Activation of carbon dioxide by new mixed sandwich uranium(III) complexes incorporating cyclooctatetraenyl and pyrrolyl, phospholide, phospholide, or arsaside ligands†

Rachel J. Kahan, a F. Geoffrey N. Cloke, * a S. Mark Roe b and François Nief b

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complex 1 displayed a different pattern of proton resonances, indicative of a more complex structure in solution (vide infra).

All three complexes form stable adducts with THF, 1-THF, 2-THF, and 3-THF, respectively. Mass spectrometry and microanalysis supported the formulation of 1-3, and the molecular structures were confirmed by single crystal X-ray diffraction studies on the THF complexes, and the structures are shown in Fig. 1 with selected data in Table 1.

High resolution data could not be obtained for 1-THF and the molecular structure of this complex therefore only illustrates connectivity. The molecular structure of 2-THF features a phosphonyl ring disordered over two positions, which has been modelled accordingly (see ESI† for full details). The three complexes are isostructural, and only small differences are observed between 2-THF and 3-THF, due to the lengthening of the U–E bond on descending the pnictogen group. These structures are similar to their carbocyclic analogue [U(COT)(CpPMe4)(THF)], demonstrating that incorporation of a pnictogen has not significantly altered the overall structural properties of the complexes. Comparison of 2-THF to the only other mixed-sandwich complex featuring a heterocyclic ligand, the U(IV) complex [U(COT)(CpPMe4)(BH4)(THF)], illustrates a similar U–Ct2 bond length (2.610(8) Å).6 However, the Ct1–U–Ct2 angle is more acute (135.6(3)°) and the U–Ct1 distance is longer (2.013(9) Å) presumably due to the presence of the BH4 group.

The molecular structure of base-free 1 was also determined by single crystal X-ray diffraction, and shows that this complex is dimeric in the solid-state (see Fig. 2). As a consequence of the dimeric structure, the Ct1–U–Ct2 angle is more acute than those in 2-THF and 3-THF, however the U–Ct1, U–Ct2 and U–O bond lengths are similar. Other heterocyclic complexes have also been reported featuring η5:η1 coordination, however only

- **Table 1**: Selected distances (Å) and angles (°) for 2-THF and 3-THF. Ct1 is defined as the COT ring centroid and Ct2 is defined as the CpPMe4 ring centroid. Numbers in brackets represent values from the alternatively positioned phosphonyl ring.

- **Fig. 2**: ORTEP diagram of 1 (thermal ellipsoids at 50% probability; hydrogen atoms and ‘Pr groups have been omitted for clarity). The latter features similar U–Ct3 distances (2.56(1) and 2.54(1) Å) to 2-THF and similar U–P bond lengths (2.945(3) and 2.995(3) Å), demonstrating that η4-coordination does not affect the η5-bonding. The dimeric structure of 1 presumably persists in solution since it would account for the more complex NMR spectra observed for 1 as opposed to those for monomeric 2 and 3; unfortunately DOSY experiments on 1 were only suggestive of a dimeric structure and its low solubility in suitable solvents precluded cryoscopy.

![Scheme 1](image1)

**Scheme 1**: Synthetic route to uranium(III) mixed-sandwich complexes.

![Fig. 1](image2)

**Fig. 1**: From left to right: ball and stick model of 1-THF, and ORTEP diagrams of 2-THF and 3-THF (thermal ellipsoids at 50% probability; hydrogen atoms and ‘Pr groups have been omitted for clarity).
Cyclic voltammetry

In order to compare their U^{IV}/U^{III} redox couples with the carbocyclic analogues, cyclic voltammetry was performed on 1–3. Complex 1 exhibits a distorted quasi-reversible wave at approximately –1.88 V vs. FeCp_{2}/C0, which is within the expected range for the U^{IV}/U^{III} redox couple. Complexes 2 and 3 also exhibit an electrochemical event at this approximate potential. However, the degree of distortion of the voltammograms becomes more pronounced descending the pnictogen group, precluding accurate determination of E_{1/2}. Two other electrochemical events were observed for the three complexes and an additional two events were observed for 1 (see ESI†). These events could however not be unambiguously assigned and demonstrate the complex behaviour of the heteroatom containing mixed-sandwich system in the cyclic voltammetry experiment, as opposed to the more straightforward behaviour of the purely carbocyclic complexes.\(^1\)

The assumed E_{1/2} value of the U^{IV}/U^{III} redox couple for 1 is slightly less negative than that for [U(COT{TIPS}2)(Cp^{Me4})](THF) (−2.08 V), demonstrating the increased thermodynamic stability of the U^{III} oxidation state relative to the U^{IV} oxidation state in 1. This is in agreement with other published studies, which found the U^{IV}/U^{III} redox couple is ca. 0.2 V anodically shifted for complexes featuring phospholyl ligands.\(^1\) This arises from loss of degeneracy of the five-membered ring e-symmetry orbitals, causing a decrease in the HOMO–LUMO gap, an effect which has also been observed in transition metal complexes;\(^1\) the low energy vacant orbital in the phospholyl complex 1 (and indeed the N and As analogues) thus likely stabilises the U([iii]) centre. Hence, whilst complexes 1–3 can still be regarded as potent reducing agents, they are somewhat less powerful than their purely carbocyclic analogues.

Reactivity with CO\(_2\)

Addition of excess carbon dioxide to 1 and 2 afforded the complexes [U(COT{TIPS}2)][μ-O](μ-O2CEC4Me4)\(_2\) (E = N (4), P (5)), which are formed by reduction of 0.5 equivalents CO\(_2\) per uranium centre to give the oxo unit. A further equivalent CO\(_2\) is inserted into the U–E bond, giving rise to the carbamate and phosphacarbonate units respectively, so that a total of 1.5 equivalents carbon dioxide are required for the transformation (Scheme 2). The reaction can be conveniently monitored by \(^{13}\)C NMR using \(^{13}\)CO\(_2\), and shows the formation of 4 and 5 by the appearance of resonances at −7.1 and −46.6 ppm corresponding to the carbamate and phosphacarbonate groups, respectively; free \(^{13}\)CO formed from the reduction of CO\(_2\) to form the bridging oxo unit was also observed in both cases.

Monitoring of the formation of 4 in C\(_7\)D\(_8\) by \(^1\)H NMR spectroscopy revealed its formation to be quantitative; however the thermal instability of this complex resulted in consistently low values of carbon by microanalysis, but 4 did display a parent ion in the mass spectrum (EI). The formation of 5 was found to proceed less cleanly and in lower yield. The \(^1\)H NMR spectrum of 5 in C\(_7\)D\(_8\) at 303 K was broad and with few clearly defined resonances. The spectrum sharpened at 363 K, (possibly due to a fluxional process, the nature of which however could not be established), allowing the assignment of all but the COT ring protons. However, microanalysis and mass spectral data (EI) agreed with the proposed formulation of 5. Attempts to react 3 with carbon dioxide were unsuccessful and resulted in decomposition of the complex to form intractable products.

The proposed structures of 4 and 5 were confirmed by single crystal X-ray diffraction (see Fig. 3 and Table 2), and to the best of our knowledge, 5 represents the first example of a phosphacarbonate ligand bound to a uranium centre. Both complexes are structurally similar, and exhibit slightly shorter U–C\(_t\) distances than the parent mixed-sandwich complexes. The oxo unit is
symmetrical in 5 but asymmetrical in 4 despite the identical U–O–U angle, but both complexes feature carboxyl fragments that are positioned off-centre between the two uranium centres.

The metrics within this unit closely resemble those in [[OTtbp]-2U(μ-O)(μ-O2COTtbp)2]U(OTtbp)2], which also exhibits a bent oxo fragment (140.4(5°) with identical U–O distances to 5 (2.095(3) Å), and asymmetrical bridging carbonate moieties.16b

However, some structural differences are observed between the carboxamidophosphacarbonate units. In 4, the nitrogen lone pair overlaps with the CO3 unit, evidenced by the short N–CO3 bonds, and with the pyrrolyl diene unit, which gives rise to near linear C12–N–C angles (169.1(13) and 179.6(12°)) and a well-separated carboxamide moiety with an aromatic pyrrolyl ring. The phosphacarbonate fragment in 5 does not exhibit this feature, and has discrete diene and P–CO3 moieties and bent C12–P–C angles (116.6(2) and 116.2(3°)), with trigonal pyramidal geometry around the phosphorus atoms.

**Conclusion**

Three new mixed-sandwich complexes of the type [U(COT2TPPS2)(CpEMe4)] (where E is N, P or As and COT2TPPS2 = C6H9(1,4-Si3Pr3)] have been synthesised featuring a heterocyclic alternative to the cyclopentadienyl ligand. These complexes are structurally comparable to their purely carbocyclic analogues, but feature slightly less negative U0/U1 redox potentials as a result of the heteroatom incorporation into the 5-membered ring. However, they are still capable of reducing CO2, but the presence of the heteroatom also results in CO2 insertion chemistry and the formation of the first uranium phosphacarbonate complex.

**Experimental**

**General considerations**

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques or under an argon atmosphere in an MBraun glovebox. Solvents were dried over appropriate drying agents (NaK, pentane; K, THF) prior to distillation under N2. Solvents were stored over K mirrors or 4 Å molecular sieves under Ar.

Vacuum distilled and stored over 4 Å molecular sieves. Deuterated solvents were dried over K, THF or 4 Å molecular sieves. 29Si{1H} NMR spectra were referenced externally to SiMe4 and 31P spectra were referenced externally to 85% H3PO4 in D2O. EI-MS was performed by Dr A. K. Abdul-Sada at the University of Sussex using a VG Autospec Fisons instrument. Elemental analyses were performed by Mikroanalytisches Labor Pascher or the University of Bristol Microanalysis Service. IR Spectra were recorded on residues between NaCl plates on a Perkin-Elmer Spectrum One FTIR instrument. The following materials were prepared according to published procedures: UI3,17 potassium tetramethylphosph(on)[referred to as K[CP3Me4]],18 potassium tetramethylpyrrolyl[referred to as K[CP2Me4]],19 potassium tetramethyl-aryl[referred to as K[CP3Ar]],20 and K2[C6H9(1,4-Si3Pr3)] (referred to as K2[COT2TPPS2]).21 CO2 (99% enrichment) was purchased from Cambridge Isotopes and transferred via a calibrated Toepfer pump.

**Syntheses**

[U(COT2TPPS2)(CpEMe4)] (1). THF (150 mL) was added to a mixture of UI3 (1.240 g, 2.000 × 10−3 mol) and K2[COT2TPPS2] (0.865 g, 1.75 mmol) in THF (50 mL) dropwise over 40 m. The mixture was warmed to ambient temperature and stirred overnight. The solution was cooled to −35 °C, and to this was added a solution of K2[COT2TPPS2] (0.618 g, 0.999 mol) in THF (30 mL) dropwise over 40 m. The mixture was warmed to ambient temperature and dried under reduced pressure, then extracted in pentane and filtered through Celite to yield a green/brown solution. Cooling the solution to −35 °C afforded deep brown crystals of 1 (0.243 g, 16%).1H NMR (C7D8): δ 1.7 (s, br, 18H, 1Pr-CH3), 1.1 (s, br, 6H, 1Pr-CH2), −0.5 (s, br, 18H, 1Pr-CH3), −5.5 (s, br, 2H, COT-CH), −6.4 (s, br, 6H, Cp-CH3), −43.9 (s, br, 2H, COT-CH), −60.4 (s, br, 2H, COT-CH), −60.9 (s, br, Cp-CH3). 29Si[1H] NMR (C7D8): δ −139.6 (SiPr3). Anal. calcd (found) for C31H22N2Si2U: C 52.55 (52.47), N 1.78 (1.85), H 7.78 (7.77). MS (EI): m/z = 776 (M+).

X-ray quality crystals of 1·THF were obtained from a saturated pentane/THF solution at −35 °C.1H NMR (C7D8): δ 8.4 (br, 8.4, br, 2H, COT-CH), 3.4 (s, br, Cp-CH3), 3.2 (s, br, 4H, THF), −1.3 (s, br, 4H, THF), −1.1 (s, br, 6H, 1Pr-CH2), −2.2 (br, 24H, 1Pr-CH3), −4.0 (s, br, 18H, 1Pr-CH3), −34.9 (s, br, Cp-CH3), −75.0 (s, br, 2H, COT-CH), −91.4 (s, br, 2H, COT-CH). 29Si[1H] NMR (C7D8): δ −141.6 (SiPr3).

[U(COT2TPPS2)(CpEMe4)] (2). A solution of K2[CP3Me4] (0.178 g, 0.999 × 10−3 mol) in THF (30 mL) was added to a suspension of UI3 (0.618 g, 0.999 × 10−3 mol) in THF (60 mL), resulting in a colour change from deep blue to green over several minutes. The mixture was stirred for a minimum of 2 h then cooled to −40 °C. To this was added a solution of K2[COT2TPPS2] (0.430 g, 0.869 × 10−3 mol) in THF (30 mL) dropwise over 20 minutes. The mixture was warmed to ambient temperature and dried

| C7D8: δ 1.7 (s, br, 18H, 1Pr-CH3), 1.1 (s, br, 6H, 1Pr-CH2), −0.5 (s, br, 18H, 1Pr-CH3), −5.5 (s, br, 2H, COT-CH), −6.4 (s, br, 6H, Cp-CH3), −43.9 (s, br, 2H, COT-CH), −60.4 (s, br, 2H, COT-CH), −60.9 (s, br, Cp-CH3). 29Si[1H] NMR (C7D8): δ −139.6 (SiPr3). Anal. calcd (found) for C31H22N2Si2U: C 52.55 (52.47), N 1.78 (1.85), H 7.78 (7.77). MS (EI): m/z = 776 (M+). X-ray quality crystals of 1·THF were obtained from a saturated pentane/THF solution at −35 °C.1H NMR (C7D8): δ 8.4 (br, 8.4, br, 2H, COT-CH), 3.4 (s, br, Cp-CH3), 3.2 (s, br, 4H, THF), −1.3 (s, br, 4H, THF), −1.1 (s, br, 6H, 1Pr-CH2), −2.2 (br, 24H, 1Pr-CH3), −4.0 (s, br, 18H, 1Pr-CH3), −34.9 (s, br, Cp-CH3), −75.0 (s, br, 2H, COT-CH), −91.4 (s, br, 2H, COT-CH). 29Si[1H] NMR (C7D8): δ −141.6 (SiPr3).

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NMR spectra were recorded on a Varian VNMR spectrometer operating at 400 MHz (1H).1H and 13C spectra were referenced internally to residual solvent signals, 29Si spectra were referenced externally to SiMe4 and 31P spectra were referenced externally to 85% H3PO4 in D2O. EI-MS was performed by Dr A. K. Abdul-Sada at the University of Sussex using a VG Autospec Fisons instrument. Elemental analyses were performed by Mikroanalytisches Labor Pascher or the University of Bristol Microanalysis Service. IR Spectra were recorded on residues between NaCl plates on a Perkin-Elmer Spectrum One FTIR instrument. The following materials were prepared according to published procedures: UI3,17 potassium tetramethylphosph(on)[referred to as K[CP3Me4]],18 potassium tetramethylpyrrolyl[referred to as K[CP2Me4]],19 potassium tetramethyl-aryl[referred to as K[CP3Ar]],20 and K2[C6H9(1,4-Si3Pr3)] (referred to as K2[COT2TPPS2]).21 CO2 (99% enrichment) was purchased from Cambridge Isotopes and transferred via a calibrated Toepfer pump.
under reduced pressure, then extracted in pentane and filtered through Celite to yield a brown solution. Cooling the solution to −35 °C yielded 2 as a purple powder (0.281 g, 32%). 1H NMR (C6D6): δ 3.43 (s, br, 2H, COT-CH2), −1.7 (s, br, 6H, 1Pr-CH3), −4.6 (s, br, 18H, 3Pr-CH3), −8.1 (s, br, 18H, 3Pr-CH3), −13.4 (s, br, 6H, Cp-CH3), −35.4 (s, br, 2H, COT-CH2), −72.5 (s, br, 2H, COT-CH2), −106.8 (s, br, 2H, COT-CH2). 29Si{1H} NMR (C7D8): δ 19.0 (s, br, 6H, Cp-C7D8): δ 90.16 (br, w/1/2 = 1433 Hz, P-‘ring’). Anal. calc’d (found) for C48H40Si4P2: C 50.76 (50.57), H 7.30 (7.291). Addition of THF (0.5 mL) to a saturated pentane solution of 2 yielded 2 THF at −35 °C. 1H NMR (C7D8): δ 14.9 (s, br, 2H, COT-CH2), 1.8 (s, br, 4H, THF), 0.8 (s, br, 4H, THF), −1.8 (s, br, 6H, 1Pr-CH3), −3.0 (s, br, 24H, 1Pr-CH3, COT-CH2), −4.8 (s, br, 18H, 3Pr-CH3), −25.7 (s, br, Cp-CH3), −73.0 (s, br, 2H, COT-CH2), −83.4 (s, br, 2H, COT-CH2). 29Si{1H} NMR (C7D8): δ −127.5 (s, P-‘ring’). 31P{1H} NMR (C7D8): δ 846.2 (br, w/1/2 = 411 Hz, P-‘ring’).

[U(OTCPTP)2](CpAsMe4) (3). A solution of [U(COTTIPS2)2] (2) (3 equivalents) 13CO2 was delivered to a solution of 2 in THF (80 mL) was added to a

\[\text{C}_{34}H_{46}Si_{10}A_{2}P_{2}S_{4} \text{U}_{2}: C 50.76 (49.52), H 7.15 (7.33) \] MS (EI): m/z = 794 (M+). Addition of THF (0.5 mL) to a saturated pentane solution of 2 yielded 2 THF at −35 °C. 1H NMR (C7D8): δ 14.9 (s, br, 2H, COT-CH2), 1.8 (s, br, 4H, THF), 0.8 (s, br, 4H, THF), −1.8 (s, br, 6H, 1Pr-CH3), −3.0 (s, br, 24H, 1Pr-CH3, COT-CH2), −4.8 (s, br, 18H, 3Pr-CH3), −25.7 (s, br, Cp-CH3), −73.0 (s, br, 2H, COT-CH2), −83.4 (s, br, 2H, COT-CH2). 29Si{1H} NMR (C7D8): δ −127.5 (s, P-‘ring’). 31P{1H} NMR (C7D8): δ 846.2 (br, w/1/2 = 411 Hz, P-‘ring’).

[U(OTCPTP)2](µ-O)(µ-n\textsubscript{3}-η\textsubscript{2}-O\textsubscript{3}C\textsubscript{6}PC\textsubscript{4}Me\textsubscript{4}) (4). An excess (3 equivalents) 13CO2 was delivered to a solution of 1 (34.2 mg, 4.40 x 10−3 mol) in C6D6 via Toeppler pump at −78 °C. Warming of the solution to ambient temperature resulted in a gradual colour change from brown to orange over 24 h. Removal of all volatiles under reduced pressure afforded an orange residue, which was extracted in hexane and cooled to −35 °C to yield crystals of 4 (22.7 mg, 62%). NMR (C6D6): δ −1.4 (s, br, 18H, 3Pr-CH3), −2.3 (s, br, 6H, 1Pr-CH3), −2.6 (s, br, 18H, 3Pr-CH3), −10.0 (s, br, 6H, Cp-CH3), −27.7 (s, br, 6H, Cp-CH3). COT ring proton resonances were not observed. 13C{1H} NMR (C6D6): δ −7.1 (s, O13CNCMe4). 29Si{1H} NMR (C6D6): δ −79.7 (s, P-‘ring’). Anal. calc’d (found) for C68H120O2N2Si4U2: C 50.76 (49.52), H 7.29 (7.201), N 1.69 (1.690). The low percentage of C and high percentage of N is attributed to the limited thermal stability of 4. MS (EI): m/z = 1692 (M+).

[U(OTCPTP)2](µ-O)(µ-n\textsubscript{3}-η\textsubscript{2}-O\textsubscript{3}C\textsubscript{6}PC\textsubscript{4}Me\textsubscript{4}) (5). A solution of 2 (191.5 mg, 2.21 x 10−3 mol) in pentane was frozen and exposed to 3.2 equivalents CO2 via Toeppler pump. Warming the solution to ambient temperature resulted in a gradual colour change from purple to red/brown. Solution was stirred for 24 h then filtered via filter cannula. Cooling the solution to −35 °C afforded crystals of 5 (47.5 mg, 25%). Repetition of the reaction with 13CO2 afforded the 13C-enriched complex. 1H NMR (C6D6): δ 3.15 (s, br, 2H, COT-CH2), −15.0 (s, br, 6H, Cp-CH3) 13C{1H} NMR (C6D6): δ −66.6 (d, 1JCP = 20.3 Hz, O13CNCMe4). 29Si{1H} NMR (C6D6): δ −75.7 (s, P-‘ring’). 31P{1H} NMR (C6D6): δ 15.0–9.0 (br, overlapping, P-‘ring’), −14.5 (br, P-‘ring’). Anal. calc’d (found) for C58H120O2P2Si4U2: C 49.69 (49.937), H 7.15 (7.332). MS (EI): m/z = 1692 (M+).

X-ray crystallographic studies

Data for 1, 2, 3 and 5 were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073) source, and data for 1 THF were collected using an Agilent Technologies Xcalibur Gemini ultra diffractometer with a Cu Kα radiation (λ = 1.54184) source at 173 K using an Oxford Cryosystems Cobra low temperature device, operating in ω scanning mode with Ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, 22 Scalepack and Denzo. 23 Absorption corrections were based on equivalent reflections using SADABS. 24 Data for 4 were collected and processed by the UK National Crystallography Service at the University of Southampton. 25 The crystals were mounted on a glass fibre with silicon grease, from dried vacuum oil kept over 4 Å molecular sieves in an MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX or Olex2 packages and software therein. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were refined using a riding model. Disordered solvent molecules were modelled using the SQUEEZE 26 function in PLATON. 27 Crystal structure and refinement data are given in Table S1 of the ESI. 28 CCDC 1051779–1051784.

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