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

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A series of uranium(III) mixed-sandwich complexes of the type [U(COTIPS2)(CpEMe4)] (E = N, P or As, and COTIPS2 = C8H8{(1,4-SiPr3})2), featuring a heterocyclic five membered ring, have been synthesised and their X-ray crystal structures determined. The redox properties of these complexes have been assessed using cyclic voltammetry and the results compared to the purely carbocyclic mixed-sandwich analogues. The reactions of [U(COTIPS2)(CpEMe4)] and [U(COTIPS2)(CpEMe4)] with CO2 afford the structurally characterised carbamate and phosphacarbonate complexes [U(COTIPS2)][µ-O][µ-η1:η1- O2CEC6Me5]2 (E = N and P respectively), arising from CO2 reduction and insertion.

Introduction

The use of carbocyclic aromatic ligands in organouranium chemistry has been prominent ever since the synthesis of [Cp2UCl] in 1956,1 and subsequent expansion of this area to include 6, 7 and 8 membered rings illustrates the versatility of aromatic ligands in this field. The cyclopentadienyl (Cp) ligand and its substituted derivatives are ubiquitous in organouranium chemistry,2 however aromatic heterocyclic analogues have received comparatively little attention. Of the few reported uranium complexes featuring heterocyclic 5-membered rings, we reported the only example of a homoleptic uranium complex, featuring the 1,3-di-tert-butyl-1,2,4-triphospholyl ligand, 3 and more extensive studies by Ephritikhine et al. for small molecule activation, have attracted significant interest; 8 allowing dimerisation of the complexes these ligands can also bond through the pnictogen lone pair, generating a uranium(IV) cation.6,7

In recent years, the use of organometallic uranium complexes for small molecule activation, has attracted significant interest,8 in the specific case of CO2 reduction to afford uranium oxo complexes and CO has been achieved previously using U(III) complexes incorporating tripodal tris(aryl)oxide9 or siloxide ligands,10 and disproportionation to CO and uranium carbonate derivatives has been described for neutral and anionic U(III) siloxide,10 and tris(aryl)oxide systems.11 In recent years, we have employed uranium(III) mixed-sandwich complexes featuring substituted COT and Cp ligands for the reductive activation of CO and CO2, and comprehensive studies have determined that the steric properties of the mixed-sandwich complexes dictate the outcome of these reactions.12,13 Hence we decided to investigate the effect of changing the electronic properties of these mixed sandwich complexes, and herein we report the results obtained from incorporation of a heterocyclic ring in to the U(III) mixed sandwich motif and subsequent reactivity towards CO2.

Results and discussion

Synthesis of mixed-sandwich complexes

The three mixed-sandwich complexes [U(COTIPS2)(CpEMe4)] (E = N (1), P (2), As (3)) were prepared by successive salt metathesis reactions of U1 with K[CpEMe4] and K2[COTIPS2] in low to moderate yield (Scheme 1). This ‘one-pot’ methodology is an adaptation of the synthetic route employed for the synthesis of [U(COTIPS2)(Cp*][THF)] and other substituted cyclopentadienyl analogues, although 1–3 are formed less cleanly and in lower yields (16–40%) than their purely carbocyclic counterparts.12

The phospholyl and arsolute mixed-sandwich complexes (2 and 3) displayed comparable, paramagnetically shifted 1H and 29Si{1H} NMR spectra, whereas the pyrrolyl mixed-sandwich...
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 phospholyl 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)(CpMe4)(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 (2.56(1) Å) and 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 CpEMe4 ring centroid. Numbers in brackets represent values from the alternatively positioned phospholyl ring.
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<tr>
<td></td>
<td>2·THF</td>
<td>3·THF</td>
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<tr>
<td>U–Ct1</td>
<td>1.974(4)</td>
<td>1.974(4)</td>
</tr>
<tr>
<td>U–Ct2</td>
<td>2.54(2)</td>
<td>2.586(2)</td>
</tr>
<tr>
<td>U–E</td>
<td>2.986(14)</td>
<td>2.776(15)</td>
</tr>
<tr>
<td>U–O</td>
<td>2.716(2)</td>
<td>2.726(4)</td>
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<tr>
<td>Ct1–U–Ct2</td>
<td>135.8(15)</td>
<td>142.4(14)</td>
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Fig. 2 ORTEP diagram of 1 (thermal ellipsoids at 50% probability; hydrogen atoms and Pr groups have been omitted for clarity). Selected distances (Å) and angles (°): U1–Ct1 1.968(3), 1.974(3); U1–Ct2 2.548(4); 2.568(4); U1–N1 2.680(5), 2.691(6); U1–N1 2.598(6), 2.615(5); Ct1–U–Ct2 138.66(11), 138.59(12).

[(U[η5-CpPMe4][μ-η5:η1-CpPMe4](BH4))]2 is comparable to 1. The latter features similar U–Ct2 distances (2.56(1) and 2.54(1) Å) to 2·THF and similar U–P bond lengths (2.94(3) and 2.99(3) Å), demonstrating that η5-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.

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 \(-1.88 \text{ V vs. } \text{FeCp}_2^{\text{u}}\), 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.\(^\text{13}\)

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 TIPS2)(CpEMe4)(THF)] (\(-2.08 \text{ V}\)), 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.\(^\text{14}\) This arises from loss of degeneracy of the five-membered ring \(\gamma\)-symmetry orbitals, causing a decrease in the HOMO–LUMO gap, an effect which has also been observed in transition metal complexes;\(^\text{15}\) 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 CO2

Addition of excess carbon dioxide to 1 and 2 afforded the complexes [U(COT TIPS2)](μ-O)(μ-O2CCEC₆Me₄)₂ (\(E = N (4), P (5)\)), which are formed by reduction of 0.5 equivalents CO₂ per uranium centre to give the oxo unit. A further equivalent CO₂ 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 \(^{13}\)CO₂, 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 CO₂ to form the bridging oxo unit was also observed in both cases.

Monitoring of the formation of 4 in C₇D₈ 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 C₇D₈ 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–C₇ 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 [[OTbpb]-2U[μ-O][μ-O2COTbpb]2U[OTbpb]2]], which also exhibits a bent oxo fragment (140.4(5)) with identical U–O distances to 5 (2.093(3) Å), and asymmetrical bridging carbonate moieties.16

However, some structural differences are observed between the carbamate and phosphocarbonate units. In 4, the nitrogen lone pair overlaps with the CO2 unit, evidenced by the short N–CO2 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 delocalised carbamate moiety with an aromatic pyrrolyl ring. The phosphocarbonate fragment in 5 does not exhibit this feature, and has discrete diene and P–CO2 moieties and bent C9–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(COTTIPS2)–(CpEMe4)] (where E is N, P or As and COT TIPS2 = C8H6{1,4-SiPr3}) have been synthesised featuring a heterocyclic alternative to the cyclopentadienyl ligand. These complexes are structurally comparable to their purely carbocyclic analogues, but feature the heteroatom incorporation into the 5-membered ring. However, they are still capable of reducing CO2, but with 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 (NaK3, pentane; K, THF) prior to distillation under N2. Solvents were stored over K mirrors or 4 Å molecular sieves. Deuterated solvents were dried over K, THF, then extracted in pentane and filtered through Celite to yield a green/brown solution. Cooling the mixture to −35 °C, and to this was added a solution of K2[UCOTTIPS2] (0.865 g, 1.75 mmol) in THF (50 mL) dropwise over 40 min. 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 K3[UCOTTIPS2] (0.178 g, 0.523 mol) in THF (60 mL), resulting in a mixture of CO2, and this was added a solution of K2[UCOTTIPS2] (0.865 g, 1.75 mmol) in THF (50 mL) dropwise over 40 min. 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 mixture to −35 °C afforded deep brown crystals of 1 (0.243 g, 16%), 1H NMR (CD2Cl2): δ 1.7 (s, br, 18H, Pr-CH3), 1.1 (s, br, 6H, Pr-CH3), −0.5 (s, br, 18H, Pr-CH3), −5.5 (s, br, 2H, COT-CH), −6.4 (s, br, 6H, COT-CH), 43.9 (s, br, 2H, COT-CH), −60.4 (s, br, 2H, COT-CH), −60.9 (s, br, COT-CH). 25Si [1H] NMR (CD2Cl2): δ −139.6 (S2Pr3). Anal. calcd (found) for C16H30NSi2U: C 52.55 (52.56), N 1.80 (1.82), H 7.78 (7.79). 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 (CD2Cl2): δ 8.4 (br, 2H, COT-CH), 3.4 (s, br, COT-CH), 3.3 (s, br, 4H, THF), −1.3 (s, br, 4H, THF), −1.1 (s, br, 6H, Pr-CH3), −2.2 (br, 24H, Pr-CH3), −4.0 (s, br, 18H, Pr-CH3), −34.9 (s, br, COT-CH), −75.0 (s, br, 2H, COT-CH), −91.4 (s, br, 2H, COT-CH). 25Si [1H] NMR (CDCl3): δ −141.6 (S2Pr3).

[U(COTTIPS2)(CpEMe4)] (2). A solution of K2[UCOTTIPS2] (0.178 g, 0.999 × 10−3 mol) in THF (30 mL) was added to a mixture of U2 (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 K3[UCOTTIPS2] (0.430 g, 0.869 × 10−3 mol) in THF (30 mL) dropwise over 20 min. The mixture was warmed to ambient temperature and dried.

### Table 2

<table>
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<tr>
<td>U–C1</td>
<td>1.908(12), 1.921(13)</td>
</tr>
<tr>
<td>U–O1</td>
<td>2.094(7), 2.074(6)</td>
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<tr>
<td>C1–O1–E1,2</td>
<td>1.381(10), 1.381(14)</td>
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<tr>
<td>U–O2–U</td>
<td>139.3(3)</td>
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C1 is defined as the COT ring centroid and C2 is defined as the CpEMe4 ring centroid.
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 (CD₂Cl₂): δ 3.43 (s, 2H, COT-CH), -1.7 (s, br, 6H, ¹Pr-CH), -4.6 (s, br, 18H, ¹Pr-CH₃), -8.1 (s, br, 18H, CP-CH₃), -13.4 (s, br, 6H, CP-CH₃), -33.5 (s, 2H, COT-CH), -72.5 (s, 2H, COT-CH), -106.8 (s, 2H, COT-CH). ²⁹Si[¹H] NMR (CD₂Cl₂): δ ~120.3 (s/Pr₃). ³¹P[¹H] NMR (CD₂Cl₂): δ ~910.6 (br, w/12 = 1433 Hz, P'-ring'). Anal. calc'd (found) for Cs₂H₂O₇Si₂P₂: C 50.76 (49.527), H 7.22 (7.33). MS (EI): m/z = 794 (M¹). Addition of THF (0.5 mL) to a saturated pentane solution of 2 THF at −35 °C yielded 2 as a purple powder (0.592 g, 0.956 mol). The solution was slowly warmed to ambient temperature and stirred overnight. The solution was cooled to −40 °C, and to this was added a solution of K[¹COT[²TIPP]²] (0.370 g, 0.747 × 10⁻³ mol) in THF (50 mL) dropwise over 30 min. The mixture was slowly warmed to ambient temperature and dried under reduced pressure, then extracted in pentane and filtered through Celite to yield a brown solution. Cooling the solution to −35 °C yielded 3 as a brown powder (0.320 g, 40%). ¹H NMR (CD₂Cl₂): δ 55.3 (s, br, 2H, COT-CH), -1.6 (s, br, 6H, ¹Pr-CH), -4.2 (s, br, 18H, ¹Pr-CH₃), -7.6 (s, br, 18H, ¹Pr-CH₃), -13.9 (s, br, 6H, CP-CH₃), -41.0 (s, br, CP-CH₃), -71.7 (s, br, 2H, COT-CH), -105.8 (s, br, 2H, COT-CH). ³¹P[¹H] NMR (CD₂Cl₂): δ ~116.3 (s/Pr₃). Anal. calc'd (found) for Cs₂H₂O₇Si₂P₂: C 50.76 (49.527), H 7.22 (7.33). MS (EI): m/z = 837 (M²). ¹H NMR (CD₂Cl₂): δ 15.4 (s, br, 2H, COT-CH), 2.5 (s, br, 4H, THF), 1.1 (s, br, 4H, THF), -1.7 (s, br, 6H, ¹Pr-CH), -2.8 (br, 24H, ¹Pr-CH₃), -3.2 (s, br, CP-CH₃), -4.6 (s, br, 18H, ¹Pr-CH₃), -28.7 (s, br, CP-CH₃), -72.6 (s, br, 2H, COT-CH), -80.5 (s, br, 2H, COT-CH). ³¹P[¹H] NMR (CD₂Cl₂): δ ~126.5 (s/Pr₃). [U(¹COT[²TIPP]²)(CpAsMe₃)]²⁺ (3). An excess (3 equivalents) ¹³C⁺CO₂ was delivered to a solution of 1 (34.2 mg, 4.40 × 10⁻³ mol) in C₆D₆ via Toepler 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 (CD₂Cl₂): δ -1.4 (s, br, 18H, ¹Pr-CH₃), -2.3 (s, br, 6H, ¹Pr-CH), -2.6 (s, br, 18H, ¹Pr-CH₃), -10.0 (s, br, 6H, CP-CH₃), -27.7 (s, br, 6H, CP-CH₃). COT ring proton resonances were not observed. ¹¹C[¹H] NMR (CD₂Cl₂): δ -7.1 (s, O₁,C₄N₃C₄Me₃). ²⁹Si[¹H] NMR (CD₂Cl₂): δ -79.7 (s/Pr₃). Anal. calc'd (found) for C₄₃H₆₀N₄O₂Si₂P₂: C 70.76 (49.527), H 7.29 (7.301), N 1.69 (2.100). The low percentage of C and high percentage of N is attributed to the limited thermal stability of 4. MS (EI): m/z = 1659 (M³).

**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 θ and ω scans to fill the Ewald sphere. The programs used for control and integration wereCollect.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 SQUEEZE26 function in PLATON.27 Crystal structure and refinement data are given in Table S1 of the ESI.28 CDC15 1051779–1051784.

**Acknowledgements**

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