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Dinuclear uranium complexation and manipulation using robust tetraaryloxides†

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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*)₃U(η¹-N₂)],³ and the first molecular uranium carbonyl [(Me₃SiC₅H₄)₃UCO] showed reversible CO binding in solution.⁴ However, two molecules of uranium tris(aryloxide) or tris(siloxide) UX₃ (X = O-2,4,6-^tBu₃C₆H₂, OSi(2,4,6-Me₃C₆H₂)₃) in combination can effect the reduction of N₂ to such an extent that the molecule [X₃U^{IV}(μ-η²:η²-N₂)U^{IV}X₃] is stable in boiling toluene, and can reductively couple CO at ambient temperature and pressure to the ynediolate complex [X₃U^{IV}(OCCO)U^{IV}X₃],^{5,6} with 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 [X₂U^{IV}(μ-η⁶:η⁶-C₆H₅R)U^{IV}X₂] (R = H, alkyl, aryl).⁷ The recently reported reductive activation of CO₂ by pairs of the uranium complexes [U(η⁶-C₈H₆{SiR₃})₂(η-Cp^R)] (R = Me, ⁱPr; R' = Me₄H, Me₅, Me₄ⁱPr, Me₅SiMe₃, Me₄Et) 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).^{8,9}

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 coordinated between the two U centres.^{10,11} Recognising the strength of the U–aryloxide bond in a range of U oxidation states,^{7,12–16} 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 H₄L^P and H₄L^M, and phenyl-substituted H₄L^{P*}, Fig. 1.

Bimetallic salts of the phenols closely related to H₄L^P and H₄L^M in Fig. 1 (with R₁ = R₂ = ^tBu) have been demonstrated to be excellent ring opening polymerisation initiators for monomers including lactide (by H₂K₂L^P and H₂K₂L^M adducts),¹⁸ epoxide (by bis-Al^{III} adducts of L^P with R₁ = R₂ = ^tBu),¹⁹ and ε-caprolactone (by bis-Nb or Ta adducts of L^P 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}

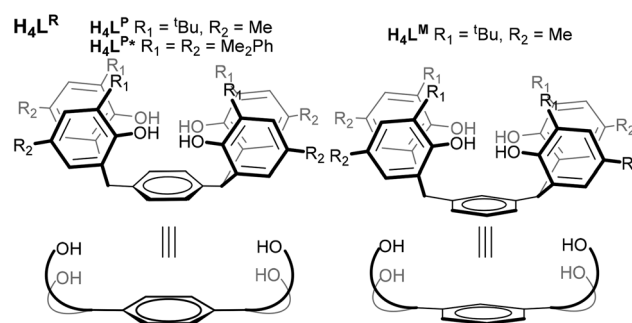


Fig. 1 The substituted tetraphenols H₄L^R (with both *para* and *meta* substituted arene cores) and the new aryl-substituted H₄L^{P*}.

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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 $\text{Ca}_2\text{L}^{\text{R}}$ ($\text{R} = \text{P}, \text{P}^*$) or tetrapotassium $\text{K}_4\text{L}^{\text{R}}$ ($\text{R} = \text{M}$) with two equivalents of $\text{U}^{\text{IV}}(\text{diox})_2$ ($\text{diox} = \text{O}(\text{CH}_2\text{CH}_2)_2\text{O}$, 1,4-dioxane) in THF or dioxane affords the green crystalline diuranium target complexes after work-up to remove salt by-products. The diuranium complexes $[\{\text{UI}_2(\text{S})_n\}_2\text{L}^{\text{R}}]$, $\mathbf{1}^{\text{R}}$, ($\text{R} = \text{P}$: $\text{S} = \text{THF}$, $n = 3$ or $\text{S} = \text{diox}$, $n = 2$; $\text{R} = \text{P}^*$: $\text{S} = \text{THF}$, $n = 2$; $\text{R} = \text{M}$: $\text{S} = \text{THF}$, $n = 2$) can be isolated after work-up in excellent yields (65–80%).

Second, treatment of the proligand $\text{H}_4\text{L}^{\text{R}}$ with two equivalents of the U^{IV} metallacyclic silylamide $\text{UN}''_2(\text{N}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2)$ results in full deprotonation of all four acidic phenols to afford the unsolvated, yellow, crystalline $[\{\text{UN}''_2\}_2\text{L}^{\text{R}}]$ $\mathbf{2}^{\text{R}}$ ($\text{R} = \text{P}, \text{P}^*, \text{M}$), after work-up to eliminate the volatile, hexane soluble by-product HN'' , in essentially quantitative yields.

Complexes $\mathbf{1}^{\text{R}}$ and $\mathbf{2}^{\text{R}}$ have been fully characterised, including by single crystal X-ray diffraction. The *in-situ* synthesis of the calcium salts are described below as they have proven ideal

metathesis precursors for some, since Group 1 bases often afford compounds that retain one or more bridging aryloxy protons.¹⁸

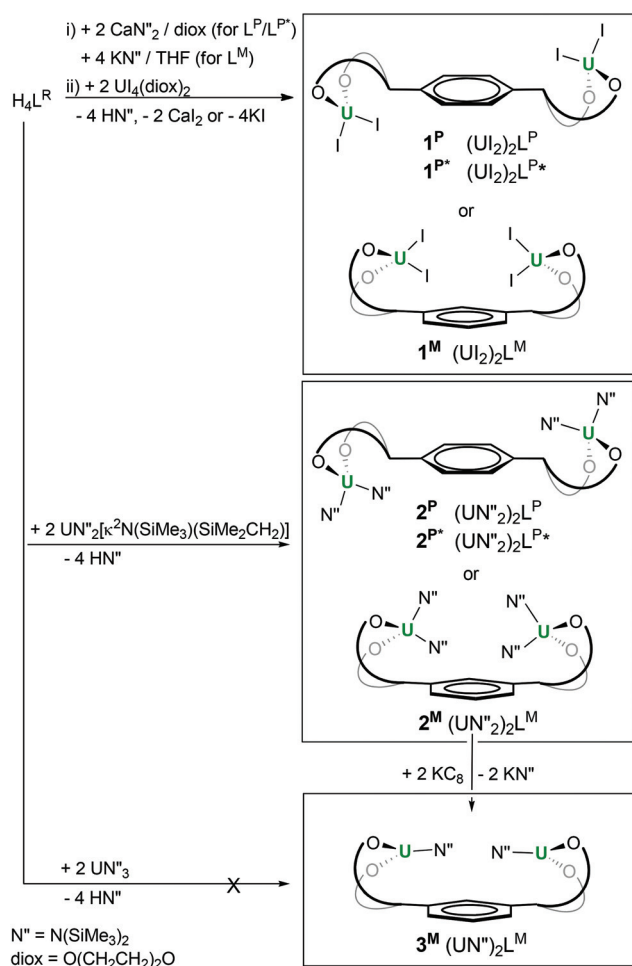
In our hands, direct syntheses of uranium(III) analogues of $\mathbf{1}^{\text{R}}$ and $\mathbf{2}^{\text{R}}$ from uranium(III) halide and amide starting materials were unsuccessful. We therefore investigated the electrochemical and chemical reduction of the uranium(IV) complexes. The $\text{U}^{\text{IV/III}}$ redox couple is known to range from -2.78 to -1.83 V *versus* ferrocene depending on the ligand environment.^{1,22,23} The cyclic voltammetry data show that the complexes $\mathbf{1}^{\text{R}}$ and $\mathbf{2}^{\text{R}}$ 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 $\text{U}^{\text{IV}}-\text{U}^{\text{IV}}$ 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 $\mathbf{2}^{\text{M}}$ with two equivalents of KC_8 affords dark purple di- U^{III} $[\{\text{UN}''_2\}_2\text{L}^{\text{M}}]$, $\mathbf{3}^{\text{M}}$ in 63% yield after workup, which has been characterised by multinuclear NMR spectroscopy and elemental analysis, Scheme 1.

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

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

Single crystals of $\mathbf{1}$ and $\mathbf{2}$ were grown, details for which are in the ESI†. The molecular structures of $\mathbf{1}^{\text{P}}$, $\mathbf{1}^{\text{P}^*}$, $\mathbf{1}^{\text{M}}$, $\mathbf{2}^{\text{P}}$ and $\mathbf{2}^{\text{M}}$ are shown in Fig. 2 and 3; that for $\mathbf{2}^{\text{P}^*}$ is in the ESI† along with the structure of a dioxane solvate of $\mathbf{1}^{\text{P}}$, $\mathbf{1}^{\text{P}}(\text{dioxane})$.

The uranium centre in $\mathbf{1}^{\text{P}}$ is seven-coordinate, adopting square face monocapped trigonal prismatic geometry, whereas the six coordinate uranium centres in $\mathbf{1}^{\text{P}^*}$ and $\mathbf{1}^{\text{M}}$ adopt distorted octahedral geometry. The dioxane adduct of $\mathbf{1}^{\text{P}}$, $\mathbf{1}^{\text{P}}(\text{dioxane})$, also displays six coordinate uranium centres in distorted octahedral geometry. The equatorial plane is occupied by the aryloxy and iodide ligands, and the axial positions occupied by coordinated dioxane molecules. The exo-



Scheme 1 Syntheses of $(\text{U}^{\text{IV}})_2$ and $(\text{U}^{\text{III}})_2$ complexes of bridged tetra-aryloxy ligands L^{P} , L^{P^*} and L^{M} .

Table 1 Selected reduction potentials *versus* Fc^+/Fc measured in THF using $0.1 \text{ M } [\text{tBu}_4\text{N}][\text{BPh}_4]$ as the supporting electrolyte

Compound	Reduction potential at $100 \text{ mV s}^{-1}/\text{V}$
$\mathbf{1}^{\text{M}}$	-2.03
$\mathbf{2}^{\text{M}}$	-1.99
$\mathbf{1}^{\text{P}}$	-2.05
$\mathbf{2}^{\text{P}}$	-2.05
$\mathbf{2}^{\text{P}^*}$	-1.53



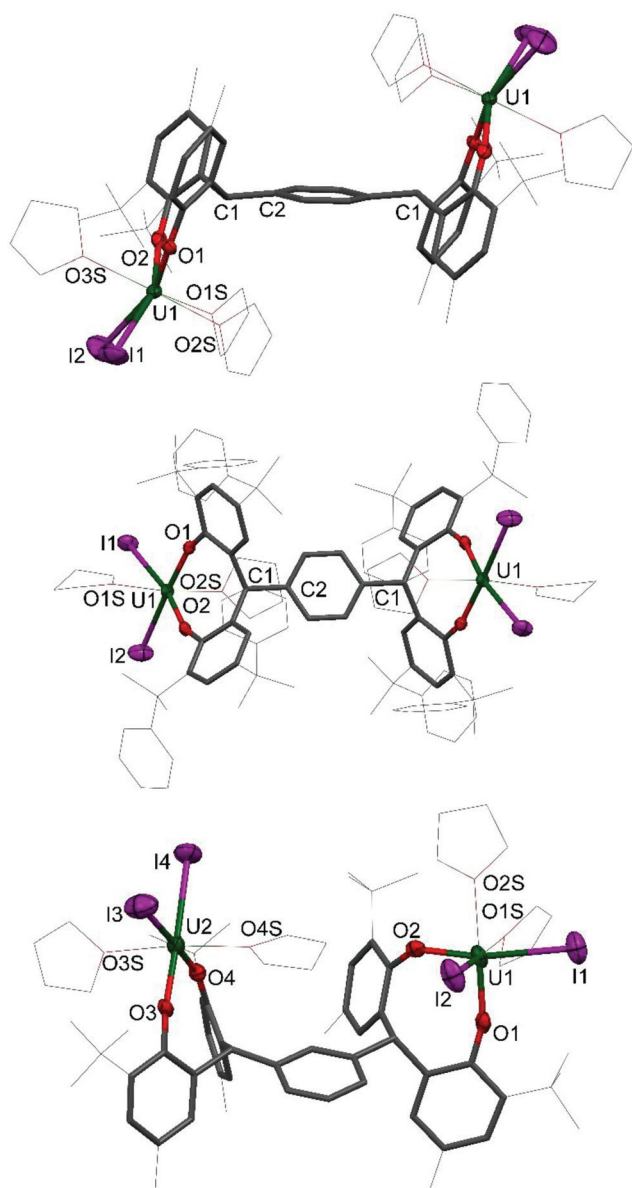


Fig. 2 Solid-state structures of **1^P** (upper, side view), **1^{P*}** (middle, top view) and **1^M** (lower, side view). For clarity, hydrogen atoms and lattice solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability, the remaining atoms and bonds shown as capped stick or wireframe). Selected bond lengths (Å) and angles (°) for **1^P**: 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 **1^{P*}**: 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 **1^M**: 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).

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 ESI† 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 aryloxo and iodide ligands occupy the

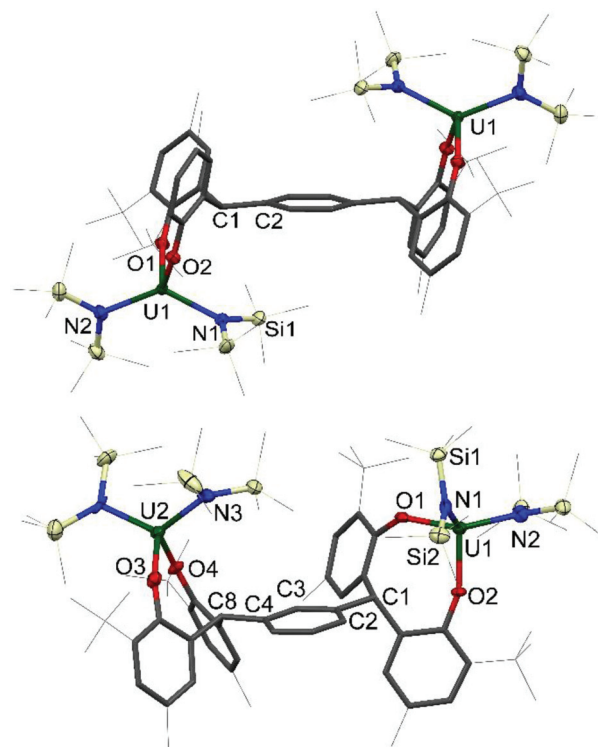


Fig. 3 Solid-state structures of **2^P** (upper, side view), and **2^M** (lower, side view). For clarity, all methyl groups, hydrogen atoms, and lattice solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability, the remaining atoms and bonds shown as capped stick). For **2^{P*}** see ESI.† Selected bond lengths (Å) and angles (°) for **2^P**: 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); **2^M**: 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).

equatorial plane about U2 with the axial positions occupied by THF donor molecules in a *trans* arrangement. The THF donors about the U1 centre, however, are mutually *cis* occupying one equatorial and one axial position. The two iodides and one aryloxo group occupy the three remaining equatorial positions and the other aryloxo occupies the axial position. This surprising feature results in unsymmetrical bond lengths and angles 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–C_{ipso} angle of 138.7(9)° compared to the average of the other three angles, 157.0(9)°.

The U–OAr bond distances in **1^P**, **1^{P*}** and **1^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(aryloxo) bis(iodo) complexes such as I₂U(ODtbp)₂(thf) (ODtbp = *O*-2,6-*t*Bu₂C₆H₄) with an average U–O bond length of 2.076 Å,¹⁴ and I₂U(OAr)₂(thf)₃ (Ar = *O*-4-*t*BuC₆H₄, *O*-2,6-Me₂C₆H₃, C₆F₅) with average U–O distances of 2.068(8) Å, 2.091(8) Å and 2.120(6) Å respectively.²⁴



Distance (Å)/angle (°)	1p	1*	1m	2p	2*	2m
U-U	—	—	9.387	—	—	10.06
U-O	2.112	2.106	2.112	2.120	2.142	2.122
U-I	3.103	3.051	3.029	—	—	—
U-N	—	—	—	2.253	2.267	2.252
OUO	88.98	91.26	92.80	98.49	96.53	98.14
IUI	81.6	84.0	91.8	—	—	—
NUN	—	—	—	127.0	107.2	115.2
UOC	157.1	156.0	152.4	149.4	150.7	148.5

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^M complexes,^{18,20} 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.

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 4 Å molecular sieves. All solvents were degassed and stored for 2 days prior to use. d_6 -Benzene and d_8 -tetrahydrofuran were freeze pump thaw degassed, refluxed over potassium for 24 hours and distilled by trap to



1^{P*} (U₂I₄L^{P*})

Made analogously to U₂I₄L^P. Green plates suitable for X-ray diffraction were grown from slow evaporation of a THF solution.

¹H NMR (*d*₈-THF, 329 K, 500 MHz) δ 7.13 (Aryl H, 2H), 7.08 (Aryl H, 8H), 6.98 (Aryl H, 4H), 6.94 (Aryl H, 4H), 6.84 (Aryl H, 2H), 6.69 (Aryl H, 2H), 6.57 (Aryl H, 8H), 6.47 (Aryl H, 4H), 6.42 (Aryl H, 2H), 5.65 (Aryl H, 4H), 2.31 (Ar₃CH₂, 1H), 2.21 (Ar₃CH₂, 1H), 1.45 (CH₃, 12H), 1.31 (Aryl H, 4H), 1.18 (CH₃, 12H), 1.02 (Aryl H, 4H), 0.78 (Aryl H, 4H).

Elemental analysis: C 53.62%, H 5.02% calculated. C 53.32%, H 5.16% found.

1^M (U₂I₄L^M)

A Schlenk flask was charged with H₄L^M (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, UI₄(OC₄H₈O)₂ (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 pale 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 (*d*₈-THF, 329 K, 500 MHz) δ 13.94 (Aryloxide H, 4H), 7.53 (Aryloxide 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 (Ar₃CH₂, 2H).

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

2^P (U₂N''₄L^P)

A Schlenk flask was charged with H₄L^P (100 mg, 0.133 mmol) and U(N'')₂(N{SiMe₃}SiMe₂CH₂) (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''₄L^P 2^P in 65% yield (247 mg). The yellow blocks were suitable for single crystal X-ray diffraction analysis.

¹H NMR (C₆D₆, 500 MHz) δ 35.34 (Aryloxide H, 4H), 19.97 (Aryloxide H, 4H), 5.51 (Aromatic H, 4H), 4.40 (CH₃, 12H), -2.90 (Ar₃CH₂, 2H), -9.62 (*t*-BuH, 36H), -18.89 (SiCH₃, 72H).

²⁹Si NMR (C₆D₆, 99.4 MHz) δ -234.6 (Me₃Si).

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

2^M (U₂N''₄L^M)

Made by an analogous procedure with recrystallisation by slow diffusion of hexane vapour into concentrated THF solu-

tions to give green blocks suitable for single crystal X-ray diffraction analysis in 60% yield.

¹H NMR (C₆D₆, 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 (Aryloxide H, 4H), 1.50 (CH₃, 12H), -3.03 (Ar₃CH₂, 2H), -9.76 (*t*-BuH, 36H), -18.51 (SiCH₃, 72H) ppm; ²⁹Si NMR (C₆D₆, 99.4 MHz) δ -230.8 (Me₃Si).

Elemental analysis: C 48.85%, H 7.23%, N 3.00% calculated. C 48.66%, 6.91%, N 2.78% found.

2^{P*} (U₂N''₄L^{P*})

Made by an analogous procedure. Green plates isolated in 65% yield. Single crystals suitable for X-ray diffraction were grown by diffusion of hexanes into a THF solution of 2*.

¹H NMR (500 MHz, THF-*d*₈) δ 13.12 (Aromatic H, 4H), 11.89 (Aromatic H, 8H), 9.05 (Aromatic H, 4H), 7.56 (Me H, 12H), 7.16 (Aromatic H, 8H), 7.05 (Aromatic H, 4H), 6.74 (Aromatic H, 4H), 6.65 (Aromatic H, 8H), 6.37 (Me H, 12H), 1.59 (Me H, 12H), 1.26 (Me H, 12H).

Elemental analysis: C 60.68%, H 6.92%, N 2.21% calculated. C 60.51%, H 6.93%, N 1.99% found.

3^M (U₂N''₂L^M)

A Schlenk flask was charged with U₂N''₄L^M (274 mg, 0.223 mmol) and KC₈ (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%).

¹H NMR (C₆D₆, 500 MHz) δ 22.22 (Aromatic H, 2H), 17.50 (Aromatic H, 1H), 14.62 (Aromatic H, 1H), 11.85 (Aryloxide H, 4H), 7.50 (Aryloxide H, 4H), 2.11 (CH₃, 12H), 0.89 (Ar₃CH₂, 2H), -7.94 (s, 36H, *t*-Bu-H), -13.33 (s, 36H, SiCH₃) ppm; ²⁹Si NMR (C₆D₆, 99.4 MHz) δ -99.93 (Me₃Si).

Elemental analysis: C 49.66%, H 6.38%, N 1.81% calculated. C 49.66%, H 6.38%, N 1.81% found.

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Notes and references

- 1 P. L. Arnold, *Chem. Commun.*, 2011, **47**, 9005.
- 2 H. S. La Pierre and K. Meyer, in *Progress in Inorganic Chemistry*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2014, vol. 58.



- 3 W. J. Evans, S. A. Kozimor and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 14264–14265.
- 4 J. G. Brennan, R. A. Andersen and J. L. Robbins, *J. Am. Chem. Soc.*, 1986, **108**, 335–336.
- 5 P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci.*, 2011, **2**, 77–79.
- 6 S. M. Mansell, J. H. Farnaby, A. I. Germeroth and P. L. Arnold, *Organometallics*, 2013, **32**, 4214–4222.
- 7 P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nat. Chem.*, 2012, **4**, 668–674.
- 8 N. Tsoureas, O. T. Summerscales, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2013, **32**, 1353–1362.
- 9 N. Tsoureas, L. Castro, A. F. R. Kilpatrick, F. G. N. Cloke and L. Maron, *Chem. Sci.*, 2014, **5**, 3777.
- 10 P. L. Arnold, C. J. Stevens, J. H. Farnaby, M. G. Gardiner, G. S. Nichol and J. B. Love, *J. Am. Chem. Soc.*, 2014, **136**, 10218–10221.
- 11 P. L. Arnold, J. H. Farnaby, R. C. White, N. Kaltsoyannis, M. G. Gardiner and J. B. Love, *Chem. Sci.*, 2014, **5**, 756–765.
- 12 W. G. Van Der Sluys and A. P. Sattelberger, *Chem. Rev.*, 1990, **90**, 1027–1040.
- 13 W. G. Van Der Sluys, C. J. Burns, J. C. Huffman and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1988, **110**, 5924–5925.
- 14 L. R. Avens, D. M. Barnhart, C. J. Burns, S. D. McKee and W. H. Smith, *Inorg. Chem.*, 1994, **33**, 4245–4254.
- 15 A. Walshe, J. Fang, L. Maron and R. J. Baker, *Inorg. Chem.*, 2013, **52**, 9077–9086.
- 16 R. J. Baker and A. Walshe, *Chem. Commun.*, 2012, **48**, 985–987.
- 17 M. Janssen, L. Bini, B. Hamers, C. Müller, D. Hess, A. Christiansen, R. Franke and D. Vogt, *Tetrahedron Lett.*, 2010, **51**, 1971–1975.
- 18 J. Zhang, C. Jian, Y. Gao, L. Wang, N. Tang and J. Wu, *Inorg. Chem.*, 2012, **51**, 13380–13389.
- 19 L. Tang, E. P. Wasserman, D. R. Neithamer, R. D. Krystosek, Y. Cheng, P. C. Price, Y. He and T. J. Emge, *Macromolecules*, 2008, **41**, 7306–7315.
- 20 Y. Al-Khafaji, X. Sun, T. J. Prior, M. R. J. Elsegood and C. Redshaw, *Dalton Trans.*, 2015, **44**, 12349–12356.
- 21 A. Cottone and M. J. Scott, *Organometallics*, 2000, **19**, 5254–5256.
- 22 D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez and J. L. Kiplinger, *Organometallics*, 2004, **23**, 5142–5153.
- 23 A. Vallat, E. Laviron and A. Dormond, *J. Chem. Soc., Dalton Trans.*, 1990, 921–924.
- 24 D. D. Schnaars, G. Wu and T. W. Hayton, *Dalton Trans.*, 2009, 3681.
- 25 J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, **114**, 10811–10821.
- 26 P. B. Hitchcock, M. F. Lappert, A. Singh, R. G. Taylor and D. Brown, *J. Chem. Soc., Chem. Commun.*, 1983, 561–563.
- 27 A. J. Lewis, K. C. Mullane, E. Nakamaru-Ogiso, P. J. Carroll and E. J. Schelter, *Inorg. Chem.*, 2014, **53**, 6944–6953.
- 28 R. K. Rosen, R. A. Andersen and N. M. Edelstein, *J. Am. Chem. Soc.*, 1990, **112**, 4588–4590.
- 29 B. S. Newell, A. K. Rappé and M. P. Shores, *Inorg. Chem.*, 2010, **49**, 1595–1606.
- 30 S. M. Mansell, B. F. Perandones and P. L. Arnold, *J. Organomet. Chem.*, 2010, **695**, 2814–2821.
- 31 O. Michel, C. Meermann, K. W. Törnroos and R. Anwender, *Organometallics*, 2009, **28**, 4783–4790.
- 32 M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031–2038.
- 33 A. Dormond, A. El Bouadili, A. Aaliti and C. Moise, *J. Organomet. Chem.*, 1985, **288**, C1–C5.
- 34 L. M. Viculis, J. J. Mack, O. M. Mayer, H. T. Hahn and R. B. Kaner, *J. Mater. Chem.*, 2005, **15**, 974.

