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Dinuclear uranium complexation and manipulation using robust tetraaryloxides

Jordann A. L. Wells,* Megan L. Seymour,* Markéta Suvova,* and Polly L. Arnold*†

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Two lower-oxidation state uranium cations can be readily combined in a robust, yet flexible and derivatisable, tetraaryloxide ligand framework, affording a new platform at which to use the multi-electron reductive capacity of the two actinide centres.

While single organometallic uranium centres are often capable of binding and reducing inert small molecules such as dinitrogen and carbon oxides, the most notable levels of activation and transformations are achieved almost exclusively by the combination of two uranium cations around one substrate.1,2

For example, dinitrogen overpressures as high as 80 psi are required to stabilise the terminal [(Cp*)2U(η6-N2)]3 and the first molecular uranium carbonyl [(Me5SiC5H4)3UCO] showed reversible CO binding in solution.4 However, two molecules of uranium tris(aryloxide) or tris(siloxide) UX3 (X = O-2,4,6-tert-Bu3C6H2, OSi(2,4,6-Me3C6H2)) in combination can effect the reduction of N2 to such an extent that the molecule [X3UIV(μ-η6-N2)UIVX3] is stable in boiling toluene, and can reductively couple CO at ambient temperature and pressure to the ynediolate complex [X3UIV(μ-η6-CO)UIVX3] and can further C-H and C-C bond formations possible. The conversion of aryl C-H to C-B bonds has also been possible in di-uranium(arene) complexes [X2UIV(μ-η6-OC6H5)UIVX3] (R = H, alkyl, aryl).5 The recently reported reductive activation of CO2 by pairs of the uranium complexes [U(η6-C6H5)(SiR3)2(η6-CP*)] (R = Me, Pr, R = MeH, Me, Me+ Pr, Me, SiMe3, Me, Et) has been particularly instructive since the product (carbonate, oxo-bridged, or desirable C-C coupled oxalate) formed by trapping between the two uranium centres depends on the steric accessibility to the two U centres (rather than the redox capability).6,9

All these results suggest that a ligand pre-organised to hold two reducing U centres would be desirable if these small molecule activations are to be rendered catalytic, or better controlled. In collaboration with Love, we recently reported the use of expanded Pacman-shaped N-donor macrocycles to combine two U(III) centres at a distance suitable for trapping a di- or triatomic fragment, but have been unable as yet to isolate complexes in which no X-ligand is accessible to the two uranium centres (rather than the redox capability).8,9

Recognising the strength of the U-aryloxide bond in a range of U oxidation states,5,12-16 we have developed a two-hour, one-pot, large-scale synthesis of three closely related analogues of a known arene-bridged tetraphenol17 in order to isolate and study the first O-donor compounds containing two discrete U(III) or U(IV) centres in a single molecule, in geometries pre-organised for small molecule binding. The three phenols used here are H4Lp and H4LM, and phenyl-substituted H4Lp*, Figure 1.

Bimetallic salts of the phenols closely related to H4LP and H4LM in Figure 1 (with R1 = R2 = tBu) have been demonstrated to be excellent ring opening polymerisation initiators for monomers including lactide (by H4K2Lp and H4K2LM adducts),18 epoxide (by bis-AlIII adducts of Lp with R1 = R2 = tBu),19 and ε-caprolactone (by bis-Nb or Ta adducts of Lp with R1 = R2 = tBu).20 X-ray structural analyses in some of these complexes demonstrate a ligand flexibility that enables the metals to reside on the same or opposite sides of the central arene bridge.19,21

Both salt metathesis and protonolysis routes allow access to diuranium complexes of the tetraphenolates, as shown in Scheme 1. First, treatment of the in-situ formed dicalcium salt Ca2Lp (R = P, P*) or tetrapotassium K4Lp (R = M) with two equivalents of [UL2(diox)]2 (diox = O(CH2CH2)2O, 1,4-dioxane) in THF or dioxane affords the green crystalline diuranium target complexes after work-up to remove salt by-products. The di-uranium complexes {[UL2(S)x]:Lp}2, I8, (R =
P: S = THF, n = 3 or S= diox, n = 2; R = P*, S = THF, n = 2; R = M, S = THF, n = 2) can be isolated after work-up in excellent yields (65-

Second, treatment of the proligand \( H_4L^R \) with two equivalents of the U(IV) metal centres at the same time, and confirming the absence of U(IV)-U(IV)

Complexes \( 1^R \) and \( 2^R \) have been fully characterised, including by single crystal X-ray diffraction. The syntheses of the calcium salts are described in the SI as they have proven ideal metathesis precursors for some, since Group 1 bases often afford salts that retain one or more bridging aryloxide protons.15

![Scheme 1 Syntheses of (U(III)) and (U(IV)) complexes of bridged tetra-aryloxide ligands L^P, L^P or L^M.

In our hands, direct syntheses of uranium(III) analogues of \( 1^R \) and \( 2^R \) from uranium(III) halide and amide starting materials were unsuccessful. We therefore investigated the electrochemical and chemical reduction of the uranium(IV) complexes. The U(IV)/U(III) redox couple is known to range from -2.78 to -1.83 V versus ferrocene depending on the ligand environment.12,22,23 The cyclic voltammetry data show that the complexes \( 1^R \) and \( 2^R \) have one wave in the negative potential region attributable to the single electron reduction of both metal centres at the same time, and confirming the absence of U(IV)/U(III) electronic communication through the ligand in all cases. The potentials of the complexes are collated in Table 1 and suggest that the uranium(III) complexes should be chemically accessible from a reaction with common one-electron reductants such as group 1 metals. The treatment of \( 2^R \) with two equivalents of KCs affords dark purple di-U(III) \( \{[UN''_2]_2LM\} \), \( 3^M \) in 63 % yield after workup, which has been characterised by multinuclear NMR spectroscopy and elemental analysis, Scheme 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reduction Potential at 100mVs(^{-1}) V</th>
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<tbody>
<tr>
<td>( 1^M )</td>
<td>-2.03</td>
</tr>
<tr>
<td>( 2^M )</td>
<td>-1.99</td>
</tr>
<tr>
<td>( 1^P )</td>
<td>-2.05</td>
</tr>
<tr>
<td>( 2^P )</td>
<td>-2.05</td>
</tr>
<tr>
<td>( 2^P* )</td>
<td>-1.53</td>
</tr>
</tbody>
</table>

Table 1 Selected reduction potentials versus Fe\(^{3+}/\text{Fc} \) measured in THF using 0.1 M \([\text{nBu}_4\text{N}]\mu\text{BPh}_4\) as the supporting electrolyte.

Complexes 1, 2 and 3 are soluble in hot THF, dioxane, pyridine and arene solvents. The \(^1H\) NMR spectra of the iodide complexes 1 are moderately shifted by the U(IV) centres with resonances in the range 14 to 0 ppm whereas the amide complexes 2 are more significantly shifted with proton resonances spanning from 40 to -20 ppm.

Interestingly, following reduction of \( 2^M \) to give \( 3^M \), the chemical shift range is decreased and proton resonances occur between 22 and -13 ppm. The \(^29\)Si resonance of the silylamide group occurs at around -230 ppm for both \( 2^P \) and \( 2^M \) and is shifted to -100 ppm in \( 3^M \).

Single crystals of 1 and 2 were grown, details for which are in the SI. The molecular structures of \( 1^P \), \( 1^P^* \), \( 1^M \), \( 2^P \) and \( 2^M \) are shown in Figures 1 and 2; that for \( 2^P* \) is in the SI along with the structure of a dioxane solvate of \( 1^P \), \( 1^P^* \) (dioxane).

The uranium centre in \( 1^P \) is seven-coordinate, adopting square faco-axial dioxanes act as a bridging ligand, linking the uranium centres in separate molecules to form a one-dimensional polymer in the solid state (see SI for further information).

The coordination environment of the two uranium centres in \( 1^M \) differs. While both metal centres have a pseudo-octahedral geometry, the aryloxide and iodide ligands occupy the equatorial plane in \( 1^P \) and \( 1^P^* \) adopt distorted octahedral geometry. The dioxane adduct of \( 1^P \), \( 1^P^* \) (dioxane), also displays six coordinate uranium centres in distorted octahedral geometry. The equatorial plane is occupied by the aryloxide and iodide ligands, and the axial positions occupied by coordinated dioxane molecules. The exo-axial dioxanes act as a bridging ligand, linking the uranium centres in separate molecules to form a one-dimensional polymer in the solid state. The U1-O2 bond length is slightly shorter than the average of the three other bond lengths (2.080(11) Å and 2.124(10) Å respectively). Perhaps most notable is the distortion of the U1-O1-Cipso angle of 138.7(9)° compared to the average of the other three angles, 157.0(9)°.

The U-OAr bond distances in \( \{[UN''_2]_2LM\} \), \( 3^M \) are very similar, with average distances of 2.112(5) Å, 2.106(4) Å and 2.120(10) Å respectively. These are comparable to previously reported uranium(IV) bis(aryloxido) bis(iodo) complexes such as \( \text{I}_2\text{U(OH)dpb)}(\text{thf}) \) (ODdpb = O-2,6-Bu_2C_6H_4) with an average U-O bond length of 2.076 Å,14 and \( \text{I}_2\text{U(OAr)}(\text{thf}) \) (Ar = O-4- BuC_6H_4, O-
2,6-Me$_2$C$_6$H$_3$, C$_6$F$_5$) with average U-O distances of 2.068(8) Å, 2.091(8) Å and 2.120(6) Å respectively.\textsuperscript{24}

**Figure 1** Solid-state structures of 1P (upper, side view), 1P* (middle, top view) and 1M (lower, side view). For clarity, hydrogen atoms and lattice solvent molecules are omitted (displacement ellipsoids are drawn at 50 % probability, the remaining atoms and bonds shown as capped stick). For 1P* see SI. Selected bond lengths (Å) and angles (°) for 1P: U1-O1 2.108(5), U1-O2 2.117(5), U1-I1 3.0970(8), U1-I2 3.1094(8), U1-O1-C11 157.4(4), U1-O1-C21 156.8(4). For 1P*: U1-O1 2.105(4), U1-O2 2.106(4), U1-I1 3.0553(4), U1-I2 3.0472(5), U1-O1-C11 152.9(3), U1-O1-C21 159.1(3). For 1M: U1-O1 2.132(12), U1-O2 2.080(11), U2-O3 2.110(9), U2-O4 2.129(10), U1-I1 3.0643(16), U1-I2 2.9860(14), U2-I3 3.0109(18), U2-I4 3.0562(14), U1-O1-C11 138.7(9), U1-O1-C21 161.1(10), U2-O3-C31 154.1(9), U2-O4-C41 156.0(9).

**Figure 2** Solid-state structures of 2P (upper, side view), and 2M (lower, side view). For clarity, all methyl groups, hydrogen atoms, and lattice solvent molecules are omitted (displacement ellipsoids are drawn at 50 % probability, the remaining atoms and bonds shown as capped stick). For 2P* see SI. Selected bond lengths (Å) and angles (°) for 2P: U1-O1 2.1033(13), U1-O2 2.1362(13), U1-N1 2.2580(16), U1-N2 2.2479(17), U1-O1-C11 152.17(12), U1-O2-C21 146.77(12), 2M: U1-O1 2.130(4), U1-O2 2.110(4), U2-O3 2.138(5), U2-O4 2.112(4), U1-N1 2.265(5), U1-N2 2.254(6), U2-N3 2.228(5), U2-N4 2.264(6), U1-O1-C11 141.5(4), U1-O2-C21 157.1(4) U2-O3-C31 138.5(4), U2-O4-C41 157.4(4).

The U-O-C$_{ipso}$ bond angles for the 1R complexes are bent, reminiscent of the homoleptic uranium(IV) complex U(OEt)$_4$,\textsuperscript{25} with angles of 157.1(4)$^\circ$, 156.0(3)$^\circ$, 152.4(9)$^\circ$ for 1P, 1P* and 1M respectively, compared to 154.04(8)$^\circ$ for U(OEt)$_4$. This is somewhat unusual, as the U-O-C$_{ipso}$ bond angles of other complexes of the type I$_2$U(OAr)$_2$ fall within the range 166.2(8)$^\circ$ to 176.9(8)$^\circ$, and could be ascribed to the constraints imposed by the ligand frame.

The four-coordinate uranium centres in complexes 2P, 2P* and 2M all adopt a distorted tetrahedral geometry. The complexes have comparable average U-O bond distances of 2.1198(13) Å, 2.1422(19) Å and 2.122(4) Å respectively, which is also true of the U-N bond distances of 2.2530(16) Å, 2.267(2) Å and 2.252(6) Å respectively. The slight elongation of U-O and U-N bonds in 2P* compared to 2P and 2M can be rationalised by the increased steric bulk around the metal centre in the larger tetraaryloxide framework interacting with the sterically demanding silylamide ligands. Similarly to the iodide complexes, the U-O-C$_{ipso}$ bond angles are closer to the homoleptic uranium(IV) aryloxide, as opposed to the I$_2$U(OAr)$_2$ analogues, with mean angles of 149.47(12)$^\circ$, 150.72(17)$^\circ$ and 148.5(4)$^\circ$ for 2P, 2P* and 2M respectively. The U-O bond distances are comparable to that of U(OEt)$_4$, as well as the tetrahedral mixed aryloxo-amido uranium(IV) complexes EthNU(OEt)$_3$ and N''3U(OEt)$_3$ with average U-O distances of 2.143(4) Å and 2.145(8) Å respectively.\textsuperscript{25,26} The U-N bond distances of 2P differ from the U-N bond distance of 2.161(5) Å exhibited by Et$_2$NU(OEt)$_3$ slightly, but agree very well with the U-N bond distances exhibited by N''3U(OEt)$_3$ and the
uranium(V) complex N\text{\textsuperscript{3}}\text{,}U(Onaph)\text{\textsubscript{2}} (napth = C\text{\textsubscript{10}}H\text{\textsubscript{7}}) of 2.284(10) and 2.222(6) Å respectively. This discrepancy in the U-N bond distance is presumably due to the difference in steric environment imposed by the bis(trimethylsilyl)amide ligand compared with that of the diethylamide ligand.

Inspection of the solid-state structures of these bimetallic derivatives, and of literature examples of other metal complexes suggests that the coordination of the two metals on the same side of the arene bridge is the preferred geometry in the meta-substituted L\text{\textsubscript{M}} complexes,\textsuperscript{3,20} but significantly rarer in the others, but is presumably not retained in solution for the smaller R substituted phenols. This could be due to the additional stability afforded by the generation of a dipole across the molecule.

<table>
<thead>
<tr>
<th>Table 2 Comparison of key metrics for the di-uranium complexes</th>
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<tr>
<td>Distance (Å/angle (°))</td>
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<tr>
<td>------------------------</td>
</tr>
<tr>
<td>U-U</td>
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<td>U-O</td>
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Conclusions

Straightforward syntheses of dinuclear U\textsuperscript{IV} complexes are possible using three different tetraphenolate ligands, in which a para- or meta-substituted phenyl backbone provide a strong yet flexible support to the two metal centres. The dinuclear U\textsuperscript{III} analogues are most readily accessible by chemical reduction. The meta-arene bridged ligand appears to favour the coordination of both metals on the same side of the bridge, a factor which may enhance the ability to reductively couple certain small molecules.

Meta- and para- functionalised aryl imido and alkynyl ligands have previously been used to demonstrate viable magnetic exchange between f\textsuperscript{1} uranium centres.\textsuperscript{25,29} The properties are switched by changing the substitution patterns of the linking arene groups, and as such could be useful in developing f-block magnetic materials for data storage, quantum computing or refrigeration applications. In addition to reactivity studies of these new potential multi-electron reductants, work is in progress to understand the magnetic behaviour of these new complexes.

Acknowledgements

We thank EaStCHEM, the University of Edinburgh and the Engineering and Physical Sciences Research Council EPSRC, grants EP/H004823/1 and EP/M010554/1. PLA also thanks the Technische Universität München – Institute for Advanced Study, funded by the German Excellence Initiative.

General details

All moisture and air sensitive materials were manipulated using standard high-vacuum Schlenk-line techniques and MBraun gloveboxes and stored under an atmosphere of dried and deoxygenated dinitrogen. All gases were supplied by BOC gases UK.

All glassware items, cannulae and Fisherbrand 1.2 µm retention glass fibre filters were dried in a 160 °C oven overnight before use.

Tetrahydrofuran and hexane for use with moisture and air sensitive compounds were dried using a Vac Atmospheres solvent purification system and stored over activated 4 Å molecular sieves. The solvent was cycled through a drying column containing molecular sieves for 12 hours before collection. 1,4-Dioxane for use with moisture and air sensitive compounds was refluxed over sodium for 3 days, distilled and collected into an ampoule containing 4Å molecular sieves. All solvents were degassed and stored for 2 days prior to use. d\textsubscript{5}-Benzenede and d\textsubscript{6}-tetrahydrofuran were freeze pump thaw degassed, refluxed over potassium for 24 hours and distilled by trap to trap distillation prior to use. All solvents were purchased from Sigma-Aldrich or Fisher Scientific.

Unless stated otherwise, all NMR spectroscopic analyses were recorded at 298 K using a Bruker Avance III 500.12 MHz spectrometer with 1H NMR spectra run at 500.12 MHz, and 29Si NMR spectra at 99.37 MHz. The 1H NMR spectra were referenced internally using residual solvent signals and are reported relative to external tetramethylsilane. Chemical shifts are quoted in ppm and coupling constants in Hz.

Experimental details

Potassium and sodium metal, 2-tert-butyl-4-methylphenol, 2,4-bis(dimethylbenzyl)phenol, and isophthalaldehyde were purchased from Sigma-Aldrich and used as received. KN(SiMe\textsubscript{3})\textsubscript{2},\textsuperscript{30} [Ca(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}],\textsuperscript{31} U\textsubscript{IV} (dioxane)\textsubscript{2},\textsuperscript{32} (((MeSi\textsubscript{2})\textsubscript{3})\textsubscript{2}U[k\textsuperscript{2}-N(SiMe\textsubscript{3})SiMe\textsubscript{2}CH\textsubscript{2}]\textsuperscript{33} and KC\textsubscript{8} were synthesised as previously described in literature procedures.\textsuperscript{34}

H\textsuperscript{I-L}\textsuperscript{P}

A two necked 250 cm\textsuperscript{3} round bottom flask was charged with 2-tert-butyl-4-methylphenol (41.80 g, 250 mmol, 4.4 eq.), terephthalaldehyde (7.5 g, 56 mmol, 1 eq.) and p-toluenesulfonic acid (1.06 g, 5.6 mmol, 0.1 eq) and equipped with a stirrer bar and an oil bubbler. The flask was placed under nitrogen flow, stirred and heated to 110 °C. The solids melted to yield a yellow solution, which darkened with time. After circa 2 hours, the reaction mixture had turned to a reddish solid. The flask was allowed to cool to room temperature, at which point 50 cm\textsuperscript{3} of 20% H\textsubscript{2}O in MeCN solution was added. The resulting beige suspension was filtered to provide an off-white solid which was collected and washed with boiling ethanol. The resulting colourless solid was dried under vacuum at 65 °C overnight and stored in a glove box. Yield 27 g (64%).

1H NMR (CD\textsubscript{2}n, 500 MHz): δ 7.12 (Arxyloide H, J = 1.9 Hz, 4H), 7.06 (Aromatic H, 4H), 6.72 (Arxyloide H, J = 1.9 Hz, 4H), 5.56 (Ar=CH\textsubscript{2}, 2H), 4.95 (ArOH, 4H), 2.06 (CH\textsubscript{3}, 12H), 1.44 (Bu H, 36H).

13C NMR (126 MHz, CD\textsubscript{2}n): δ 151.2, 140.0, 107.2, 136.0, 130.1, 129.6, 128.1, (Aromatic C), 34.6 (C=CH\textsubscript{2}), 29.6 (C(CH\textsubscript{3}))\textsubscript{2}, 20.7 (CH\textsubscript{3}).

Mass Spectrometry: (ESI) m/z 777.4850 [L\textsuperscript{P}+Na\textsuperscript{+}].

H\textsuperscript{I-L}\textsuperscript{M}

A two necked 250 cm\textsuperscript{3} round bottom flask was charged with 2-tert-butyl-4-methylphenol (26.94 g, 161 mmol, 4.4 eq.), isophthalaldehyde (5.0 g, 37 mmol, 1 eq) and p-toluensulfonic acid (9.71 g, 3.8 mmol, 0.1 eq) and equipped with a stirrer bar and an oil bubbler. The flask was placed under nitrogen flow, stirred and heated to 110 °C. The solids melted to yield a yellow solution, which darkened with time. After circa 2 hours, the reaction mixture had turned to a reddish solid. The flask was allowed to cool to room temperature, at which point 30 cm\textsuperscript{3} of MeCN was added. The resulting...
beige suspension was filtered to provide a colourless solid which was collected by filtration and washed with MeCN. The resulting colourless solid was dried under vacuum at 65 °C overnight and stored in a glove box. Yield 22.9 g (82%).

1H NMR (CD_{2}D, 500 MHz) δ 7.09 (Aryloxide H, s, 4H), 7.06-6.96 (Aromatic H, m, 4H), 6.68 (ArylOH, s, 4H), 5.47 (ArCH, s, 2H), 4.90 (ArOH, s, 4H), 2.05 (CH3, s, 12H), 1.43 (Bu H, s, 36H).

13C NMR (CD_{2}D, 126 MHz) δ 151.1, 141.8, 137.6, 130.7, 129.6, 128.4, 128.0 (Aromatic C), 47.6 (ArCH), 34.5 (C(CH3)), 29.61 (C(CH3)3), 20.73 (CH3).

Elemental analysis: C 82.71 %, H 8.81 % calculated. C 82.83 %, 8.92 % found.

H₂L^* Analogous procedure to that used to synthesise H₂L. 82% yield.

1H NMR (CD_{2}D, 600 MHz) δ 7.34 – 7.28 (Aromatic H, 12H), 7.20 (Aromatic H, 8H), 7.12 (Aromatic H, 8H), 7.07 (Aromatic H, 4H), 7.03 (Aromatic H, 4H), 6.99 (Aromatic H, 8H), 6.96 – 6.90 (Aromatic H, 4H), 6.89 (Aromatic H, 4H), 5.98 (ArCH, 2H), 4.48 (ArOH, 4H), 1.65 (CH4), 1.47 (CH4).

13C NMR (CD_{2}D, 151 MHz) δ 151.6, 150.2, 149.1, 142.0, 140.8, 135.4, 131.6, 129.4, 129.0, 127.4, 127.1, 126.6, 126.1, 125.8, 124.0 (Aromatic C), 44.6 (PhCH), 43.0 (CCH3), 42.3 (CCH3), 31.4 (CH3), 31.3 (CH3), 30.0 (CH3), 29.8 (CH3).

Mass Spectrometry: (ESI) m/z 777.4850 [LM+Na]^+.

1⁠M (U₂N"₄L₄) A Schlenk flask was charged with H₄L^* (1.00 g, 1.32 mmol) and KN" (1.06 g, 5.30 mmol) and equipped with a stirrer bar. THF was added and the yellow solution was stirred for 1 hour at room temperature. To this solution, Ua(OOC-H₂O)₄ (2.44 g, 2.65 mmol) in THF was added by cannula transfer from a separate Schlenk flask. The resulting dark green solution was stirred at room temperature for 48 hours, yielding a light green suspension. The colourless precipitate was removed by filtration and the solvent was removed under reduced pressure giving a light green solid. (1.87 g, 82 %). Green plate crystals suitable for single crystal X-ray analysis were grown from slow evaporation of concentrated benzene or thf solutions at room temperature.

1H NMR (d₆-THF, 329K, 500 MHz) δ 13.94 (Aryloxide H, 4H), 7.53 (Aryl H, 4H), 7.18 (t-Bu H, 36H), 6.92 (Aromatic H, 1H), 5.93 (CH3, 12H), 5.60 (Aromatic H, 1H), 2.20 (Aromatic H, 2H), 0.90 (ArCH, 2H).

Elemental analysis: C 40.37 %, H 4.68 % calculated. C 40.27 %, 4.55 % found.

2⁠P (U₂N"₄L₄) A Schlenk flask was charged with H₂L^* (100 mg, 0.133 mmol) and U(N"₃)₅(N(SiMe₃)₂) (N" = N(SiMe₃)₂) (200 mg, 0.278 mmol, 2.1 eq.), a stirrer bar and hexanes (15 ml). The resulting dark brown suspension was allowed to stir at room temperature for 16 h during which time a colour change to olive green occurred. The reaction mixture was allowed to stand, and the off-white precipitate was isolated by filtration. The product was recrystallized from benzene solutions allowed to stand at room temperature to afford yellow plates of U₂N"₄L₄. 2⁠P in 65 % yield (247 mg). The yellow blocks were suitable for single crystal X-ray diffraction analysis.

1H NMR (CD₃, 500 MHz) δ 35.34 (Aryloxide H, 4H), 19.97 (Aryl H, 4H), 5.51 (Aromatic H, 4H), 4.40 (CH3, 12H), -2.90 (ArCH, 2H), -9.62 (t-BuH, 36H), -18.89 (SiCH3, 72H).

2⁠M (U₂N"₄L₄) Made by an analogous procedure with recrystallisation from slow diffusion of hexane vapour into concentrated THF solutions to give green blocks suitable for single crystal X-ray diffraction analysis in 60% yield.

1H NMR (CD₃, 500 MHz) δ 41.19 (Aromatic H, 2H), 31.62 (Aromatic H, 1H), 27.73 (Aromatic H, 1H), 16.71 (Aryloxide H, 4H), 3.90 (Aryl H, 2H), 1.50 (CH3, 12H), -3.03 (ArCH, 2H), -9.76 (t-BuH, 36H), -18.51 (SiCH3, 72H) ppm.

Elemental analysis: C 48.85 %, H 7.23 %, N 3.00 % calculated. C 48.03 %, H 7.10 %, N 2.90 % found.

2⁠M (U₂N"₄L₄) Made by an analogous procedure with recrystallisation from slow diffusion of hexane vapour into concentrated THF solutions to give green blocks suitable for single crystal X-ray diffraction analysis in 60% yield.
COMMUNICATION

A Schlenk flask was charged with $\text{U}_2\text{N}_2\text{d}_M$ (274 mg, 0.223 mmol) and KCs (64 mg, 0.447 mmol) and equipped with a stirrer bar. Toluene was added and the resulting dark green solution was stirred for 16 hours at room temperature, turning dark purple. The toluene was removed under reduced pressure and the product was extracted into heptane. The dark purple product was obtained as a powder following removal of volatiles under reduced pressure, (0.31 g, 74%).

Notes and references

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