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Isolation of a Uranium(III) Benzophenone Ketyl Radical that Displays Redox-Active Ligand Behaviour

Ellen M. Matson, John J. Kiernicki, Nickolas H. Anderson, Phillip E. Fanwick, Suzanne C. Bart*

The first uranium(III) charge separated ketyl radical complex, $\text{Tp}^*\text{U}(\text{OC}\cdot\text{Ph}_3)$, has been isolated and characterized by infrared, $^1\text{H}$ NMR, and electronic absorption spectroscopies, along with X-ray crystallography. $\text{Tp}^*\text{U}(\text{OC}\cdot\text{Ph}_3)$ is a potent two-electron reductant towards $\text{N}_2\text{Mes}$ ($\text{Mes} = \text{2,4,6-trimethylphenyl}$) and ($\text{2,2',6,6'-tetramethyl-piperidin-1-yl}$)oxyl (TEMPO), with reducing equivalents derived from the metal centre and the redox-active benzophenone.

Alkali metals,$^{1-3}$ transition metals,$^{4, 5}$ and lanthanides$^{6, 7}$ have been studied extensively for their ability to reduce the π-bond in carbonylated substrates. Single electron transfer from these metals results in the formation of charge separated radical ketyl complexes, which are highly reactive and thus typically invoked as intermediates in C-C coupling reactions. The oxophilicity and highly reducing nature of low-valent uranium renders this metal a prime candidate for such chemistry. Uranium mediated pinacolate coupling, in which two ketyl radicals are formed and subsequently coupled, has also been proposed to occur through radical intermediates.$^{8-10}$ For instance, treating trivalent $\text{Cp}_3\text{U}$ with benzophenone results in dimeric $\text{Cp}_3\text{U}(\text{OC}\cdot\text{Ph}-\text{CPh}_3\cdot\text{O})\text{UCp}_3$, proposed to form via a uranium(IV) ketyl radical intermediate, $\text{Cp}_3\text{U}(\text{OC}\cdot\text{Ph}_3)$, produced by electron transfer from U(III) to the ketone followed by coupling with the para-carbon radical. By analogy, $\{(\text{4ArO})\text{tacn}\}\text{U}(\text{OC}\cdot\text{Ph}-\text{CPh}_3\cdot\text{O})(\{(\text{4ArO})\text{tacn}\})$ has been formed in low yields from addition of benzophenone to trivalent $\{(\text{4ArO})\text{tacn}\}$, proposed to occur by generation of the uranium(IV) charge separated ketyl species, $\{(\text{4ArO})\text{tacn}\}\text{U}(\text{OC}\cdot\text{Ph}_3)$.^{11}

Recently, work from our lab has demonstrated reductive heterocoupling of ketyl radical intermediates with redox-active ligands. For instance, C-C bond formation occurs between a proposed furanaldehyde ketyl radical and the dianionic $\{\text{Mes-PDI}\}$,$^{12}$ ligand in tetravalent $\text{Cp}^\text{IV}\text{UI}\{(\text{Mes-PDI})\}$, forming a tetradeinate chelate.^{10} We have also demonstrated that exposure of trivalent $\text{Cp}^\text{IV}\text{U}(2,2'-\text{bpy})$, which contains a radical bipyridine ligand, to both aldehydes and ketones results in reductive C-C heterocoupling of the carbonyl-carbon and 2,2'-bipyridine to form the uranium(IV) family, $\text{Cp}^\text{IV}\text{U}\{(\text{NC}3\text{H}_4)\text{NC}3\text{H}_4\cdot\text{CH}=\text{C}(\text{R'R})\text{O}\} (\text{R} = \text{R}' = \text{Ph}; \text{R} = \text{R}' = \text{Me}; \text{R} = \text{H}, \text{R}' = \text{tolyl}; \text{R} = \text{H}, \text{R}' = \text{furanyl})$.^{13} The coupled products are proposed to form via a ketyl radical intermediate that is generated upon carbonyl coordination.

Isolation of uranium ketyl radical species has proven more challenging but has been demonstrated with the formation of $\{(\text{4-8ArO})\text{tacn}\}\text{U}(\text{OC}3\text{Mes-Ph}_3)$, which was recently fully characterized by Meyer and co-workers.$^{12}$ Using the para-tert-butyl substituted benzophenone prevents the C-C coupling previously observed in the adamantyl derivative. This species was found to be quite reactive, readily abstracting an H atom from THF solvent or other H-donor substrates such as 1,4-cyclohexadiene. Interestingly, the isolation of the corresponding uranium(III) ketyl radical intermediate has remained elusive. We reasoned that making use of the sterically bulky hydridoris(3,5-dimethylpyrazolyl)borate (Tp*) ligand framework could make isolation of such a reactive species possible. Herein, we report the characterization of a rare uranium(III) charge separated ketyl complex, $\text{Tp}^*\text{U}(\text{OC}\cdot\text{Ph}_3)$. Unlike previous examples, this complex resists H-atom abstraction and C-C coupling. Reactivity studies show the ketyl radical is truly redox-active, using electrons derived both from the metal centre and the ketyl for reduction of organic substrates.

An initial attempt at formation of the trivalent uranium ketyl species was made by reduction of $\text{Tp}^*\text{U}(\text{1-UI})$ with KC$_8$ in the presence of an equivalent of benzophenone, which resulted in a bright purple reaction mixture (Eq. 1). Analysis of an aliquot of this solution by vibrational spectroscopy did not show a carbonyl stretch, suggesting reduction of the C=O multiple bond occurred (Figure S2). Analysis by $^1\text{H}$ NMR spectroscopy revealed thirteen...
paramagnetically broadened resonances ranging from -227 to 93 ppm, suggestive of a C₃ symmetric complex in solution (Figure S1). To aid in the spectral assignment, the analogous species was synthesized with benzophenone-d₈ and characterized by 1H NMR spectroscopy. For the latter, the absence of the furthest two upfield (-227.59 ppm, 2H; -178.86 ppm, 4H) and downfield (93.86 ppm, 4H) resonances confirmed these as protons arising from coordinated benzophenone. Protons proximal to ligand radicals on uranium have been previously observed to have far-ranging chemical shifts, as is the case with Tp*U(2,2'-bpy) (1-U(bpy)) (-254.80, -134.80 ppm).¹⁹ Cp*U(2,2'-bpy) (93.91, -81.40 ppm).¹⁵ and Cp*U[(O:C₃Ph)₂(PDipp)₂] (-310.96, 177.43 ppm).¹⁵ Similarly, sp² hybridization at the ipso carbons (C46-C41-C42 = 124.8(7)°, C56-C51-C52 = 120.1(8)°) suggests a single reduction of benzophenone, whereas a significant decrease in this angle has been observed for the benzophenone dianion.¹⁹

Crystals of 2 suitable for X-ray crystallographic analysis were obtained from a concentrated solution of n-pentane and toluene (20:1) at -35 °C. Refinement of the data set revealed a seven coordinate uranium species, Tp*U(OC•Ph₂), in a distorted pentagonal bipyramidal geometry (Figure 1, Table 1). The U-N distances for the Tp* ligands range from 2.551(6) to 2.703(6) Å and are consistent with previously reported his(Tp*) uranium complexes.¹⁶ The U1-O4 distance of 2.240(5) Å is significantly longer than that of the uranium(III) aryloxide Tp*U[ODipp] (Dipp = 2,6-diisopropylphenyl) (2.159(10) Å) reported by Marques and co-workers.¹⁷ This observation is consistent with data for [[(tBuArO):tpacn]U[OC•Ph₂]], which has an elongated U-O bond distance (2.178 Å) as compared to its corresponding uranium(IV) methoxide, [[(tBuArO):tpacn]-U[OC•Ph₂]] (2.077(3) Å).¹² Further evidence for the formation of the ketyl species was obtained by examination of intraligand distances of the newly formed ligand. The O4-C4 distance in complex 2 (1.339(10) Å) is significantly longer than that reported for free benzophenone (1.23(1) Å),¹⁸ but consistent with that of the allali metal-ketyl complex, [(HMPA)(Ph₂CO)Na₂ (1.299(10) Å)¹³ and [(tBuArO):tpacn]U[OC•Ph₂] (1.334(6) Å).¹² The C-O distance in 2 is shorter than that reported for the benzophenone dianion, [Na₂(Ph₂CO)(tetracylglyme)] (1.40(1) Å),¹⁹ supporting the formulation of 2 as a uranium(III) species. Furthermore, the bond angles around the ketyl carbon sum to 360° (118.8(8)°, 116.4(7)°, 124.8(7)°), suggesting retention of sp² hybridization at C4. Similarly, sp² hybridization at the ipso carbons (C46-C41-C42 = 124.8(8)°; C56-C51-C52 = 120.1(8)°) suggests a single reduction of benzophenone, whereas a significant decrease in this angle has been observed for the benzophenone dianion.¹⁹

Complex 2 crystallizes in the same unit cell (P-1) as the isostructural samarium(III) ketyl radical complex, Tp*Sm(OC•Ph₂), synthesized by Takats and co-workers.²⁰ Like the uranium examples, the Sm-O distance of 2.201(3) Å is longer than that of reported Sm(III)-OR alkoxy complexes.²¹² Complex 2 is similar to that of Tp*Sm(OC•Ph₂) (1.322(6) Å), making 2 the first isolated and crystallographically characterized uranium(III) charge separated ketyl complex.

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The electronic absorption spectrum for 2 was collected from 400 to 2100 nm in THF at ambient temperature (Figure 2). Complex 2 exhibits an intense, color-producing absorption in the visible region at 556 nm (ε = 863 M⁻¹cm⁻¹). This absorption is representative of the π-π* transition of a benzophenone radical bound to a uranium centre, as previously observed in the electronic absorption spectrum for [[(tBuArO):tpacn]U[OC•Ph₂]] (562 nm) and the fleeting [[(tBuArO):tpacn]U[OC•Ph₂]] (550 nm).¹² This transition is blue-shifted from the π-π* transitions of sodium benzophenone ketyl (624 nm).²³ A trend previously observed for both transition metal⁵ and lanthanide⁷ complexes. The near-infrared region is comprised of broad, ill-defined transitions of moderate intensity (ε = 25 – 150 M⁻¹cm⁻¹) characteristic of a uranium(III) centre.²⁴

The reactivity of benzophenone with Tp*U(2,2'-bpy) (1-U(bpy)) was investigated to determine if reductive heterocoupling of the carbonyl substrate would occur by analogy to Cp*U(2,2'-bpy) that we observed previously.¹³ Exposure of a brown THF solution of 1-U(bpy) to one equivalent of benzophenone resulted in a gradual colour change to purple (Eq. 1). Following workup, inspection of the product by 1H NMR spectroscopy surprisingly revealed the formation of 2 as well as an equivalent of

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**Table 1** Experimental structural parameters of 2

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**Figure 1** Molecular structure of 2 displayed at 30% probability ellipsoids. Co-crystallized solvent molecules and selected hydrogen atoms have been removed for clarity.
uranium(IV) is only observed in the case of Cp*O π-bond, formation of a new C-C bond and oxidation to

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uncoordinated 2,2'-bipyridine. While both trivalent uranium bipyridine complexes, 1-U(bpy) and Cp*U(2,2'-bpy), reduce the C-

O π-bond, formation of a new C-C bond and oxidation to uranium(IV) is only observed in the case of Cp*U(2,2'-bpy), whereas the trivalency of 1-U(bpy) is maintained in formation of 2. We attribute this difference in reactivity to the increased sterically bulk of the ancillary Tp* ligand framework, which cannot accommodate a bulky tridentate heterocoupled ligand.

In order to determine how trivalent 2 compares to previously observed uranium ketyl radicals, reactivity studies were undertaken. Exposure of 2 to an additional equivalent of benzophenone resulted in decomposition to an unidentified complex commonly observed with this ligand system, suggesting formation of a pinacolate ligand is sterically inaccessible with the bis(Tp*) framework. This was corroborated by treating Tp*UCl2 with one equivalent of 1,1,2,2-tetraphenyl-1,2-ethanediol in the presence of KCH2Ph, which resulted in a complex mixture of uranium containing products. Complex 2 also did not show similar reactivity to [(t-BuArO)3 tacn]U[OC(t-Bu)Ph2]12 as addition of 1,4-cyclohexadiene to a THF solution of 2 yielded no reaction with neither consumption of cyclohexadiene nor C-C coupling apparent.

Next, the reducing ability of 2 was tested. Addition of N3Mes to a solution of 2 resulted in an immediate colour change to pink with concomitant loss of dinitrogen as indicated by effervescence of the reaction mixture (Eq. 2). Inspection of the crude product mixture by infrared spectroscopy revealed the formation of a carbonyl stretch at 1660 cm⁻¹ (Figure S7) suggesting oxidation of the C-O single bond in 2. 1H NMR spectroscopy of the crude reaction mixture displayed a single product, Tp*UNMes (3-UNMes), as the sole product in high purity as well as an equivalent of uncoordinated, neutral benzophenone (Figure S6). Interestingly, 3-UNMes was previously found to react with aldehydes to form the corresponding aldmine and Tp*UO (3-

UO)27 however, in the presence of the sterically more demanding benzophenone, 3-UNMes is stable.

To determine whether this redox-active nature of benzophenone was general, complex 2 was exposed to an equivalent of TEMPO (TEMPO = 2,2,6,6-tetramethyl-piperidin-1-yl)oxyl) resulting in an immediate colour change to light pink. Inspection of the crude sample by infrared spectroscopy revealed the same carbonyl stretch observed in the reaction with N3Mes, suggesting reformation of uncoordinated benzophenone (Figure S5). 1H NMR spectroscopy displayed a single product, 3-UO,27 as well as two organic products, benzophenone and 2,2,6,6-tetramethylpiperidine (TMP) (formed by H-atom abstraction from solvent) (Figure S4). To our knowledge, this is the first homogeneous system in which benzophenone acts as a redox-active ligand by first accepting an electron in the formation of 2 and then ejecting this electron in the formation of 3-UNMes and 3-UO.

In summary, the first trivalent charge separated radical ketyl complex of uranium, Tp*U[OC•Ph]2 (2), has been synthesized. X-ray crystallography was used to establish structural parameters which were found to be consistent with a reduced benzophenone ligand, while electronic absorption spectroscopy confirmed the U(III) oxidation state. Complex 2 displays reactivity in sharp contrast to literature precedent by resisting both H-atom abstraction and C-C coupling. Alternately, 2 can perform the two electron reduction of organic oxidants by using reducing equivalents derived from the metal centre and the ketyl ligand, demonstrating the redox-active behaviour of the latter.

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Notes and references
