Carbon Dioxide Activation by a Uranium(III) Complex Derived from a Chelating Bis(aryloxide) Ligand

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Supporting Information Placeholder

ABSTRACT: The new dianionic ligand, C₆H₄(p-C(CH₃)₃C₆H₄Me₃O)₂ (p-Me₂bp), featuring two aryloxide donors and a central arene ring, has been synthesized, and used to prepare the mixed-ligand U(III) compound, [U(Cp*)(p-Me₂bp)] which exhibits an η⁶-interaction with the uranium center. Reductive activation of CO₂ was investigated using [U(Cp*)(p-Me₂bp)] in supercritical CO₂, which gave a dinuclear uranium carbonate complex, {U(Cp*)(p-Me₂bp)}₂(μ-η²:η⁶-CO₂), cleanly and selectively. Reactivity studies in conventional solvents using lower pressures of CO₂ showed the formation of a rare U(IV) oxalate complex, {U(Cp*)(p-Me₂bp)}₂(μ-η²:η⁶-C₂O₂), alongside {U(Cp*)(p-Me₂bp)}₂(μ-η²:η⁶-CO₂). The relative ratio of the latter two products is temperature dependent: at low temperatures (-78 °C) oxalate formation is favored, whilst at room temperature the carbonate is the dominant product. The U(IV) iodide, [U(Cp*)(p-Me₂bp)]I, was also synthesized and used as part of an electrochemical study, the results of which showed that [U(Cp*)(p-Me₂bp)] has a U⁴⁺/U¹⁻ redox couple of -2.18 V vs FeCp₂⁺/⁰ as well as an possible electrochemically accessible U⁵⁺/U¹⁻ reduction process at -2.56 V vs FeCp₂⁺/⁰.

INTRODUCTION

Since the development of easily accessible U(III) starting materials, the field of uranium(III) chemistry has flourished, utilizing a wide range of ligands to stabilize uranium in this oxidation state—of particular current interest in the context of small molecule activation.¹ Aryloxide groups provide a hard oxygen donor atom, well suited to binding oxophilic uranium in the +3 and higher oxidation states,²,³ and homoleptic U(III) derivatives of bulky aryloxide ligands have been shown to reductively activate N₂ and CO₂, and insert CO₂.⁴ Meyer et al. pioneered the use of the tripodal ligands derived from phenols of the type ((R³ArOH)₃mes) which incorporates three aryloxide arms and a central arene ring which provides additional electronic stabilization via a δ interaction with the uranium center.⁵ This approach has led to the successful synthesis of a U(II) complex,⁶ and the uranium(III) complex [(Ad₃Me₃ArO)₂mes]U which electrocatalytically generates dihydrogen from water.⁷ Arnold et al. have also reported a tetraaryloxide variant which facilitates the complexation of two uranium centers.⁸

Uranium(III) complexes featuring a variety of ancillary ligand sets have been shown to disproportionate CO₂ to form CO₃²⁻ complexes and CO.⁹ Furthermore, we and others have also reported the reductive coupling of CO₂ to yield bridging oxalate U(IV) complexes, which is a rare transformation in uranium chemistry (and indeed in the d-block elements).¹⁰¹¹ Our work to date on small molecule activation chemistry has focused on the use of a "soft" ligand set around U(III), in the form of a mixed sandwich framework incorporating a cyclopentadienyl ligand and a dianionic aromatic...
cyclooctatetraene or pentalene ligand.10,12 Hence we were interested in the effect of changing the dianionic ligand in the latter for an alternative, "harder" chelating ligand with tunable steric demands. Here we report a new bidentate ligand featuring two dimethyl functionalized aryloxide rings and a central arene ring, and the synthesis of its Cp*U(III) derivative and reactivity towards CO2 thereof. Beyond simply providing steric bulk, the arene is centrally situated to promote stabilization of low valent U centers via δ-backbonding (vide supra).

RESULTS AND DISCUSSION

Ligand synthesis

The neutral bisphenol (p-Me2-bp)H2 (1) was prepared via a modification of a procedure reported in the patent literature.13 α,α,α',α'-Tetramethyl-1,4-benzenedimethanol undergoes an acid catalyzed condensation reaction with 2,4-dimethylphenol (excess, as solvent) to give crude 1 (Scheme 1). Recrystallization from Et2O gave 1 as white crystals in 40-50% overall yield, with analytical purity confirmed by elemental analysis.

Figure 1. ORTEP diagram for molecular structure of compound 1. Disordered C6D6 solvent omitted for clarity; thermal ellipsoids at 50%. The numbering scheme is used for NMR spectroscopy assignments. Selected structural parameters (Å, deg): C12–C13 = 1.390(17), C12–C14 = 1.3933(18), C6–C9–C12 = 109.05(10), C1–O1 = 1.3843(15).

1H and 13C NMR spectroscopic data show two-fold symmetry, indicating that in solution the phenol rings freely rotate around the C(CH3)2 units linking them and the central arene ring.

Bisphenol 1 is readily deprotonated by 2 equivalents of KH in 1,2-dimethoxyethane (DME) to give the dipotassium salt (p-Me2-bp)K2(DME)n (2) as a fractional solvate (n = 1.5 - 2) in 85-95% yield. The crude material thus obtained returned elemental analyses which were slightly high in C and H, however it was successfully used in subsequent salt metathesis reactions without further purification. Compound 2 is sufficiently soluble in d5-pyridine to allow the degree of DME solvation in individual samples to be determined by 1H NMR spectroscopy, however, these solutions were too dilute to allow acquisition of 13C NMR spectroscopic data.

Mixed Ligand uranium(III) complex

Dipotassium salt 2 reacts with 1 equivalent of [UCp*]2(THF)3 (prepared in situ in THF) to give, after workup, the mononuclear U(III) complex [U(Cp*)(p-Me2-bp)] (3) as dark green-black plates in yields of 60 - 75% (Scheme 2).

Scheme 1. Synthesis of (p-Me2-bp)H2 (1)

\[
\text{HO} \quad \text{OH} \quad \text{OH} \quad \text{(excess, as solvent)} \quad 150^\circ \text{C}, 4 \text{~h} \quad \text{HO} \quad \text{OH}
\]

\[\text{p-TSA} = \text{para-Toluenesulfonic acid}\]

The solid state molecular structure of 1 was determined by X-ray diffraction, and is shown in Figure 1, together with selected bond lengths and angles. The phenol rings adopt an antiperiplanar conformation with respect to the central arene, and the quaternary sp3 carbon (C9) linking the phenol and arene rings is tetrahedral (C6–C9–C12 angle of 109.05(10)) consistent with a lack of strain. The central arene C–C distances are essentially the same as those observed in the solid state structure of p-xylene (1: av. 1.3930 Å; p-xylene: av. 1.392 Å) and the central arene displays almost no ring torsion (1: +/- 0.15°, p-xylene: +/- 0.10°).14 The two phenol rings are related via a crystallographic inversion center and the angle between the planes of the central arene and each phenol ring is 81.51°.
The ¹H NMR spectrum of paramagnetic 3 contains resonances over the range 18.3 to −13.5 ppm. Both the CH₃ groups of the bridging arms and the central arene protons appear as two distinct sets of resonances due to the reduced symmetry imposed by a rigid arylxide and Cp⁺ coordination environment.

**Carbon dioxide activation**

The reaction of gases with f-element complexes in the solid state (i.e. solvent-free) has recently been reported as a potentially high yielding and selective approach to exploring subsequent reduction chemistry.¹⁹ Recent work from our own laboratory has used supercritical CO₂ to promote the exclusive formation of U(IV) bridging carbonate complexes,¹⁰ and this approach was used to investigate the reductive activation of CO₂ by 3 (Scheme 3).

**Scheme 3. Synthesis of [U(Cp*)(p-Me₂bp)]₂([μ-η³:η³-CO₃]) (4)**

The reaction of solid 3 in supercritical CO₂ resulted in an immediate color change from green-black to orange, and the resultant orange powder contained only one major product (>96% by ¹H NMR spectroscopy), confirming the highly selective nature of the reaction. The product was identified as the bridging carbonate complex [U(Cp*)(p-Me₂bp)]₂([μ-η³:η³-CO₃]) (4) by X-ray diffraction studies crystals of 4.CdH₆ obtained from CdH₆ at ambient temperature. The degree of solvation in 4.CdH₆ was determined by ¹H NMR spectroscopy in d₅-THF, and satisfactory elemental analysis obtained for this solvate.
shift expected for a paramagnet, but there was no resolution to a discrete, higher symmetry species even at 100 °C.

The reductive activation of 13CO2 by 3 was also investigated in solution (Scheme 4). An excess (ca. 2 equivalents) of 13CO2 was added to a solution of 3 in Cd(DCD): at −78 °C using a Töpler pump. Upon warming to ambient temperature the colour changed from black to orange, and the 1H NMR spectrum showed the presence of a mixture of products, including 4 (ca. 40%). In addition to excess 13CO2 and free 13CO (arising from the reductive disproportionation of 13CO2 to form 4), three paramagnetically shifted resonances were observed in the 13C[1H] NMR spectrum of the reaction mixture. A singlet at −101 ppm, which was assigned to the bridging 13CO in 4, and two mutually coupled doublets at −130 and −199 ppm; all three resonances remained unchanged in the 1H coupled spectrum. The observed coupling in the latter is consistent with coupling between two proximal, inequivalent 13C atoms (JCC = 70 Hz), thus pointing towards the formation of an oxalate complex resulting from the reductive coupling of 13CO2.

Figure 3. ORTEP diagram for molecular structure of compound 4; 50 % thermal ellipsoids shown. Solvent masking was employed to remove a highly disordered CdH6 from the refinement. Selected crystallographic units (Å, deg): average U–O(aryloxide) = 2.175, η1–Cp–O5 2.162(11), average η2–U–O = 2.448, average U–C(arene) = 3.124, Ct(arene)–U = 2.7902(3), Cτ(Cp*)–U = 2.4958(3), O1–U1–O2 = 161.6(3).

The solid state molecular structure of 4 is shown in Figure 3, together with selected bond distances and angles, and reveals a dinuclear structure with a η1-η2-bound carbonate bridging two uranium centers. The central CO2− unit is disordered in the crystal, resulting in superposition of η1-η2 and η2-η3 binding modes with 50:50 occupancy. The resulting model required isotropic refinement for the central carbonate (which has a regular planar triangular structure), and as a result the bond lengths and angles within the central carbonate unit cannot be determined accurately. The η1–U–O distance (2.162(11) Å) is shorter than the η2–U–O distances (av. 2.448(15) Å), a feature which was also observed in the mixed sandwich U(IV) carbonate complex [{U(η1–Cp)5H5{SiPrMe2–1,4}2(η2–C6Me5H)}2(μ-η1-η2-η3-CO3)3 (η3–C; av. 2.227(12) Å, η3: av. 2.422(10) Å). Each U center is chelated by a pair of bisaryloxy ligands (av. U–O = 2.175 Å), with the central U–arene interaction (av. U–C(arene) = 3.124 Å) significantly weaker than observed in 3, possibly due to the larger number of O donors and greater steric congestion in 4. This weak U–arene interaction is consistent with a pair of U(IV) centers each binding to a neutral, unreduced central arene. The complex is twisted around the central carbonate unit to minimise steric interaction between opposite bisaryloxy ligands (torsion as measured between opposite arene centroids Cτ(Arene)–Uτ–Cτ′(Arene) = 67.95°).

The torsion observed in the solid state structure of 4.CdH6 persists in solution. At 0 °C the 1H NMR spectrum of 4 (Cd(DCD)) consists of eight CH resonances, eight CH3 resonances and one resonance for the two freely rotating Cp* ligands paramagnetically shifted between 33.0 and −67.1 ppm. Above 10 °C the aryloxide resonances exhibited varying degrees of coalescence in addition to the changes in chemical

Scheme 4. Synthesis of {U(Cp*)(η-MeCp)}2(μ-η1-η2-CO3) (4) and {U(Cp*)(η-MeCp)}2(μ-η2-η2-C2O3) (5)

Fractional crystallization from benzene and then diethyl ether produced yellow crystals of the bridging oxalate complex 5 suitable for single crystal X-ray diffraction. The molecular structure is shown in Figure 3, together with selected bond lengths and angles, and shows a η2-η2 bridging oxalate unit in which the two carbons are inequivalent (the two Cp* ligands are effectively cis to one another), and hence consistent with 13C NMR data. Of note is the O1–C1–C2–O2 torsion angle of 22.2(12)° which is not seen in the molecular structures of {U(η5–C5H4{SiMe2–1,4}2(η3–C5Me5Pr)}3(μ-η2-η2-C2O3)10 or {((η5–MeArO)2Cacn)U(η5–C5Me5Pr)}3(μ-η2-η2-C2O3)11} possibly due to the steric hindrance around the uranium center. The U–O(oxalate), and oxalate C–C and C–O bonds are, however, consistent with those found in the latter U(IV) oxalate complexes. The arene centroid to uranium distance of 3.151 Å indicates that there is no interaction between the uranium center and the central arene ring in 5.
To gain further insight into the distribution of products 4 and 5 formed from 3 and $^{13}$CO$_2$, the reaction was repeated but the reaction mixture was allowed to react at $-78^\circ$C for two days followed by slow warming to room temperature over one day. This furnished a mixture of 4:5 in a ratio of 30:70 as judged by the relative integration of the Cp$^*$ resonances in the $^1$H NMR spectrum of the crude reaction mixture. When addition of $^{13}$CO$_2$ to 3 at $-78^\circ$C was followed by rapid equilibration to room temperature the ratio of 4:5 was found to be 83:17 suggesting that 5 is the kinetic product while 4 is the thermodynamic product. The above observations suggest that the formation of 4 competes with the formation of 5 and the two pathways can be kinetically manipulated.

**Uranium(IV) iodide complex**

An attempt to prepare 3 using DME as solvent instead of THF using an equimolar amount of 2 and [U(Cp*)I$_2$(DME)$_2$] produced in-situ from UI$_3$ and KCp$^*$ in DME, resulted in white solids (presumed to be KI) and a dark brown solution which contained several new products, but no 3 by $^1$H NMR spectroscopy (Scheme 5). The uranium (IV) iodo complex 6 was isolated from this solution as a microcrystalline red powder in 29% yield, and its formation from a U(III) starting material must presumably involve a disproportionation reaction, thus explaining the modest yield of 6. Single crystals of 6 suitable for X-ray diffraction were obtained from THF and furnished 6.THF which was used for NMR and MS studies. Satisfactory elemental analysis results were obtained for 6.THF.

The molecular structure of 6 displays a syn-aryl oxide chelating to a U center which is $\eta^6$-bound to the central arene weakly (av. U–C(arene) = 2.985 Å), consistent with a U(IV) center (Figure 4). The U–O distances (av. 2.149 Å) are similar to those observed in the U(IV) complex 4 and the U–I bond length of 3.0573(6) Å is typical for a U(IV) iodide, e.g. 3.059(2) Å in Cp$_3$UI$_3$. Complex 6.THF is soluble in ethers and aromatic solvents, and the $^1$H NMR spectrum (CD$_2$Cl$_2$) of 6.THF shows eleven peaks paramagnetically shifted over the range 37.2 to $-64.9$ ppm. Two sets of meso-CH$_3$ and central arene proton resonances indicate a nonfluctional bisaryl oxide coordination environment, as observed for 3.

**Scheme 5.** Synthesis of [U(Cp*)(p-Me$_2$bp)]I (6)

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**Electrochemistry**

To investigate the redox behavior of the bis(aryl oxide)/Cp$^*$ complexes and enable comparison with similar U(III) and U(IV) systems, voltammetric data for 3, 4, 5 and 6 were obtained in [*Bu$_4$N][B(C$_6$F$_5$)$_4$]/THF. Tabulated...
electrochemical data can be found in the Supporting Information.

The cyclic voltammogram of 3 is quite complex and displays several processes as shown in Figure 5. Four quasi-reversible processes were observed at −2.56, −2.18, −1.71 and +0.13 V vs FeCp₂^{+/0}. In addition, the CV of 3 shows a minor oxidation feature at ca. −1 V vs FeCp₂^{+/0}.

Figure 5. Overlaid CV scans (10 cycles) for 3 in THF / 0.05 M [¹⁷Bu₃N][B(C₆F₅)₄], scan rate 100 mV s⁻¹.

Cyclic voltammetry was carried out on the U(IV) derivative 6 to gain insight into the nature of the processes seen in 3. Complex 6 shows an irreversible reduction wave at −2.19 V vs FeCp₂^{+/0} (Figure S4) which is in excellent agreement with the quasi-reversible process at −2.18 V vs FeCp₂^{+/0} seen in 3 and is assigned to the U(IV)/U(III) couple in this system. This value is similar to other U(IV)/U(III) redox couples found in other U(III) systems studied by us and others and is consistent with a strongly reducing metal center. Further supporting this assignment is the observation of a single quasi-reversible reduction process at −2.19 V vs FeCp₂^{+/0} in the dinuclear U(IV) complex, 4 (Figure S2).

Upon scanning to more negative potentials 3 and 6 showed a quasi-reversible process observed at −2.56 and −2.59 V vs FeCp₂^{+/0} respectively. This process lies at an extremely negative potential and may be attributable to a ligand based reduction, however, the free ligand 2 did not show a cathodic process within this potential region (Figure S1). Another possibility is a U(III)/U(II) reduction process, and Meyer and co-workers have recently reported a trivalent uranium monocyclopentadienyl complex derived from the chelating tris(aryloxide)arene ligand, [[(ArO)₃Mes]U(II)], which shows a nearly reversible and chemically accessible reduction at −2.495 V vs FeCp₂^{+/0}.

When 4 was studied in 0.1 M [¹⁷Bu₃N][PF₆] / THF the first U(IV)/U(III) reduction event occurs at −2.25 V vs FeCp₂^{+/0} (Figure S3). For comparison reduction processes in the carbonate-bridged complexes based on the [U(η⁶-C₅H₅)(SiMe₂(1,4,1)R)] (R = Et, 'Pr or 'Bu) mixed-sandwich ligand system were observed between −2.11 and −2.17 V vs FeCp₂^{+/0} in 0.1 M [¹⁷Bu₃N][PF₆] / THF.

CONCLUSION

The combination of the soft pentamethylcyclopentadienyl ligand and a hard, chelating aryloxide ligand affords the U(III) complex [U(Cp*)(p-Me₂-bp)] whose U(IV)/U(III) redox couple is essentially identical to that of the mixed sandwich complexes of the type U(η₆-C₅H₅(SiR₂(1,4,1))(η-6-C₅Me₂R)). The work presented here demonstrates that the new ligand, (p-Me₂-bp)²⁻, in [U(Cp*)-(p-Me₂-bp)] can significantly alter the reactivity towards CO₂. The new bidentate ligand presented can be synthesized cleanly in moderate yield and provide a system analogous to the COT and pentalone based mixed sandwiches already established in actinide chemistry. Using this ligand a U(III) complex has been used to reductively disproportionate and reductively couple CO₂ to give uranium carbonate and oxalate complexes respectively. Studies have shown reactivity towards CO₂ can be controlled via temperature. Electrochemical studies show the U(IV)/U(III) couple has a reduction potential of −2.18 V vs FeCp₂^{+/0}, indicating this system is an ideal candidate to support metal centers for the activation of small molecules.

Future studies will focus on the reactivity of [U(Cp*)(p-Me₂-bp)] towards other small molecules, alongside the modification of the (p-Me₂-bp)²⁻ ligand which may lead to the discovery of new reactivity towards substrates.
EXPERIMENTAL SECTION

General Information. All manipulations involving air- or moisture-sensitive materials were performed under an inert atmosphere of argon using standard Schlenk techniques, or in an MBraun N2 or Ar-filled glovebox. Solvents were dried over appropriate drying agents (NaK:5Et2O, pentane, Et2O, BuOMe; K: THF, benzene, toluene) before distilling under N2 and degassing before use. Solvents were stored over K mirrors with the exception of THF and Et2O, which were stored over activated 4Å molecular sieves. Deuterated solvents were dried over K, vacuum distilled and freeze-pump-thawed before storage under N2. NMR spectra were recorded on a Varian VNMRS 400 MHz spectrometer at 303 K, with 1H NMR spectra run at 399.5 MHz and 13C NMR spectra run at 100.5 MHz. Chemical shifts are quoted in parts per million and are referenced internally to residual protic solvent shifts (D) or deuterated solvent shifts (DCl). El-MS was performed by Dr. A. K. Abdul-Sada at the University of Sussex using a VG Autospec Fisons instrument (EI at 70 eV). Elemental analyses were performed by Mikroanalytisches Labor Pascher or Bristol University Microlaboratory. COCl2 (99.7% enrichment) gas was purchased from Eurostop and was transferred via an accurately calibrated Töpler pump. The reaction with supercritical CO2 (99.999% BOC) was performed in a 10 mm sapphire NMR tube equipped with a titanium valve, connected to a high pressure stainless steel line equipped with a high pressure piston pump (High Pressure Equipment Company).

Caution: Depleted uranium is a weak α-emitter (4.197 MeV) with a half-life of 4.47 × 1017 years. All manipulations should be undertaken in a well ventilated and monitored fume hood or under an inert atmosphere in a glovebox, and uranium containing residues should be disposed of according to local regulations.

(p-Me2Bp)2H (1). a,a,a’,a’-tetramethyl-1,4-benzenediamethanol (10 g, 50 mmol) dissolved in 2,4-dimethylphenol (20 g) was added with stirring over 4 h to 2,4-dimethylphenol (45 g) containing p-tolylsulfonic acid (0.30 g, 1.5 mmol, 3 mol %) at 150 °C. NaClO4 (0.60 g, 5 mmol) was added to neutralise the catalyst and the mixture stirred another 40 min. Excess 2,4-dimethylphenol was distilled off under vacuum and the solid, beige coloured residue taken up in Et2O, rinsed with NaOH (0.6 M, 1 x 100 mL), water (3 x 150 mL), brine (2 x 100 mL), under vacuum and the solid, beige coloured reside taken up in Et2O and stripped to provide a crude white solid. Recrystallisation from Et2O at -50 °C and drying for 2 h (80 °C, 0.01 mbar) provided 1 as a white powder (9.5 g, 23.6 mmol, 47 %).

1H NMR (assigned according to Figure 1) (CDCl3, 303 K): δ 7.36 (s, 4H, H13,14), 7.18 (s, 2H, H5), 6.95 (s, 2H, H3), 4.28 (s, 2H, OH), 2.39 (s, 6H, H8), 2.18 (s, 6H, H7), 1.73 ppm (s, 12H, H10,11).

13C[1H] NMR (assigned as per Figure 1) (CDCl3, 303 K): δ 149.9 (C2), 147.3 (C12), 134.6 (C6), 130.4 (C3), 129.1 (C4), 127.1 (C13,14), 126.2 (C1), 124.9 (C5), 41.7 (C9), 30.0 (C10,11), 21.2 (C8), 16.4 ppm (C7). Anal. Calcd for CaH24O2: C, 83.54; H, 8.51. Found: C, 83.26; H, 8.49. MS (El): m/z 402 (M+).

(p-Me2Bp)K2(DME)2 (2). A solution of 1 (2.66 g, 6.62 mmol) in DME (40 mL) was added dropwise over 1 h to a stirred suspension of KH (0.533 g, 13.3 mmol) in DME (60 mL). After 18 h the reaction mixture was cooled to -30 °C for 1.5 h, filtered through a frit, and the solids thus obtained dried in vacuo for 2.5 h to give the product as a white powder of sufficient purity for further reactions (3.95 g, 95 %).

1H NMR (CD3N, 303 K): δ 7.43 (s, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 3.51 (s, 6H, DME CH3s, 6H, DME CH2s), 3.29 (s, 9.9H, DME CH3s), 2.54 (s, 6H, Ar-CH3), 2.33 (s, 6H, Ar-CH3) 1.90 (s, 12H, CH(C2H5)s). Anal. Calcd for Cs6H14O2K2: C, 66.2; H, 7.79. Found: C, 69.2; H, 8.19.

[U(Cp*)(p-Me2Bp)]2CO3 (4). A deep blue-green solution of [U(Cp*)(THF)]2 was prepared by adding THF (70 mL) to KCO3 (0.35 g, 2.0 mmol) and U1 (1.24 g, 2.0 mmol), with overnight stirring followed by filtration. To this was added (p-Me2Bp)K2(DME)2 (1.12 g, 1.7 mmol, 0.85 equivalents) as a suspension in THF (15 mL). The dark brown reaction mixture was stirred overnight before being stripped to dryness, taken up in pentane (60 mL), filtered through Celite and reduced to ca. 15 mL. Slow cooling to -50 °C gave 3 as dark olive green platelets which were rinsed with pentane and dried in vacuo (0.94 g, 72 %). Analytically pure 3 was obtained by recrystallisation from pentane at -50 °C. 1H NMR (CD3CN, 303 K): δ 18.28 (s, 2H, Ar-H), 10.05 (s, 2H, Ar-H), 9.05 (s, 2H, Ar-H), 4.54 (s, 6H, CH3), 4.14 (s, 6H, CH3), -2.24 (s, 6H, CH3), -3.89 (s, 15H, Cp*), -13.56 (s, 2H, Ar-H). Anal. Calcd for C20H20O2U3: C, 58.98; H, 6.12. Found: C, 58.96; H, 6.35.

[U(Cp*)(p-Me2Bp)]2CO3 (5). A 50 ml Young’s ampoule with a was charged with 3 (300 mg, 0.386 mmol) and toluene (3 ml). The solution was cooled to -78 °C and degassed and 4 equivalents of CO2 gas added. A colour change from black to orange was observed shortly after the addition of CO2. The reaction mixture was left to stir at -78 °C for 2 d and then at room temperature for 1 d. Volatiles were removed in vacuo, benzene (5 ml) was added and the suspension heated at almost reflux and left to cool to ambient temperature overnight to afford 4. CaH24 was obtained by recrystallisation from acetone. The latter was collected by filtration, washed with benzene (3 x 3 ml) and the washings combined with the original filtrate. This solution was then concentrated to ca. 3 ml and allowed to stand at room temperature overnight, depositing a further, small amount of the CaH24 which was filtered off. Finally, the filtrate from this, second crystallization was pumped to dryness, dissolved in Et2O (3 ml) and stored at -35 °C to give small yellow crystals of 5 (52 mg, 10 %). 1H NMR (CD3CN, 273 K): δ 39.34 (s, 12 H, CH3), 31.67 (s, 4 H, Ar-H), 25.45 (s, 4 H, Ar-H), 22.68 (s, 12 H, CH3), 14.82 (s, 12 H, CH3), -3.77 (s, 12 H, CH3), -7.62 (s, 30 H, Cp*), -53.91 (s, 4 H, Ar-H), -62.33 (s, 4 H, Ar-H). Anal. Calcd for C90H84O2U2: C, 57.28; H, 5.79. Found: C, 57.00; H, 6.02.


