elemental analysis as $[U\{(Ar^{tBu2}OAr)_2Me_2\text{-cyclam}\}(CH_3CN)_2][BPh_4]_2$ (**3**). The ^1H NMR pattern and chemical shifts of the $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ signals of **3** in acetonitrile-d_3 are very close to those found in **2-I** and **2-BPh$_4$** in the same solvent (Figure S6 in the Supporting Information). The resonances due to the $[BPh_4]^-$ anions appear as three signals, in the diamagnetic region, with a relative $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}/[BPh_4]^-$ integration intensity of 1:2. This result suggests that the monocationic species **2-I** and **2-BPh$_4$** were converted into the dicationic compounds $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(CH_3CN)_2][I][X]$ (X = I, BPh_4) in acetonitrile solutions. Acetonitrile is known to induce the dissociation of the labile I^- from U−I complexes, favoring the formation of polycationic species;[63,66] such behavior was, for instance, observed for the U(IV) complex $[UCp^*{}_2I_2]$ in acetonitrile.[63]

Attempts to obtain single crystals adequate to X-ray diffraction analysis from acetonitrile solutions were not successful. However, a few crystals were grown from a dichloromethane-d_2 solution of **3**. While the quality of the structure of the U(IV) dication $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(CH_3CN)_2]^{2+}$ is not sufficient to discuss the metrical parameters, it clearly allowed to confirm the identity of **3** as a monomeric dicationic U(IV) complex and confirm the C_2 symmetry in the solid state (Figures S7 and S8 in the Supporting Information). The infrared spectrum of **3** also confirmed the coordination of acetonitrile molecules to the uranium center. One band at 2260 cm^{-1}, corresponding to the vibrational frequencies of bound nitriles, is observed. The increase of the nitrile CN stretching frequencies with respect to free acetonitrile (2254 cm^{-1}) reflects the σ-donor character of the acetonitrile ligand.[67]

Reactivity of 1 with MN_3 (M = Na, Cs). Alkali metal azides have been used as precursors for the synthesis of nitride complexes, including transition metals allowing the two-electron transfer $N_3^- + 2e \rightarrow N^{3-} + N_2$.[68,69] Their reactivity is particularly attractive for use in uranium chemistry as it offers a means of accessing uranium−nitrogen multiple bonds.[24,28,30,32] A relevant result was the synthesis of the first terminal U(V) nitride $[UN(Tren^{TIPS})][Na(12C4)_2]$ ($Tren^{TIPS}$ = $N(CH_2CH_2NSi^{iPr3})_3{}^{3-}$; 12C4 = crown ether 12-crown-4) from the reaction of the U(III) complex $[U(Tren^{TIPS})]$ with sodium azide.[32] Given our interest in metal−ligand multiple bond chemistry, we thought that the reaction of MN_3 with the new bis(phenolate) cyclam U(III) precursor **1** could give access to a U(V) nitride complex.

One equivalent of sodium azide was added to a solution of **1** in THF, resulting in a gradual color change from dark violet to olive oil green, over ∼18 h. Analysis of the ^1H NMR spectrum of the crude reaction mixture in tetrahydrofuran-d_8 revealed a combination of products but with the formation of a major one (Figure S9 in Supporting Information). After workup of the reaction residue, the one-electron oxidized bis(azido) species $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(N_3)_2]$ (**4**) was isolated as a pale green solid in 62% yield, instead of the intended U(V) nitride complex $[U(N)\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}]$. Complex **4** was alternatively synthesized in high yield by reaction of **2-I** with excess of NaN_3 (Scheme 2). The reaction of **1** with cesium azide in THF at room temperature also afforded **4** as the major product. Mazzanti and co-workers also observed that the reaction of an anionic U(III) siloxide complex with 1 equiv of CsN_3 in THF led to the formation of a mixture of compounds, including the U(IV) azide compound $[K(18c6)][U(N_3)(OSi(O^tBu)_3)_4]$,[24] although in this case it was also possible to isolate a few crystals of the di-μ-nitrido diuranium(V/V) complex $K[U(\mu\text{-}N)\{OSi(O^tBu)_3\}_3]_2$.[24] With our experimental conditions, no evidence of the formation of a bridged or terminal

U(V) nitride was observed. Nevertheless, the addition of 1 equiv of cesium azide to an NMR tube containing a solution of **1** in pyridine-d_5 at room temperature was accompanied by gas evolution, and after 3 d a few brown crystals were formed and analyzed by X-ray diffraction, showing that the nitride-bridged diuranium(IV/IV) complex $[(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)U(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})]$ (**5**) was formed. The in situ ^1H NMR spectrum of the reaction mixture revealed several resonances of difficult interpretation and attempts to scale up and prepare **5** pure failed, preventing further characterization of this species.

Complex **4** is soluble in THF, acetonitrile, and pyridine and was fully characterized, including by ^1H NMR, IR, elemental CHN, and X-ray crystallographic analyses. The ^1H NMR spectrum of **4** in acetonitrile-d_3 solution (or THF-d_8: see Experimental) shows 17 paramagnetically shifted and relatively sharp resonance signals, ranging from 179.76 to −99.50 ppm, suggestive of C_2 symmetry, and with a pattern for the chelating ligand very similar to those observed in the NMR spectra of **2-I** and **2-BPh₄** in acetonitrile-d_3. Thus, three signals are observed at 13.02, −10.21, and −8.72 ppm, in a 9:9:3 ratio, assignable to two ^{t}Bu group resonances and to one methyl NCH_3 group resonance of the bis(phenolate) cyclam ligand, respectively, and 14 resonances for the macrocycle core, benzylic, and aromatic protons of the ligand.

The infrared spectrum of **4** is consistent with the coordination of azide ligands, as a strong stretching band is observed at 2068 cm^{-1}, which falls within the range observed for other uranium(IV) azido complexes (2055−2100 cm^{-1}).[8,11,16,70−73]

The solid structure of **4** was unambiguously established by X-ray diffraction analysis of green crystals obtained from a concentrated solution of **4** in acetonitrile-d_3 (or in non-deuterated acetonitrile; Table 2 and Figure 3). The bis(azide) uranium complex crystallizes with one acetonitrile in the lattice, in the triclinic space group $P\bar{1}$, and the molecular structure shows that the uranium bis(azide) is a mononuclear complex and exhibits a distorted square antiprismatic geometry, with the uranium center ligated by the $\kappa^6\text{-}O_2N_2N'_2$ donor ligand and two azide ligands. The almost coplanar four nitrogen atoms of the macrocycle define one of the quadrangular faces, and the other one is defined by the two phenolate oxygens and the two coordinated azide nitrogens. Although the crystallographic structure results in the absence of symmetry, the arrangement of the donor atoms around uranium approximates C_2 symmetry, which is consistent with the solution NMR data of **4**. The $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligand coordinates to the U(IV) center with an O−U−O angle of 126.74(7)°, with average U−O, U−N, and U−N′ bond distances of 2.129(6), 2.813(4), and 2.785(11) Å, respectively, and the phenolate rings are arranged in the structure with a dihedral angle of 77.4(1)°.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 4 and 5

		5	
	4	**U1**	**U2**
U−O	2.125(2); 2.133(2)	2.194(3); 2.251(3)	2.206(3); 2.196(3)
$U-N_{benzyl}$	2.811(2); 2.815(2)	2.716(3)	2.703(4); 2.685(3)
$U-N_{CH3}$	2.776(2); 2.794(2)	2.727(3)	2.771(4)
$U-N_{azide}$	2.361(2); 2.407(2)	2.348(4)	
$U-N_{nitride}$		2.086(3)	2.035(3)
O−U−O	126.74(7)	149.43(10)	97.96(10)
$N_{benzyl}-U-N_{benzyl}$	116.12(6)		104.50(10)
$N_{CH3}-U-N_{CH3}$	98.26(7)		
$N_{azide}-U-N_{azide}$	125.40(8)		
$N_{azide}-U-O$	78.85(8); 78.27(8); 77.64(8); 77.79(8)	79.44(12); 90.67(12)	

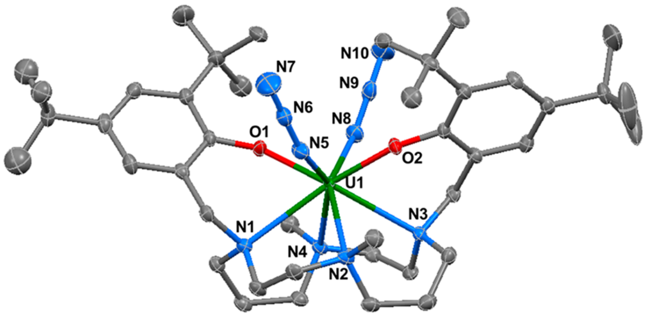


Figure 3. Solid-state molecular structure of $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)_2]$ (**4**) in **4**·CH_3CN with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and cocrystallized solvent molecule are omitted for clarity.

The two azide ligands are bent to the uranium center with $U-N_\alpha-N_\beta$ bond angles of 150.9(5)° (U1−N5−N6) and 138.5(5)° (U1−N8−N9). The average $U-N_{azide}$ bond length in **4** of 2.384(2) Å falls within the range found in other structurally characterized uranium(IV) azido complexes with terminal coordination mode (2.219(6)−2.562(12) Å)[70−78] and is comparable with the value found in the eight-coordinate compound $[U(N_3)_4(py)_4]$ (2.314(3) Å).[73] The two azide moieties are nearly linear ($N_\alpha-N_\beta-N\gamma$ = 178.9(4)° and 178.0(3)°), and the $N_\alpha-N_\beta$ and $N_\beta-N\gamma$ distances are slightly different (N5−N6: 1.188(3) Å and N6−N7: 1.151(4) Å; N8−N9: 1.197(3) Å and N9−N10: 1.150(4) Å), indicative of slight coordination-induced activation of the azide moiety.[78]

The structural characterization of complexes with a monobridged nitride ligand and two uranium U(IV) centers remains rare, having also been achieved from the reduction of NaN_3 with homoleptic U(III) amide complexes.[24,30,31] However, to the best of our knowledge, compound **5** is an unprecedented neutral bimetallic uranium(IV) nitride complex possessing an almost linear $U(IV)-N^{3-}-U(IV)$ motif (Figure 4).

The overall neutral charge of **5** is consistent with a formal +4 oxidation state for the two uranium centers that is balanced by the bridging N^{3-}, two $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligands, and one N_3^- ligand. The presence of a bridging O^{2-} cannot be ruled out; in this case, one of the uranium centers would be trivalent (U2) and the other tetravalent (U1). However, the formation of a mixed-valent U(III)/U(IV) complex by reaction with residual oxygen is not expected, since U(III) complexes are highly reactive with oxygen. When the X-ray refinement was tried with a bridging O^{2-}, the bond distances were similar to the ones obtained with N^{3-}, but the checkCIF report presents an alert indicating that the oxygen could be wrongly assigned (see Supporting Information). Moreover, the two uranium centers present the same coordination number (6), and if we analyze the average U−O(phenolate) distances, the values are

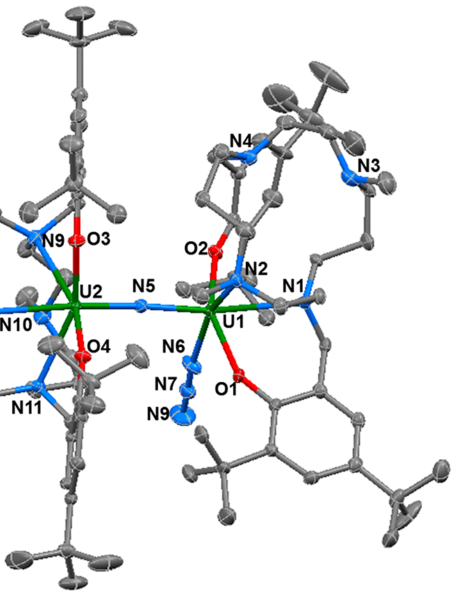


Figure 4. Solid-state molecular structure of $[(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})(N_3)U(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})]$ (5) in $5\cdot 3C_5D_5N$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

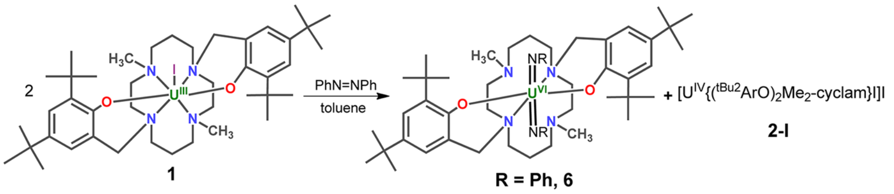
very similar (U1: 2.22(3) and U2: 2.20(1) Å, see Table 2), consistent with the presence of uranium centers in the same oxidation state.

The two uranium atoms are ligated by a bridging N^{3-} ligand in a nearly linear mode (U1−N−U2 angle of 173.2(2)°), and the coordination environments around the two U(IV) cations are different resulting in an asymmetric structure. While U1 is coordinated to two amine nitrogens and two phenolate oxygens of the $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligand, one azide ligand and the N^{3-}bridged nitride ligand, with a $U{-}N_{nitride}$ bond distance of 2.086(3) Å, in a distorted octahedral geometry, U2 is coordinated to three amine nitrogens and two phenolate oxygens of the ancillary ligand and the nitride ligand, with a $U{-}N_{nitride}$ bond distance of 2.035(3) Å, also in a distorted octahedral geometry. The slightly different $U{-}N_{nitride}$ bond lengths are suggestive of partially localized U1−N═U2 bonding, such as observed in $[Na(DME)_2(TMEDA)][(NR_2)_2U(\mu\text{-}N)U(CH_2SiMe_2NR)(NR_2)_2]$ (1.95(1) and 2.12(1) Å),[30] and differ from the almost equivalent $U{-}N_{nitride}$ bonds observed in the complex featuring a linear U(IV)−N−U(IV) motif $[N(n\text{-}Bu)_4][(\mu\text{-}N)(U\{N(t\text{-}Bu)Ar\}_3)_2]$ (2.080(4) and 2.077(4) Å).[31] The distance U···U between the two cation units is 4.114 Å. The ligand $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ coordinates to the U1 cation in $\kappa^4\text{-}O_2NN'$ coordination mode, with an O−U−O angle of 149.43(10)° and a dihedral angle between the two phenolate rings of 63.6(1)°, and through one NCH_2Ar and one NCH_3 of the tetraazamacrocycle core forming a five-membered $\{U{-}N{-}(CH_2)_2{-}N\}$ metallacycle. The nitride ligand and the $N1CH_2Ar$ nitrogen amine are found in a *trans* arrangement (N1−U1−N5 angle of 151.94(11)°). In the second moiety of the dinuclear species **5**, the chelating ligand coordinates to the U2 center in $\kappa^5\text{-}O_2N_2N'$ mode with a smaller O−U−O bond angle (97.96(10)°) and a dihedral angle between the two phenolate rings of 8.0(2)° (almost coplanar). The nitride ligand lies in the apical position in opposition with the $N12CH_3$ nitrogen amine, with the N5−U−N12 bond angle much closer to linearity than in the U1 center (166.70(11)°), and in agreement with the partially localized U1−N═U2 bonding. The distinct coordination modes and conformations exhibited by the $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ in the dinuclear complex **5** highlights the flexibility of this chelating ligand to adapt to different coordination environments. The mean values of the U−O and the U−N bond distances for both uranium centers of the bimetallic complex **5** are similar (U1−O 2.22(3), U2−O 2.20(1), U1−N 2.72(1), and U2−N 2.72(5) Å). The $U1{-}N_{azide}$ bond distance of 2.348(4) is slightly shorter than the mean value found for the eight-coordinated bis(azide) U(IV) compound **4** (2.384(2) Å) but still in the range found for other U(IV) azide complexes.[70−78] While azido ligands typically adopt bent coordination orientations as in the case of **4**, the azido ligand in **5** adopts a practically linear $U{-}N_\alpha{-}N_\beta{-}N_\gamma$ arrangement with U1−N6−N7 and N6−N7−N8 angles of 172.4(3)° and of 177.7(5)°, respectively. The N−N−N angle and distances (N6−N7 1.175(5) and N7−N8 1.158(5) Å) are more identical to the free azide anion in 1,1-dimethylhydrazinium azide.[79]

The formation of the linear bridged nitride U(IV) complex $[(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})(N_3)U(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\})]$ could be postulated to arise from the formation of a U(III) azido intermediate $[U\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\}U(N_3)]$ followed by two-electron reduction of one azide ligand by two U(III) centers, as hypothesized for other nitride-bridged diuranium(IV/IV) complexes,[30,31] The isolation of a few crystals of **5** is an encouraging result and suggests that it might be possible to identify the adequate experimental conditions for synthesizing dinuclear and mononuclear uranium nitride species using dianionic bis(phenolate) cyclam derivatives as supporting ligands.

Reactivity of 1 with Azobenzene. The reaction with azobenzene was used to probe the ability of **1** to undergo U−N multiple-bond formation with uranium in higher oxidation states. The addition of 1 equiv of azobenzene to 2 equiv of $[U\{(^{tBu2}ArO)_2Me_2\text{-}cyclam\}I]$ (**1**) in toluene, after 2 h of stirring at room temperature, resulted in the four-electron cleavage of PhN═NPh, with formation of the soluble bis-imido uranium(VI) complex $[U\{(^{tBu2}OAr)_2Me_2\text{-}cyclam\}(NPh)_2]$ (**6**) and of the insoluble U(IV) cation **2-I** in 1:1 ratio (Scheme 3). The different solubilities of **6** and **2-I** allowed to easily isolate

Scheme 3. Synthesis of the *trans*-Bis(imido)uranium(VI) Complex 6



both compounds, after workup, with 75% and 60% yields, respectively.

Complete cleavage of azobenzene to NPh^{2-} imido ligands requires either a metal ion capable of transferring four electrons, such as W(II),[80] the additional use of a redox-active coordinating ligand,[81] or addition of multiple equivalents of the reducing species. Burns and co-workers proposed that 2 equiv of the trivalent uranium complex $[UCp^*_2Cl_2Na]$ are necessary to reduce azobenzene to make a mixture of the uranium(VI) bis(imido) $[UCp^*_2(NPh)_2]$ and the uranium(IV) complex $[UCp^*_2Cl_2]$.[19] The proposed mechanism involves two-electron transfer with formation of an unstable U(V) complex $[UCp^*_2Cl(\eta^2\text{-PhNNPh})]$, with a $PhNNPh^{2-}$ ligand, followed by comproportionation of the U(V) intermediate with the second equivalent of the U(III) compound to yield the unstable U(IV) compound $[UCp^*_2(\eta^2\text{-PhNNPh})]$ and the bis-chloride $[UCp^*_2Cl_2]$. Then the uranium oxidation state in the η^2-azobenzene U(IV) species changes from +4 to +6 by two-electron reduction of the $PhNNPh^{2-}$ ligand with NN bond cleavage and formation of the bis(imido) uranium(VI) complex.[19,82,83] Although to our knowledge the formation of uranium species with the dianionic azobenzene form $PhNNPh^{2-}$ has not been reported until now, the mechanism proposed by the authors can be invoked for the formation of **6** and **2-I** (Scheme S1 in Supporting Information). Nevertheless, the hypothesis of formation of the uranium(VI) bis(imido) $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(NPh)_2]$ (**6**) and the U(IV) $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}I]I$ (**2-I**) from the disproportionation of an unstable U(V) compound $[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}I(PhNNPh)]$ cannot be excluded.

The ^1H NMR spectrum of **6** is characteristic of a diamagnetic compound (Figure S11 in Supporting Information), as expected for an f^0 uranium compound, and displays resonances for the ligand $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ and phenyl imido groups in an integration ratio of 1:2. Only one set of phenyl imido resonances is observed for the ortho, meta, and para proton resonances, located at 5.04, 6.97, and 5.46 ppm, respectively. This pattern is consistent with a C_2 symmetric compound in solution and indicative of free rotation of the two equivalent imido phenyl rings. This symmetry is also evidenced by the equivalent phenolate arm proton resonances. Two resonances are observed at 1.83 and 1.60 ppm, attributed to the ^tBu groups, and an AB system is seen centered at 6.48 and 3.79 ppm assigned to the diastereotopic benzylic protons. The $^{13}C\{^1H\}$ NMR spectrum (Figure S12 in Supporting Information) presents only one set of four resonances for the imido phenyl carbons, one set of resonances for the phenolate arms and five carbon resonances for the tetraazamacrocycle core, confirming all the conclusions drawn from the ^1H NMR spectrum analysis.

The IR spectrum of the bis(imido) complex **6** shows one strong vibration at 1259 cm^{-1}, which is in the region expected for a *trans* imido complex.[84,26]

Crystallization of **6** by slow evaporation of a toluene/diethyl ether solution and subsequent analysis by X-ray diffraction further confirmed the formation of the bis(imido) U(VI) complex (Figure 5).

Complex **6** crystallizes in the triclinic space group $P\bar{1}$ and features one monomeric molecule in the asymmetric unit with a distorted octahedral geometry around the uranium ion. The axial positions are occupied by two coordinated phenyl imido ligands in a *trans* arrangement and with short $U{-}N_{imido}$ bonds (1.895(2) and 1.907(2) Å), consistent with uranium−nitrogen multiple-bonding character. These distances fall in the range found for bis(imido) U(VI) complexes reported in the literature (1.840(4)−1.946(4) Å),[19,24−26,85−91] and are slightly shorter than those observed for the *cis*-bis(imido)-$[UCp^*_2(NPh)_2]$ (1.952(7) Å),[91] being more close to those found in the *trans*-bis(imido)$[U(NPh)_2I_2(THF)_3]$ (1.866(2) and 1.859(2) Å), reported by Boncella and co-workers.[25,26] The N5−U−N6 angle of 172.95(8)° is nearly linear. The *trans*-$\{RN{=}U(VI){=}NR\}^{2+}$ core in complex **6** can be considered as a nitrogen analogue of the uranyl ion UO_2^{2+}.

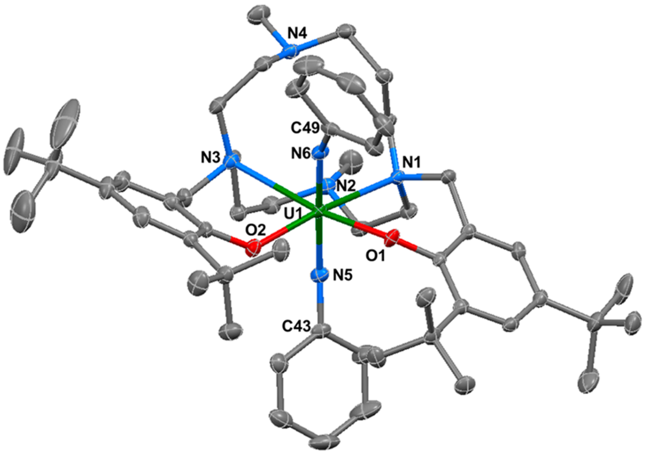


Figure 5. Solid-state molecular structure of $[U(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(NPh)_2]$ (**6**) with thermal elipsoides drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): U1−N5 1.895(2), U1−N6 1.907(2), U1−O1 2.158(2), U1−O2 2.161 (2), U1−N1 2.740(2), U1−N3 2.729(2), N5−U−N6 172.95(8), C43−N5−U1 154.9(2), C49−N6−U1 153.7(2), O1−U−N3 171.32(6), O2−U−N1 169.66(6), O2−U−O1 105.35(6).

The $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligand adopts a κ^4 coordination mode, with two amine nitrogens of the tetraazamacrocycle and the two phenolate oxygens as coordinating atoms, with an angle O−U−O of 105.4(1)°, lying in the equatorial plane of the octahedron (mean deviation from the plane of 0.19 Å). The average U−O distance of 2.159(3) Å is smaller than the corresponding distances in the uranyl(VI) pentagonal bipyramidal complex $[UO_2(^tBu_2\text{-salan})(py)]$ (2.22(2) Å), as expected for a less coordinated metal center.[92] However, the average U−N bond distance of 2.734(7) Å in our macrocycle derivative **6** is much longer than in the uranyl salan-$^tBu_2$ complex (2.645(9)Å).[92]

For the formation of the *trans*-bis(imido)$[U\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\}(NPh)_2]$ (**6**), 1 equiv of the U(III) complex **1** performs a three-electron reduction of the azobenzene, assisted by one additional equivalent of **1** as a sacrificial one-electron reductant. Complete cleavage of azobenzene to form bis(imido) uranium(VI) complexes has been achieved with cyclopentadienyl uranium(III) complexes as reductants,[19−23] however, and most likely due to steric pressure imposed by the cyclopentadienyl rings, only led to the *cis*-bis(imido) species $[UCp^*_2(NPh)_2]$. The $(^{tBu2}ArO)_2Me_2\text{-cyclam}^{2-}$ ligand flexibility and the weak interactions of the amines with the metal center permit the uncoordination of two nitrogen atoms to accommodate the imido groups in a *trans* configuration and form the first *trans*-bis(imido)uranium(VI) complex from the four-electron reduction of azobenzene. Few examples of U(VI) complexes presenting the *trans* imido configuration $\{RN{=}U{=}$

NR}$^{2+}$ have been isolated using alternative oxidative or metathetic synthetic methods,[24−26,34,85−91] including two complexes prepared from the reduction of organic azides with low-valent uranium complexes.[24,34]

■ CONCLUSIONS

The dianionic hexadentate 1,4,8,11-tetraazacyclotetradecane-based bis(phenolate) ligand $(^{tBu2}ArO)_2Me_2$-cyclam^{2-} allowed to isolate an unprecedented stable monoiodide U(III) complex anchored on a polyamine bis(phenolate) ligand by salt metathesis reaction with $[UI_3(THF)_4]$.

The enhanced reactivity of the new complex $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I]$ as reductant allowed to synthesize and structurally characterize a series of new uranium species in different oxidation states. The one-electron oxidation of the new monohalide U(III) complex with molecular iodine or $TlBPh_4$ led to the formation of the monoiodide cationic U(IV) species $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})I][X]$ (X = I, BPh_4). Reaction with inorganic azides permitted to characterize by single-crystal X-ray diffraction the bis(azide) $[U(\kappa^6\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)_2]$ complex and the unprecedented neutral monobridged nitride U(IV) complex $[(\kappa^4\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})(N_3)U(\mu\text{-}N)U(\kappa^5\text{-}\{(^{tBu2}ArO)_2Me_2\text{-cyclam}\})]$. Utilizing the reactive nature of the new U(III) compound and taking advantage of the hemilabile behavior of the bis(phenolate) cyclam ligand, the four-electron cleavage of the N═N bond of azobenzene occurred to generate a rare linear *trans*-bis(imido) uranium complex, {PhN═U(VI)═NPh}$^{2+}$, supported by a macrocycle derivative ligand and unprecedented using the azobenzene reduction route.

To summarize, we demonstrated that the bis(phenolate) tetraazamacrocycle derivative provides a new example of effective supporting ligand for stabilizing uranium species in the +3, +4, and +6 oxidation states. Moreover, the reaction with azobenzene was used to probe the ability of the new U(III) bis(phenolate) cyclam to undergo high-valent uranium−nitrogen multiple-bond formation. It is anticipated that these first reactivity studies will open new avenues in the study of U−E multiple bonds.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed under an inert atmosphere of nitrogen with the rigorous exclusion of oxygen and water (<2 ppm) using standard Schlenk techniques or a nitrogen-filled glovebox.

THF, toluene, and *n*-hexane were predried using 4 Å molecular sieves, distilled from Na alloy under nitrogen, and deoxygenated immediately prior use. THF-d_8, benzene-d_6, and toluene-d_8 were dried over sodium-benzophenone. Acetonitrile, acetonitrile-d_3, and dichloromethane-d_2 were distilled from P_2O_5 under nitrogen and maintained in contact with molecular sieves several days before use.

$[UI_3(THF)_4]$[93] and $H_2(^{tBu2}ArO)_2Me_2$-cyclam[38] were prepared as previously reported. $K_2(^{tBu2}ArO)_2Me_2$-cyclam was prepared upon reaction of $H_2(^{tBu2}ArO)_2Me_2$-cyclam with excess of KH in THF. $TlBPh_4$ was precipitated as a white solid by mixing aqueous solutions of $NaBPh_4$ and $TlNO_3$. The compound was then washed with hot water followed by *n*-hexane and dried under vacuum for 48 h. Molecular iodine and azobenzene were sublimed prior to use. All other reagents were purchased from commercial suppliers and dried in vacuum during 24 h. ^1H and ^{13}C NMR spectra were recorded in a Varian 300 MHz or in Bruker AVANCE 300 or 400 MHz. ^1H and ^{13}C chemical shifts were referenced to external $SiMe_4$ using the residual proton or carbon of the solvents as internal standards. IR spectra were recorded as mineral oil mulls between CsBr round cell windows on a Bruker Tensor 27 spectrophotometer. CHN elemental analyses were performed using a CE Instruments EA1110 automatic analyzer.

Synthesis of $[U\{(^{tBu2}ArO)_2Me_2cyclam\}I]$, ***1.*** A THF solution (15 mL) of $K_2(^{tBu2}ArO)_2Me_2$-cyclam (669 mg, 0.902 mmol) was added to a blue solution of $[UI_3(THF)_4]$ (818 mg, 0.902 mmol) in THF (15 mL), and the mixture was stirred overnight at room temperature. After centrifugation to remove the KI, the supernatant was decanted off, and the solvent was removed under reduced pressure. The product was extracted with toluene and recrystallized from a concentrated toluene solution layered with *n*-hexane. The resulting solid was washed with *n*-hexane, and **1** was isolated as a dark-violet crystalline solid in 79% yield (731 mg, 0.711 mmol). Single crystals suitable for X-ray analysis were grown from a benzene-d_6 solution. Analysis for $C_{42}H_{70}IN_4O_2U$: Calcd C, 49.07; H, 6.86; N, 5.45; Found C, 48.86; H, 6.91; N, 5.47.

^1H NMR (300 MHz, THF-d_8, 23 °C): δ (ppm) 90.23 (1H), 83.08 (1H), 52.87 (1H), 40.07 (1H), 39.18 (1H), 35.34 (1H), 33.84 (1H), 29.23 (1H), 27.22 (1H), 22.78 (1H), 21.56 (1H), 13.30 (1H), 12.48 (1H), 8.50 (9H, $C(CH_3)_3$), 7.64 (1H), 7.29 (9H, $C(CH_3)_3$), 6.48 (9H, $C(CH_3)_3$), −0.08 (1H), −0.98 (1H), −2.48 (1H), −4.48 (1H), −5.62 (1H), −7.53 (1H), −8.33 (9H, $C(CH_3)_3$), −9.39 (1H), −10.97 (1H), −14.76 (1H), −22.67 (1H), −28.46 (1H), −33.58 (1H), −34.70 (1H), −41.38 (1H), −49.44 (3H, NCH_3), −66.07 (3H, NCH_3).

^1H NMR (300 MHz, C_6D_6, 23 °C): δ (ppm) 88.21(1H), 81.10 (1H), 50.83 (1H), 36.56 (1H), 36.25 (1H), 31.24 (1H), 29.07 (1H), 28.49 (1H), 26.24 (1H), 22.37 (1H), 20.38 (1H), 13.01 (2H), 11.49 (1H), 8.38 (9H, $C(CH_3)_3$), 6.76 (9H, $C(CH_3)_3$), 6.63 (9H, $C(CH_3)_3$), 5.80 (2H), −3.15 (2H), −5.92 (1H), −6.76 (1H), −7.76 (9H, $C(CH_3)_3$), −10.86 (3H), −13.51 (1H), −16.46 (1H), −24.97 (1H), −28.47 (1H), −34.59 (1H), −36.09 (1H), −42.38 (1H), −48.77 (3H, NCH_3), −66.39 (3H, NCH_3).

*Synthesis of $[U\{(^{tBu2}ArO_2)_2Me_2\text{-cyclam})\}I]I$ (**2-I**).* To a stirring violet solution of **1** (0.150 g, 0.146 mmol) in THF (10 mL) was added a solution of 0.5 equiv of I_2 (0.018 g, 0.073 mmol) in THF (1 mL). After it was stirred for 1 h at room temperature, the reaction mixture turned yellow-green with precipitation of a yellow-green solid. The solid was separated by centrifugation, washed with THF and *n*-hexane, and vacuum-dried. Compound **2-I** was isolated as a crystalline green solid in 67% yield (0.113 g, 0.098 mmol) after recrystallization by slow evaporation of an acetonitrile solution. X-ray quality single crystals were obtained similarly. Analysis for $C_{42}H_{70}I_2N_4O_2U.CH_3CN$: Calcd C, 44.19; H, 6.15; N, 5.86; Found: C, 44.37; H, 6.41; N, 5.73.

^1H NMR (300 MHz, acetonitrile-d_3, 23 °C): δ (ppm) 173.40 (2H), 67.30 (2H), 47.30 (2H), 35.61 (2H), 24.30 (2H), 23.30 (2H), 11.3 (2H), 9.93 (18H), 7.44 (2H), 6.72 (2H), −8.71 (18H, $C(CH_3)_3$), −13.79 (6H, NCH_3), −36.94 (2H), −39.86 (2H), −47.57 (2H), −86.54 (2H), −87.66 (2H).

^1H NMR (300 MHz, dichloromethane-d_2, 23 °C): δ (ppm) 113.76(1H), 96.79 (1H), 74.65 (1H), 68.34 (1H), 53.49 (1H), 48.21 (1H), 45.61 (1H), 35.13 (1H), 34.37 (1H), 30.69 (1H), 24.66 (1H), 22.06 (1H), 15.73 (1H), 14.54 (1H), 10.03 (9H, $C(CH_3)_3$), 9.21 (1H), 7.86 (9H, $C(CH_3)_3$), 5.64 (1H), 4.62 (1H), 1.25 (9H, $C(CH_3)_3$), −5.00 (1H), −6.83 (1H), −10.60 (9H, $C(CH_3)_3$), −10.80 (1H), −14.97 (1H), −18.20 (1H), −19.81 (1H), −21.97 (1H), −23.38 (1H), −25.52 (1H), −32.20 (1H), −39.41 (3H, NCH_3), −53.60 (1H), −61.30 (3H, NCH_3).

*Synthesis of $[U\{(^{tBu2}ArO_2)_2Me_2\text{-cyclam})\}I][BPh_4]$ (**2-BPh$_4$**).* To a stirring solution of **1** (0.215 g, 0.209 mmol) in THF (10 mL) was added $TlBPh_4$ (0.109 g, 0.209 mmol). After it was stirred during 2 h at room temperature, a dark-green solid precipitated and was separated by centrifugation and vacuum-dried. The solid was extracted with acetonitrile and separated from a gray solid by centrifugation. The solvent was then removed in vacuum to give **2-BPh$_4$** as a green microcrystalline powder (0.210 g, 0.156 mmol, 75%). Crystals were obtained by slow concentration of a CH_3CN/pyridine solution of **2-BPh$_4$**. Analysis for $C_{66}H_{90}BIN_4O_2U$: Calcd C, 58.84; H, 6.73; N, 4.16; Found: C, 58.23; H, 6.82; N, 4.27. The small differences between the calculated and the experimental values can be assigned to the presence of residual Tl.

Table 3. Crystal Data and Structure Refinement of 1, 2-I, 4, 5, and 6[a]

	$1\cdot C_6D_6$	$2\text{-I}\cdot CH_3CN$	$4\cdot CH_3CN$	$5\cdot 3(C_5H_5N)$	6
empirical formula	$C_{54}H_{82}IN_4O_2U$	$C_{44}H_{73}I_2N_5O_2U$	$C_{44}H_{73}N_{11}O_2U$	$C_{99}H_{155}N_{15}O_4U_2$	$C_{54}H_{80}N_6O_2U$
formula weight	1184.17	1195.90	1026.16	2095.44	1083.27
cryst system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.7160(5)	12.8034(4)	10.1487(2)	14.9305(6)	13.3031(2)
b[Å]	38.9963(18)	12.8473(3)	13.5956(2)	17.8268(7)	13.9263(2)
c [Å]	9.9102(4)	16.0756(4)	19.218(4)	18.5796(8)	16.7844(3)
α [deg]	90	95.0382(7)	72.143(2)	91.177(2)	103.1520(10)
β [deg]	96.258(2)	98.0529(7)	75.293(2)	97.279(2)	109.5310(10)
γ [deg]	90	111.8370(8)	69.7870(10)	95.629(2)	106.6290(10)
V, [Å^3]	5269.1(4)	2401.97(11)	2335.8(5)	4879.0(3)	2622.03(7)
Z	4	2	2	2	2
calculated density (mg/m^{-3})	1.493	1.654	1.459	1.426	1.372
μ (mm^{-1})	3.708	4.702	3.522	3.372	3.139
T_{min}/T_{max}	0.6646/0.9295	0.2549/0.6506	0.3332/0.7196	0.4311/0.7742	0.3028/0.6019
$F(000)$	2380	1172	1044	2140	1108
θ_{max} (deg)	25.68	25.68	25.68	25.68	25.68
reflections collected	26 863	16 988	32 494	53 957	35 967
unique refl (R_{int})	9952 (0.0819)	8986 (0.0271)	8849 (0.0359)	18446 (0.0502)	9668 (0.0275)
$R_1[I > 2\sigma(I)]$	0.0462	0.0231	0.0223	0.0338	0.0198
wR_2 (all data)	0.0731	0.0558	0.0531	0.0784	0.0493
parameters	600	502	564	1072	580
GOF on F^2	0.914	1.046	1.041	1.025	1.059
largest diff peak, hole, e Å^{-3}	0.839, −0.772	0.736, −0.664	0.804, −0.581	1.221, −0.744	1.524, −0.855

[a] Crystallographic data for **1**, **2-I**, **4**, **5**, and **6** were deposited with the Cambridge Crystallographic Data Centre with Nos. CCDC-1411625 and CCDC-1411628−31.

^{1}H NMR (300 MHz, acetonitrile-d_3, 23 °C): δ (ppm) 173.87 (2H), 67.43 (2H), 47.33 (2H), 35.74 (2H), 24.37 (2H), 23.26 (2H), 11.31 (2H), 10.01 (18H, C(CH_3)$_3$), 7.37 (2H), 7.11 (8H, BPh$_4$), 6.92 (8H, t, BPh$_4$), 6.79 (4H, t, BPh$_4$), 6.69 (2H), −8.73 (18H, C(CH_3)$_3$), −13.85 (6H, NCH_3), −37.09 (2H), −39.99 (2H), −47.77 (2H), −86.78 (2H), −87.98 (2H).

*Synthesis of [U{(^{tBu2}ArO$_2$)$_2$Me$_2$-cyclam}(CH$_3$CN)$_2$][BPh$_4$]$_2$ (**3**).* To a stirring solution of **2-I** (80 mg, 0.0693 mmol) in 10 mL of acetonitrile was added 2 equiv of TlBPh$_4$ (73 mg, 0.139 mmol). After it was stirred at room temperature during 2 h, a yellow precipitate of TlI was separated by centrifugation from a yellow-green solution. The solvent of the supernatant was removed in vacuo, and the solid was dissolved in 4 mL of acetonitrile. Slow evaporation of the yellow-green solution resulted in the precipitation of a microcrystalline green solid, which was collected and dried in vacuo, yielding **3** in 53% yield (60 mg, 0.0370 mmol). Analysis for $C_{94}H_{116}B_2N_6O_2U$: Calcd C, 69.62; H, 7.21; N, 5.18; Found: C, 69.34; H, 7.10; N, 5.15%.

^{1}H NMR (300 MHz, acetonitrile-d_3, 23 °C): δ (ppm) 172.01 (2H), 66.73 (2H), 46.75 (2H), 35.55 (2H), 24.29 (2H), 23.00 (2H), 11.28 (2H), 10.00 (18H, C(CH_3)$_3$), 7.32 (2H), 7.14 (16H), 6.94 (16H), 6.81 (8H), 6.63 (2H), −8.60 (18H, C(CH_3)$_3$), −13.74 (6H, NCH_3), −36.64 (2H), −39.52 (2H), −47.27 (2H), −85.70 (2H), −87.20 (2H). IR spectrum (mineral oil): ν(CN) = 2260 cm^{-1}.

*Reaction of [U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}I] with NaN$_3$. Isolation of [U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(N$_3$)$_2$] (**4**). Method 1.* To a solution of [U{(^{tBu2}OAr)$_2$Me$_2$-cyclam}I] (**1**) (178 mg, 0.173 mmol) in THF (15 mL) was added 1 equiv of NaN$_3$ (11 mg, 0.173 mmol). The mixture was vigorously stirred during 18 h, and the color changed from dark violet to olive oil green. The solvent was removed in vacuum, and the resulting residue was extracted with acetonitrile and concentrated yielding a pale green microcrystalline solid. The solid was collected by centrifugation, washed with n-hexane, and dried under vacuum to give **4** as a pale green solid (106 mg, 0.107 mmol, 62%). Green crystals of **4** suitable for X-ray diffraction were grown from a concentrated solution in acetonitrile-d_3 after 2 d.

Method 2. To a suspension of **2-I** (91 mg, 0.079 mmol) in THF was added excess of NaN$_3$ (15 mg, 0.230 mmol). The mixture was stirred during 16 h at room temperature. To the pale green solution obtained was added 2 mL of n-hexane, and then the mixture was centrifuged to separate the white precipitate from the compound solution. To the solution was added 25 mL of n-hexane, and after 1 d a green microcrystalline solid of **4** was isolated by centrifugation, washed with n-hexane, and dried under vacuum. Yield: 87% (68 mg, 0.069 mmol). Analysis for $C_{42}H_{70}N_{10}O_2U$: Calcd C, 51.21; H, 7.16; N, 14.22; Found: C, 51.02; H, 7.30; N, 14.13. IR (mineral oil): $\nu(N_3)$ = 2068 cm^{-1}.

^{1}H NMR (300 MHz, acetonitrile-d_3, 23 °C): δ (ppm) 179.76 (2H), 61.81 (2H), 51.64 (2H), 43.09 (2H), 30.13 (2H), 28.24 (2H), 20.61 (2H), 13.02 (18H), −0.41 (2H), −0.66 (2H), −8.72 (6H), −10.21 (18H), −47.18 (2H), −49.78 (2H), −53.45 (2H), −96.56 (2H), −99.50 (2H).

^{1}H NMR (300 MHz, THF-d_8, 23 °C): δ (ppm) 181.90 (2H), 62.22 (2H), 51.85 (2H), 44.23 (2H), 31.11 (2H), 29.55 (2H), 20.70 (2H), 13.51 (18H), 0.078 (2H), −0.73 (2H), −8.47 (6H), −10.41 (18H), −48.47 (2H), −51.66 (2H), −55.02 (2H), −99.35 (2H), −101.70 (2H).

*Reaction of **1** with CsN$_3$ in Pyridine-d_5. Isolation of [{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(N$_3$)U(μ-N)U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**5**).* An NMR tube was charged with a solution of [U{(^{tBu2}ArO)$_2$Me$_2$-cyclam}I] (**1**; 30 mg, 0.029 mmol) in pyridine-d_5, and CsN$_3$ (5.0 mg, 0.029 mmol) was added. After the solution rested for 3 d at room temperature, a few brown crystals of $5\cdot 2(C_5D_5N)$ suitable for X-ray diffraction analysis were grown from this mixture.

*Reaction of **1** with PhNNPh. Isolation of [U{(Ar^{tBu2}O)$_2$Me$_2$-cyclam}(NPh)$_2$] (**6**).* To a stirring violet toluene (10 mL) solution of **1** (340 mg, 0.331 mmol, 2 equiv) was added a 0.5 mL toluene solution of azobenzene (30 mg, 0.165 mmol, 1 equiv). Upon addition, the solution color changed to brown, and the reaction mixture was vigorously stirred during 1.5 h at room temperature. A yellow-green solid precipitate was formed and separated from the resulting brown solution by centrifugation. The supernatant was taken to dryness. The resulting solid was washed with n-hexane, dried in vacuo, and dissolved in a mixture of toluene and diethyl ether (20/80). Crystals were grown by slow evaporation of this solution. The crystals were dried in vacuo to give **6** as a brown crystalline solid (135 mg, 0,125 mmol, 75%). Brown crystals of **6** suitable for single-crystal X-ray diffraction analysis were grown similarly. The yellow-green solid, identified as **2-I** by ^{1}H NMR, was isolated in 60% yield (116 mg, 0.100 mmol) after being washed with THF, *n*-hexane, and vacuum-dried. Analysis for $C_{54}H_{80}N_6O_2U$: Calcd C, 59.87; H, 7.44; N, 7.76; Found: C, 59.64; H, 7.53; N, 7.63.

^{1}H NMR (300 MHz, benzene-d_6, 23 °C): δ (ppm) 7.91 (d, $^4J_{HH}$ = 2.4 Hz, 2H, Ar−H), 7.67 (d, 2.3 Hz, $^4J_{HH}$ = 2.4 Hz, 2H, Ar−H), 6.97 (t, J_{HH} = 7.8 Hz, *m*-Ar (imido), 4H), 6.48 (d, J_{HH} = 12.1 Hz, NCH_2Ar, 2H), 5.56 (m, CH_2, 2H), 5.46 (t, J_{HH} = 7.5 Hz, *p*-Ar (imido), 2H), 5.04 (d, J_{HH} = 7.5 Hz, *o*-Ar (imido), 4H), 3.84 (m, CH_2, 2H), 3.79 (d, J_{HH} = 12.1 Hz, NCH_2Ar, 2H), 3.23 (t, CH_2, 2H), 3.09 (m, CH_2, 2H), 2.78 (t, CH_2, 2H), 2.61 (m, $CH_2CH_2CH_2$, 2H), 2.04 (s, NCH_3, 6H), 1.91 (m, CH_2, 2H), 1.83 (s, $C(CH_3)_3$, 18H), 1.60 (s, $C(CH_3)_3$, 18H), 1.62 (br, $CH_2CH_2CH_2$, 2H), 1.57 (br, CH2, 2H), 1.44 (br, CH_2, 2H). ^{13}C NMR (75.4 MHz, benzene-d_6, 23 °C): δ (ppm) 166.41 (ArC-O), 154.00 (*ipso*-Ar (imido)), 141.46 (Ar), 139.39 (Ar), 129.06 (*o*-Ar (imido)), 126.84 (ArC-H), 126.71 (Ar), 126.69 (*p*-Ar (imido), 124.64 (*m*-Ar (imido)), 123.98 (ArC-H), 63.51 ($ArCH_2N$), 58.99 (CH_2), 56.77 (CH_2), 55.97 (CH_2), 55.86 (CH_2), 43.26 (NCH3), 36.01 ($C(CH_3)_3$), 34.25 ($C(CH_3)_3$), 32.66 ($C(CH_3)_3$), 31.12 ($C(CH_3)_3$), 25.26 ($CH_2CH_2CH_2$).

X-ray Diffraction Analysis. Crystallographic and experimental details of data collection and crystal structure determinations for the compounds are given in Table 3. Suitable crystals of compounds **1**, **2-I**, **2-BPh4**, **3**, **4**, **5** and **6** were selected and coated in Fomblin oil under an inert atmosphere. Crystals were then mounted on a loop, and the data were collected 150 K using graphite-monochromated Mo Kα (α = 0.710 73 Å) on a Bruker AXS-KAPPA APEX II area detector. Cell parameters were retrieved using Bruker SMART and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.[94] The structures were solved by direct methods using either SHELXS-97[95]or SIR-97[96] and refined using full-matrix least-squares refinement against F^2 using SHELXL-97.[95] In the former case, all programs are included in the package of programs WINGX-version 1.64.05.[97] All non-hydrogen atoms were refined anisotropically, unless it was mentioned in the CIF files of the structures, and all hydrogen atoms were placed in idealized positions and allowed to refine riding on the parent carbon atom. In complexes **1**, **4**, and **5** some carbons of the ligand are disordered, and a constraint model was used (see CIF files and Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01547.

> X-ray crystallographic data for structures of complexes **1**, **2-I** and **4–6** (CIF)
>
> X-ray crystallographic data for structures of complexes **2-BPh$_4$** and **3**. (CIF)
>
> NMR spectra for compounds **1–4** and **6**, illustrated molecular structures of compounds **2-BPh$_4$** and **3**, supporting crystallographic data for compounds **2-BPh$_4$**, **3** and **5**, and scheme with a plausible pathway for the formation of compound **6**. (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank A. Cruz for experimental assistance. This work was supported by Fundação para a Ciência e a Tecnologia (FCT) under the Ciência 2008 Programme and through Projects UID/Multi/04349/2013 and RECI/QEQ-QIN/0189/2012.

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