Dalton
Transactions

COMMUNICATION

Cite this: *Dalton Trans.*, 2014, **43**, 17885

Received 3rd June 2014,
Accepted 11th July 2014

DOI: 10.1039/c4dt01636j

www.rsc.org/dalton

Isolation of a uranium(III) benzophenone ketyl radical that displays redox-active ligand behaviour†

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The first uranium(III) charge separated ketyl radical complex, $Tp^*_2U(OC{\cdot}Ph_2)$, has been isolated and characterized by infrared, ^1H NMR, and electronic absorption spectroscopies, along with X-ray crystallography. $Tp^*_2U(OC{\cdot}Ph_2)$ is a potent two-electron reductant towards N_3Mes (Mes = 2,4,6-trimethylphenyl) and (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 Cp_3U with benzophenone results in dimeric $Cp_3U(OC(Ph)Ph\text{-}CPh_2O)UCp_3$,[11] proposed to form *via* a uranium(IV) ketyl radical intermediate, $Cp_3U(OC{\cdot}Ph_2)$, produced by electron transfer from U(III) to the ketone followed by coupling with the *para*-carbon radical. By analogy, $[((^{Ad}ArO)_3\text{tacn})U(OC(Ph)Ph\text{-}CPh_2O)U((^{Ad}ArO)_3\text{tacn})]$ has been formed in low yields from addition of benzophenone to trivalent $[((^{Ad}ArO)_3\text{tacn})U]$, proposed to occur by generation of the uranium(IV) charge separated ketyl species, $[((^{Ad}ArO)_3\text{tacn})U(OC{\cdot}Ph_2)]$.[12]

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 $[^{Mes}PDI^{Me}]^{2-}$ ligand in tetravalent $Cp^RUI(^{Mes}PDI^{Me})$, forming a tetradentate chelate.[10] We have also demonstrated that exposure of trivalent $Cp^*_2U(2,2'\text{-bpy})$, 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, $Cp^*_2U[(NC_5H_4)\text{-}NC_4H_3CH\text{-}C(R'R)O]$ (R = R′ = Ph; R = R′ = Me; R = H, R′ = tolyl; R = H, R′ = 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 $[((^{t\text{-}Bu}ArO)_3\text{tacn})U(OC{\cdot}^{tBu}Ph_2)]$, 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 ligand 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 hydrotris-(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, $Tp^*_2U(OC{\cdot}Ph_2)$. 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 Tp^*_2UI (**1-UI**) with KC_8 in the presence of an equivalent of benzophenone, which resulted in a bright purple reaction mixture (eqn (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 (Fig. S2†). Analysis by ^1H NMR spec-

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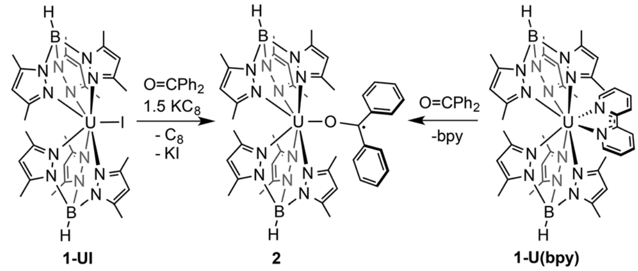
† Electronic supplementary information (ESI) available: Full experimental procedures, spectroscopic and crystallographic data. CCDC 1003448. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01636j

troscopy revealed thirteen paramagnetically broadened resonances ranging from −227 to 93 ppm, suggestive of a C_2 symmetric complex in solution (Fig. S1†).



(1)

To aid in the spectral assignment, the analogous species was synthesized with benzophenone-d_{10} and characterized by ^{1}H 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 $Tp^*_2U(2,2'\text{-bpy})$ (**1-U(bpy)**) (−254.80, −134.80 ppm),[14] $Cp^*_2U(2,2'\text{-bpy})$ (−93.91, −81.40 ppm),[15] and $Cp^PU(O_2C_2Ph_4)(^{Mes}PDI^{Me})$ (−310.96, 177.43 ppm).[10] Thus, the purple product was tentatively assigned as the charge-separated ketyl radical species, $Tp^*_2U(OC{\cdot}Ph_2)$ (**2**).

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, $Tp^*_2U(OC{\cdot}Ph_2)$, in a distorted pentagonal bipyramidal geometry (Fig. 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 bis(Tp*) uranium complexes.[16] The U1–O4 distance of 2.240(5) Å is significantly longer than that of the uranium(III) aryloxide $Tp^*_2U(ODIPP)$ (DIPP = 2,6-diisopropylphenyl) (2.159(10) Å) reported by Marques and co-workers.[17] This observation is consistent with data for $[((^{tBu}ArO)_3tacn)U^{IV}](OC{\cdot}{}^{tBu}Ph_2)$, which has an elongated U–O bond distance (2.178 Å) as compared to its corresponding uranium(IV) methoxide, $[((^{tBu}ArO)_3tacn)U^{IV}(OCH^{tBu}Ph_2)]$ (2.077(3) Å).[12]

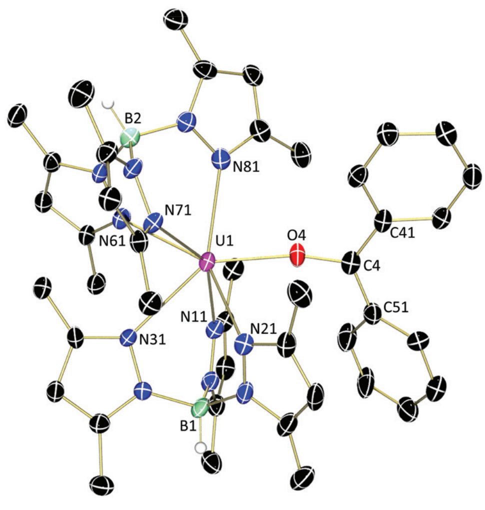


Fig. 1 Molecular structure of **2** displayed at 30% probability ellipsoids. Co-crystallized solvent molecules and selected hydrogen atoms have been removed for clarity.

Table 1 Experimental structural parameters of **2**

Bond	Distance (Å)	Bond	Angle (°)
U1–N11	2.551(6)	U1–O4–C4	162.7(6)
U1–N21	2.586(7)	C41–C4–C51	124.8(7)
U1–N31	2.703(6)	O4–C4–C41	118.8(8)
U1–N61	2.602(6)	O4–C4–C51	116.4(7)
U1–N71	2.594(6)	C42–C41–C46	124.4(8)
U1–N81	2.634(7)	C52–C51–C56	120.1(8)
U1–O4	2.240(5)		
O4–C4	1.339(10)		

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 alkali metal-ketyl complex, $[(HMPA)_2(Ph_2CO)Na]_2$ (1.299(10) Å)[3] and $[((^{tBu}ArO)_3tacn)U^{IV}](OC{\cdot}{}^{tBu}Ph_2)$ (1.334(6) Å).[12] The C–O distance in **2** is shorter than that reported for the benzophenone dianion, $[Na_2(Ph_2CO)(tetraglyme)]_\infty$ (1.401(4) 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 sp^2 hybridization at C4. Similarly, sp^2 hybridization at the *ipso* carbons (C46–C41–C42 = 124.4(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 ($P\bar{1}$) as the isostructural samarium(III) ketyl radical complex, $Tp^*_2Sm(OC{\cdot}Ph_2)$, 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 alkoxide complexes.[21,22] The O–C distance in **2** is similar to that of $Tp^*_2Sm(OC{\cdot}Ph_2)$ (1.322(6) Å), making **2** the first isolated and crystallographically characterized uranium(III) charge separated ketyl complex.

The electronic absorption spectrum for **2** was collected from 400 to 2100 nm in THF at ambient temperature (Fig. 2). Complex **2** exhibits an intense, color-producing absorption in the visible region at 556 nm (ε = 863 M^{-1} cm^{-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 $[((^{tBu}ArO)_3tacn)U^{IV}](OC{\cdot}{}^{tBu}Ph_2)$ (562 nm) and the fleeting $[((^{Ad}ArO)_3tacn)U^{IV}(OC{\cdot}Ph_2)]$ (550 nm).[12] This transition is blue-shifted from the π–π* of sodium benzophenone ketyl (624 nm),[23] a trend previously observed for both transition metal[5] and lanthanide[7] complexes. The near-infrared region is comprised of broad,

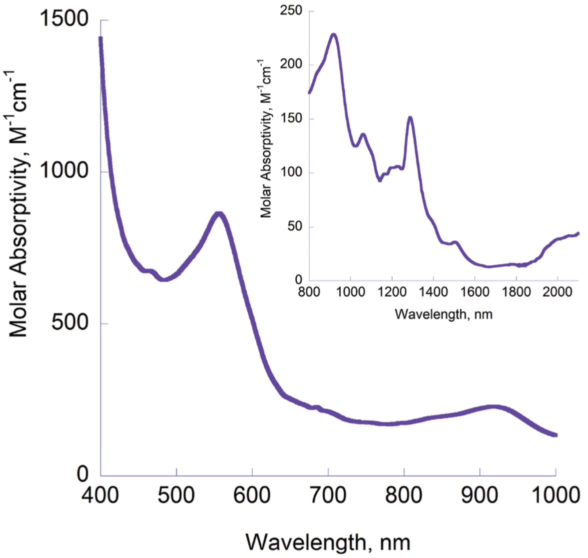


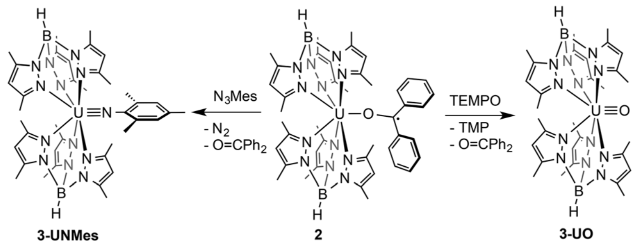
Fig. 2 Electronic absorption spectrum of **2** recorded in tetrahydrofuran from 400–2100 nm. Solvent overtones from 1670–1760 nm have been removed for clarity.

ill-defined f–f transitions of moderate intensity (ε = 25–150 M^{-1} cm^{-1}) characteristic of a uranium(III) centre.[24]

The reactivity of benzophenone with $Tp^*_2U(2,2'\text{-bpy})$ (**1-U(bpy)**) was investigated to determine if reductive heterocoupling of the carbonyl substrate would occur by analogy to our previous observations with $Cp^*_2U(2,2'\text{-bpy})$.[13] Exposure of a brown THF solution of **1-U(bpy)** to one equivalent of benzophenone resulted in a gradual colour change to purple (eqn (1)). Following workup, inspection of the product by ^1H NMR spectroscopy surprisingly revealed the formation of **2** as well as an equivalent of uncoordinated 2,2′-bipyridine. While both trivalent uranium bipyridine complexes, **1-U(bpy)** and $Cp^*_2U(2,2'\text{-bpy})$, 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 $Cp^*_2U(2,2'\text{-bpy})$, whereas the trivalency of **1-U(bpy)** is maintained in formation of **2**. We attribute this difference in reactivity to the increased steric 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 $Tp^*_2UCl_2$ [25] with one equivalent of 1,1,2,2-tetraphenyl-1,2-ethanediol in the presence of KCH_2Ph, which resulted in a complex mixture of uranium containing products. Complex **2** also did not show similar reactivity to $[((^{t\text{-Bu}}ArO)_3tacn)U(OC\cdot{}^{t\text{Bu}}Ph_2)]$,[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 N_3Mes 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 (eqn (2)). Inspection of the crude product mixture by infrared spectroscopy revealed the formation of a carbonyl stretch at 1660 cm^{-1} (Fig. S7†) suggesting oxidation of the C–O single bond in **2**. ^1H NMR spectroscopy of the crude reaction revealed the previously characterized uranium(IV) imido species, Tp^*_2UNMes (**3-UNMes**),[26] as the sole product in high purity as well as an equivalent of uncoordinated, neutral benzophenone (Fig. S6†). Interestingly, **3-UNMes** was previously found to react with aldehydes to form the corresponding aldimine and Tp^*_2UO (**3-UO**);[27] however, in the presence of the sterically more demanding benzophenone, **3-UNMes** is stable.



(2)

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 N_3Mes, suggesting reformation of uncoordinated benzophenone (Fig. 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) (Fig. 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, $Tp^*_2U(OC\cdot Ph_2)$ (**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.

We gratefully acknowledge funding by the National Science Foundation (CAREER grant to SCB, CHE-1149875).

Notes and references

‡ Crystal data for **2**: $C_{43}H_{54}B_2N_{12}OU$, 0.5(C_7H_7), M_r = 1060.199; triclinic; space group $P\bar{1}$; a = 11.0395(8), b = 13.5231(9), c = 17.6638(18) Å; α = 72.590(5), β = 86.210(5), γ = 67.426(4)°; V = 2320.04 Å^3; Z = 2; ρ = 1.518 g cm^{-3}; T = 150(1) K; R_1 = 0.068; wR_2 = 0.179.

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