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Carbon Dioxide Reduction by Multimetallic Uranium(IV) Complexes Supported by Redox-Active Schiff Base Ligands

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ABSTRACT: The synthesis, structure and the reactivity with CO₂ and CS₂ of new U(IV) complexes with a redox-active Schiff base are reported. The reaction of UI₃ with the heptadentate Schiff base ligand 2,2',2''-tris(salicylideneimino)triethylamine (trensai) did not lead to the formation of a U(III) complex but to the reductive coupling and C–C bond formation between two imino groups of the Schiff base, yielding the U(IV) complex [U₂(bis-trensai)], **1**. Further reduction of **1** led to the dinuclear macrocyclic complex [{K(THF)₃}₂U₂(cyclo-trensai)], **3-THF**, through a second C–C bond formation reaction between two additional imino groups. Complexes **1** and **3** are oxidized by AgOTf resulting in the cleavage of the C–C bonds and leading to the formation of the U(IV) complex [U(trensai)]OTf, **2**. Complex **1** does not reduce CO₂ or CS₂ but undergoes insertion of CO₂ into one of the U–N bonds. In contrast the reaction of **3** with 2 equivalents of CO₂ leads to the reductive disproportionation of CO₂ to afford carbonate in 80% yield. In the presence of a large excess of CO₂ multiple reactions take place, as supported by the isolation of the crystals of [{K(THF)₃}₂U₂(μ-O)(CO₂-CO-cyclo-trensai)(U(trensai))], **4**. The higher reductive activity towards CO₂ of complex **3** compared to previously reported U(IV) complexes of reduced Schiff bases is interpreted in terms of its redox properties.

INTRODUCTION

Redox-active ligands which are able to participate in electron transfer processes together with the metal, are being increasingly used to expand metal reactivity and application in catalysis.¹ Redox-active ligands facilitate the storage and release of electrons during substrate transformation, without involving metal oxidation state changes. In some cases, electron storage in redox-active ligand can be effected via the formation of new C–C bonds.² Reduced uranium complexes supported by redox-active ligands, are attractive because of the high electronic flexibility that such ligands can confer to the metal center which can result in novel reactivity.³

Metal-based multi-electron transfer is accessible in uranium chemistry^{3f, 3g, 4} but uncommon. In contrast, the combination of low valent uranium with redox active ligands facilitates multielectron transfer to substrates^{3g, 5}

which is an important requirement in the activation of small molecules such as CO₂ or N₂.

Notably, Bart and coworkers showed that the electrons stored in the ligand of a uranium(IV) bound pyridine(diimine) complex can effect the reductive cleavage of the azobenzene double bond^{5a} and the multi electron reduction of carbonyl substrates.^{3d} The same authors also showed that redox-active ligands can be used to promote the functionalization and the scission of uranyl(IV)-oxo bonds.⁶

However, the use of redox-active ligands to promote electron transfer in f elements compounds⁷ and in uranium chemistry^{2e, 5e, 8} in particular remains significantly rarer than in d block chemistry.^{1a-f}

Scheme 1. The reduction of bis-Schiff base complexes of U(IV) with alkali metals leads to intermolecular (top) or intramolecular C–C bond formation (bottom). The two electrons stored in the C–C bonds can be used to reduce oxidizing substrates

Scheme 2. U(III) reduces the two imino groups of the tetradentate Schiff base salophen leading to intermolecular C–C bond formation

Schiff bases were shown more than 20 years ago to act as redox-active ligands in complexes of d block elements⁹ leading to intramolecular or intermolecular C–C bond formation.

In contrast, the use of Schiff base ligands in uranium chemistry was originally mostly limited to the uranyl(VI) species¹⁰ but an increasing number of U(V)¹¹, and U(IV)^{2e} Schiff base complexes has been reported in recent years.^{2e, 8a, 12–13}

Our group demonstrated that Schiff bases act as redox active ligands also when combined to f block metals^{2e, 7c, 8a} and to low valent uranium in particular. Notably we showed that the reduction of U(IV) complexes of tetradentate^{2e, 12b} and tridentate Schiff bases^{8a} (Scheme 1) results in the reduction of the imino group of the ligand followed by formation of intermolecular or intramolecular C–C bonds. Reduction of the Schiff base imino group and formation of a new C–C bond was also observed when the Schiff base salophen (salophen: N,N'-disalicylidene-o-phenylenediamine) is directly reacted with an uranium(III) precursor (Scheme 2). Reactivity and electrochemical studies on Schiff base complexes of d block metals suggest that the electrons stored on the ligand framework may become available for CO₂ reduction.^{9a, 14}

In contrast such reactivity has not been yet observed for Schiff base complexes of the f elements. To further explore the possibility of using electrons stored on uranium complexes of Schiff bases for the reduction of small molecules we have explored the chemistry of the heptadentate tripodal ligands 2,2',2''-tris(salicylideneimino)triethylamine (H₃trensall) with low valent uranium.

We have recently shown that the heptadentate tripodal ligand 2,2',2''-tris(salicylideneimino)triethylamine (H₃trensall) allows the isolation of stable complexes of uranium in oxidation states ranging from +VI to +IV.^{11a} The trensal ligand can also be used to build heterobimetallic uranyl-Fe complexes.^{11a}

Here we show that the reaction of U₃(THF)₄ with the K₃R^{trensall} (R = H and ^tBu) ligand results in the reduction of one imino group of the trensal ligand and in the formation of a C–C bond between two trensal ligands affording the dimeric complexes [U₂(bis-R^{trensall})], **1** and **1a** (Scheme 3). Two imino groups of complex **1** can be further reduced to afford a diuranium(IV) complex supported by a macrocyclic tetra-amido-bis-imino-tetra-phenolate ligand, [K(THF)₃]₂U₂(cyclo-trensall), **3-THF**. Complexes **1** and **3** are oxidized by AgOTf to afford [U^{IV}(trensal)]OTf, **2**. Complex **1** does not reduce CO₂ or CS₂ but undergoes insertion of CO₂ into one of the U–N bonds. In contrast complex **3** effects the reductive disproportionation of CO₂ to afford carbonate. Remarkably and in contrast to the previously reported uranium complexes of redox-active Schiff base ligands, complexes **1** and **3-THF** show high reactivity towards carbon dioxide and are able to promote both insertion and reduction of CO₂.

EXPERIMENTAL SECTION

General Considerations Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. Glassware was dried overnight at 140°C before use.

NMR experiments were carried out using NMR tubes adapted with J. Young valves. ¹H, ¹⁹F and ¹³C{¹H} NMR spectra were recorded on a Bruker 400 or 600 MHz spectrometers. NMR chemical shifts are reported in ppm with solvent as internal reference.

Mass spectrometry was performed on a LTQ Orbitrap FTMS instrument (LTQ Orbitrap Elite FTMS, Thermo Scientific, Bremen, Germany) operated in the positive mode coupled with a robotic chip-based nano-ESI source (TriVersa Nanomate, Advion Biosciences, Ithaca, NY, U.S.A.). A standard data acquisition and instrument control system was utilized (Thermo Scientific), whereas the ion source was controlled by Chipsoft 8.3.1 software (Advion BioScience). The experimental conditions for the ionization voltage was +5.8 kV and the gas pressure was set at 0.30 psi. The temperature of ion transfer capillary was 275 °C. Data were analyzed using XCalibur (Thermo Scientific) and MS tools available at <http://ms.cheminfo.org>.

Electrochemical Methods. Cyclic Voltammetry experiments were carried out at room temperature in an argon-filled glovebox described above. Data were collected using a Biologic SP-300 potentiostat connected to a personal computer. All samples were 4 mM in complex with 0.1 M [Bu₄N][PF₆] supporting electrolyte in pyridine or THF solution. The experiments were carried out with a platinum disk (d = 5 mm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The experiments were repeated on independently synthesized samples to assess the reproducibility of the measurement.

Potential calibration was performed at the end of each data collection cycle using the ferrocene/ferrocenium $[(C_5H_5)_2Fe]^{+/0}$ couple as an internal standard.

The **UV-Visible spectra** were recorded as 5 mM solutions in THF using 1 mm cuvettes equipped with a J-Young valve and a Perkin Elmer 950 spectrometer.

Elemental analyses were performed using a Thermo Scientific Flash 2000 Organic Elemental Analyzer at the Institut of Chemistry and Chemical Engineering at EPFL.

Starting materials Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, hexane, pyridine and THF). Depleted uranium was purchased from Ibilabs, Florida, USA. The ligands $H_3trensals$,¹⁵ $K_3trensals$ ^{11a} and $H_3^tBu-trensals$ (tris[4-(2-hydroxy-3-tert-butylphenyl)-3-aza-3-butenyl]amine),¹⁶ $UI_3(THF)_4$,¹⁷ UCl_4 ¹⁸ and $UI_4(OEt)_2$ ¹⁹ were prepared according to the published procedures. $^{13}CO_2$ (93.13% ^{13}C) was purchased from Cortecnet and transferred prior to use in a flask in equipped with a Young valve and containing activated 3 Å molecular sieves.

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α - and β -counting equipment.

Synthesis $K_3^tBu-trensals$. A white suspension of potassium hydride (44.4 mg, 1.11 mmol, 3.2 equiv) in THF (0.8 mL) was added to a yellow solution of $^tBu-trensals$ (275.2 mg, 0.3461 mmol, 1 equiv) in THF (3.0 mL) and the resulting reaction mixture was left stirring at room temperature overnight. The resulting suspension was filtered to yield a yellow solution. The latter was dried and washed twice with hexane (1.0 mL each) to afford $K_3^tBu-trensals$ as a pale yellow powder (272.5 mg, 85.8% yield).

Anal. Calcd for $K_3^tBu-trensals(Hexane)_{0.1}$ $C_{54.6}H_{76.4}N_4O_3$: C, 67.51%; H, 8.39%; N, 6.10%. Found: C, 66.98%; H, 8.83%; N, 5.66%.

1H NMR (400 MHz, $pyr-d_5$, 298 K): δ = 1.51 (s, 27H), 1.77 (s, 27H), 2.63 (s, 6H), 3.59 (s, 6H), 3.71 (s, 3H), 7.65 (s, 3H), 8.47 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $pyr-d_5$, 298 K): δ = 30.41, 32.04, 33.69, 35.68, 58.28, 60.33, 121.32, 126.14, 129.43, 141.00, 169.14, 171.17.

Synthesis $[U_2(bis-trensals)]$, **1.** A white suspension of $K_3trensals$ (57.0 mg, 0.0911 mmol 1 equiv) in THF (1.2 mL) was added to a blue solution of $UI_3(THF)_4$ (82.7 mg, 0.0912 mmol 1 equiv) in THF (1.0 mL) (Figure 1). The mixture turned immediately orange and KI precipitated out of the solution. The reaction mixture was filtered, yielding a dark orange filtrate. Slow diffusion of hexane into the orange solution gave $[U_2(bis-trensals)](THF)$, complex **1**, as a pale

orange powder (88.5 mg, 66.6% yield). 1H NMR (400 MHz, $THF-d_8$, 298 K): δ = -66.01 (s, 1H), -52.07 (s, 1H), -45.32 (s, 1H), -37.74 (s, 1H), -34.61 (s, 1H), -32.17 (s, 1H), -30.69 (s, 1H), -20.46 (s, 1H), -16.69 (s, 1H), -13.44 (s, 1H), -5.76 (s, 1H), -4.92 (s, 1H), -2.36 (s, 1H), -0.11 (s, 1H), 0.70 (s, 1H), 13.66 (s, 1H), 15.70 (s, 1H), 23.15 (s, 1H), 23.92 (s, 1H), 24.68 (s, 1H), 26.52 (s, 1H), 35.75 (s, 1H), 38.05 (s, 1H), 41.81 (s, 1H), 46.26 (s, 1H), 63.27 (s, 1H). Anal. Calcd for $[U_2(bis-trensals)](THF)$ $C_{58}H_{62}N_8O_7U_2$: C, 47.74; H, 4.28; N, 7.68. Found: C, 48.12; H, 4.55; N, 7.38. Crystallization trials were unsuccessful.

UV-Vis (THF) λ_{max} : 275 nm, ϵ = 9324 $M^{-1} \cdot cm^{-1}$, λ_{max} : 290 nm, ϵ = 9589 $M^{-1} \cdot cm^{-1}$, λ_{max} : 360 nm, ϵ = 8567 $M^{-1} \cdot cm^{-1}$

Complete removal of KI from **1** is difficult and in large synthesis small amount of KI may remain leading to the presence of KI in the synthesis of complexes **2** and **3**.

Isolation of crystals of $[U_2(bis-^tBu-trensals)]$, **1a.** The compound **1a** was isolated following the procedure used for **1**, by adding a white suspension of $K_3-^tBu-trensals$ (50.0 mg, 0.0550 mmol, 1 equiv) in THF (1 mL) to a blue solution of $UI_3(THF)_4$ (50.0 mg, 0.0551 mmol, 1 equiv) in THF (1 mL). Slow diffusion of hexane or toluene into the reaction mixture yielded brown crystals of $[U_2(bis-^tBu-trensals)]$, **1a**. Isolation of analytically pure complex **1a** is not reproducible because of the presence of side products that can cocrystallize with **1a**. The proton NMR of the isolated compound is given in the Figure S4.

Synthesis $[U(trensals)](OTf)$, **2.** To an orange solution of complex **1** (18.7 mg, 0.0134 mmol, 1 equiv) in THF (1 mL), 2 equivalents of solid $AgOTf$ (6.9 mg, 0.027 mmol, 2 equiv) were added. The reaction mixture turned immediately dark brown. The mixture was filtered to eliminate $Ag(0)$. Single crystals suitable for X-ray diffraction, of the triflate anion complex $[U(trensals)](OTf)$, **2** were obtained by slow diffusion of toluene into a THF reaction mixture (16.4 mg, 70% yield). Anal. Calcd for $[U(trensals)](OTf) \cdot (KI)_{0.15}$ $C_{28}H_{27}N_4O_6U_1F_3S_1 \cdot (KI)_{0.15}$: C, 38.77%; H, 3.14 %; N, 6.46%. Found: C, 39.2%; H, 3.49%; N, 5.78%.

1H NMR (400 MHz, $THF-d_8$, 298 K): δ = -8.65 (s, 6H), 2.76 (s, 6H), 5.33 (s, 3H), 8.61 (s, 3H), 10.61 (s, 3H), 13.19 (s, 3H), 34.87 (s, 3H).

^{19}F NMR (376.5 MHz, $THF-d_8$, 298 K): δ = -83.26 (free OTf)

UV-Vis (THF) λ_{max} : 275 nm, ϵ = 9029 $M^{-1} \cdot cm^{-1}$, λ_{max} : 290 nm, ϵ = 9059 $M^{-1} \cdot cm^{-1}$, λ_{max} : 360 nm, ϵ = 8284 $M^{-1} \cdot cm^{-1}$

Reaction of $[U_2(bis-trensals)]$ with CO_2 . An orange solution of complex **1** (16.2 mg, 0.006 mol, 1 equiv) in $THF-d_8$ (0.5 mL) was degassed by freeze-pump-thawing and then an excess (1 atm) of CO_2 was added. The 1H NMR spectrum of the crude mixture shows the disappearance of the starting material within six days. After six days an orange powder representing the 62% of the initial mass (10.1 mg of powder) is formed. The proton NMR spectrum of the pale orange solution obtained after removal of the precipitate shows a new set of signals. 1H NMR of the reaction mixture (400 MHz, $pyr-d_5$, 298 K): δ = -60.72 (s, 1H), -57.64 (s, 1H), -56.63 (s, 1H), -53.62 (s, 1H), -45.18 (s, 1H), -41.64 (s, 1H), -41.43 (s, 1H), -41.02 (s, 1H), -25.20 (s, 1H), -21.38 (s, 1H), -10.88 (s, 1H), -10.70 (s, 1H), -10.48 (s, 1H), -9.68 (s, 1H),

-8.33 (s, 1H), -6.98 (s, 1H), -5.93 (s, 1H), -3.66 (s, 1H), -3.39 (s, 1H), -2.78 (s, 1H), -2.60 (s, 1H), -1.47 (s, 1H), -0.02 (s, 1H), 0.38 (s, 1H), 1.34 (s, 1H), 2.54 (s, 1H), 6.78 (s, 1H), 7.49 (s, 1H), 7.88 (s, 1H), 8.03 (s, 1H), 8.41 (s, 1H), 9.07 (s, 1H), 9.89 (s, 1H), 12.63 (s, 1H), 12.94 (s, 1H), 13.12 (s, 1H), 15.79 (s, 1H), 16.79 (s, 1H), 17.36 (s, 1H), 18.85 (s, 1H), 22.57 (s, 1H), 22.96 (s, 1H), 23.15 (s, 1H), 25.96 (s, 1H), 26.61 (s, 1H), 27.39 (s, 1H), 30.03 (s, 1H), 30.81 (s, 1H), 37.68 (s, 1H), 40.49 (s, 1H), 60.12 (s, 1H), 70.66 (s, 1H). ESI-MS: m/z = 1431.6 ($[U_2(\text{bis-trensal})(CO_2)]^+$).

The reaction performed with different stoichiometries of $^{13}CO_2$ (2, 10 and 100 equiv) shows only different reaction rates, but in all cases the 1H and ^{13}C -NMR spectra of the supernatant were the same. 1H NMR (400 MHz, THF- d_8 , 298 K): δ = -71.53, -63.4, -62.5, -56.3, -49.77, -49.10, -44.20, -42.35, -36.87, -34.27, -21.02, -15.91, -15.5, -11.6, -11.3, -9.53, -7.89, -5.63, -5.06, -4.64, -2.03, -1.33, 0.88, 2.10, 2.23, 4.98, 8.00, 8.32, 10.03, 10.48, 13.48, 15.22, 15.44, 16.67, 18.01, 21.95, 23.26, 24.29, 24.52, 26.70, 28.37, 29.04, 29.39, 32.23, 35.99, 36.71, 38.52, 40.09, 65.88, 88.89. $^{13}C\{^1H\}$ NMR (100 MHz, THF- d_8 , 298 K): δ = 202 (C=O). 1H NMR (400 MHz, pyr- d_5 , 298 K): δ = -60.72, -57.64, -56.63, -53.62, -45.18, -43.17, -41.64, -41.43, -41.02, -25.50, -21.38, -10.88, -10.70, -9.68, -8.33, -6.98, -5.93, -3.66, -3.39, -2.78, -2.60, -1.47, -0.02, 1.34, 2.54, 6.78, 7.88, 8.03, 8.41, 9.07, 9.89, 12.94, 13.12, 15.79, 16.79, 17.36, 18.85, 22.57, 22.96, 23.15, 25.96, 26.61, 27.39, 30.03, 36.81, 37.68, 40.49, 60.12, 70.80, $^{13}C\{^1H\}$ NMR (100 MHz, pyr- d_5 , 298 K): δ = 190.8 (C=O).

$^{13}C\{^1H\}$ NMR (100 MHz, D_2O , 298 K): δ = 162.5 (NC=O); δ = 178.1 assigned to carbamate and its hydrolysis product.

Removal of the solvent from the supernatant afforded a brown solid. Anal. Calcd for $[U_2(\text{bis-trensal})(CO_2)](THF) \cdot (KI)_{0.25} C_{55}H_{54}N_8O_8U_2 \cdot (THF)(KI)_{0.25}$: C: 45.87%; H: 4.05%; N: 7.25%. Found: C: 46.02%; H: 4.45%; N: 6.81%.

The orange powder from the reaction mixture dissolves in pyridine and shows several signals in the carbon NMR, suggesting the presence of $[U_2(\text{bis-trensal})(CO_2)]$ and of additional insertion products $^{13}C\{^1H\}$ NMR (100 MHz, D_2O , 298 K): δ = 162.5 (C=O); 164.5 (C=O); 169.2 (C=O).

Dissolution of the powder or supernatant in D_2O (pD=12) does not show the presence of CO_2 reduction products, such as oxalate or carbonate.

Synthesis of $[K_2U_2(\text{cyclo-trensal})]$, **3.** To an orange solution of complex **1** (26.2 mg, 0.019 mmol, 1 equiv) in THF (1 mL), 2 equivalents of KC_8 (5.3 mg, 0.039 mmol, 2 equiv) were added. The resulting dark brown reaction mixture was filtered to afford a brown solution. The 1H NMR spectrum of the solution did not show any signal. Upon slow diffusion of hexane into the solution, complex $[K(THF)_3]_2U_2(\text{cyclo-bis-trensal})$, **3-THF** could be isolated as a brown powder (19.6 mg, 65% yield). Anal. Calcd for $[K_2U_2(\text{cyclo-trensal})](THF) \cdot (KI)_{0.25} C_{54}H_{54}N_8O_6U_2 \cdot (THF)(KI)_{0.25}$: C: 44.12%; H: 3.96%; N: 7.10%. Found: C: 44.49%; H: 4.25%; N: 6.68%.

UV-Vis (THF) λ_{max} : 275 nm, ϵ = 9529 $M^{-1} \cdot cm^{-1}$, λ_{max} : 290 nm, ϵ = 9020 $M^{-1} \cdot cm^{-1}$, λ_{max} : 360 nm, ϵ = 8341 $M^{-1} \cdot cm^{-1}$.

Single crystals suitable for X-ray diffraction of $[K(Py)_3]_2U_2(\text{cyclo-trensal})$, **3-py**, were obtained by slow diffusion of toluene into a pyridine solution of **3-THF**.

Reaction of $[K(THF)_3]_2U_2(\text{cyclo-trensal})$, **3-THF with 2 eq of $AgOTf$.** A brown solution of complex **3-THF** (5.0 mg, 0.0026 mmol, 1 equiv) in THF (0.5 mL) was added to solid $AgOTf$ (1.4 mg, 0.054 mmol, 2 equiv). The reaction mixture turned immediately dark orange. The mixture was filtered to eliminate $Ag(0)$. The 1H NMR (THF- d_8 , 400 MHz, 298 K) spectrum of the dark orange solution shows only the signals assigned to complex **1**.

Reaction of $[K(THF)_3]_2U_2(\text{cyclo-trensal})$, **3-THF with 4 eq of $AgOTf$.** A brown solution of complex **3-THF** (8.1 mg, 0.0055 mmol, 1 equiv) in THF (1 mL) was added to solid $AgOTf$ (5.7 mg, 0.022 mmol, 4 equiv). The reaction mixture turned immediately dark brown. The mixture was filtered to eliminate $Ag(0)$. The 1H NMR (THF- d_8 , 400 MHz, 298 K) spectrum of the dark brown solution shows only the signals assigned to complex **2**.

Reaction of $[K(THF)_3]_2U_2(\text{cyclo-trensal})$, **3-THF with $^{13}CS_2$.** Complex **3-THF** was prepared in situ from the reduction of $[U_2(\text{bis-trensal})]$ (8.3 mg, 0.006 mmol, 1 equiv) in THF (0.5 mL) with a suspension of KC_8 (1.7 mg, 0.0126 mmol, 2 equiv) in THF (0.3 mL). After removal of KI , all volatiles were removed *in vacuo* from the resulting brown solution of **3-THF**. The brown solid was dissolved in THF- d_8 (0.7 mL) and $^{13}CS_2$ (1.4 μ L, 0.023 mmol, 4 equiv) was added. Upon addition of CS_2 a dark orange suspension is formed. After two days, a pale orange powder comes down and a dark orange supernatant is formed. The 1H NMR spectrum of the solution taken shows only the signals assigned to complex **1**, and the $^{13}C\{^1H\}$ NMR spectrum (THF- d_8 , 100 MHz, 298 K) shows three peaks at 128.97 ppm (new species), 193.56 ppm (free $^{13}CS_2$) and 248.71 ppm (new species). After removing the solvent and dissolving the residue in DMSO- d_6 , the 1H NMR spectrum shows the signals assigned to complex **1** and the ^{13}C NMR spectrum (DMSO- d_6 , 100 MHz, 298 K) shows peaks at 145.01 ppm, 203.57 ppm ($^{13}C_2S_5^{-2}$), 263.88 ppm ($^{13}C_2S_4^{-2}$) and 266.92 ppm ($^{13}CS_3^{-2}$) assigned to CS_2 reduction products.²⁰

Reaction of $[K(THF)_3]_2U_2(\text{cyclo-trensal})$, **3-THF with CO_2 .**

Reaction of **3-THF with 1, 2, 4, 100 equiv. of $^{13}CO_2$**

Complex **3-THF** was prepared in situ from the reduction of $[U_2(\text{bis-trensal})]$ (9.4 mg, 0.068 mmol, 1 equiv) in THF (0.6 mL) with a suspension of KC_8 (1.9 mg, 0.0140 mmol, 2 equiv) in THF (0.2 mL). After removal of KI , the resulting brown solution of **3-THF** was degassed by freeze-pump-thawing and 2 eq of $^{13}CO_2$ were added. The 1H NMR spectrum of the reaction mixture taken immediately after addition of 2 equiv. of $^{13}CO_2$ show only signals assigned to complex **1**.

The reaction was repeated in similar manner for 1, 4 and 100 equiv. of $^{13}CO_2$. The 1H NMR spectrum of the reaction mixture taken immediately after addition of 4 equiv. of $^{13}CO_2$ shows only signals assigned to complex **1**, but after 4 days signals assigned to insertion products are observed.

After 7 days, the $^{13}C\{^1H\}$ NMR spectrum of all the reaction mixtures (THF- d_8 , 151 MHz, 298 K) shows only the signal at δ = 125.0 ppm of free $^{13}CO_2$. Upon removal of the solvent in *vacuo* and after dissolution in basic D_2O (pD=12),

quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were performed (^{13}C -labelled sodium acetate as reference).

The yields in carbonate correspond to 79.5%, 80.6%, 78.2% and 91.2% (calculated with respect to the value expected if only two molecules of CO_2 react with **3**) when 1, 2, 4 and 100 equiv. of $^{13}\text{CO}_2$ are added per dinuclear complex, respectively.

$^{13}\text{C}\{^1\text{H}\}$ NMR experiments carried out after quenching in basic D_2O (pD=12) the reaction mixture after addition of 100 equivalents of CO_2 shows in addition to the signals assigned to carbonate signals at 162.45 ppm and 162.31 ppm assigned to insertion products.

Reaction of **3-THF** with 1atm CO_2

Complex **3-THF** was prepared in situ from the reduction of $[\text{U}_2(\text{bis-trens})]$ (30.9 mg, 0.022 mmol, 1 equiv) in THF (1 mL) with a suspension of KC_8 (6.0 mg, 0.044 mmol, 2 equiv) in THF (1.0 mL). After removal of KI, the resulting brown solution of **3-THF** was degassed by freeze-pump-thawing and 1 atm of CO_2 was added. Upon addition of CO_2 the solution turned from brown to colorless and an orange precipitate appeared within 3 hours. The precipitate represents the 81.2% of the mass of the starting material (25.3 mg). The mixture was centrifuged, the solid washed twice with THF (1 mL) and partially dissolved in pyridine. Upon slow diffusion of hexane into the pyridine solution of the reaction mixture a powder formed together with a few single crystals of a minor product suitable for X-ray diffraction, of $[\{\text{K}(\text{THF})_3\}\text{U}_2(\mu\text{-O})(\text{CO}_2\text{-CO-cyclo-trens})](\text{U}(\text{trens}))]$, complex **4**. The formation of the crystals was not reproducible.

X-ray Crystallography The diffraction data (except compound **4**) were collected at 100 K using $\text{Mo } K_\alpha$ radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The dataset were reduced by *EvalCCD*²¹ and then corrected for absorption.²² The data for crystal structure **4** was collected at 140 K using $\text{Cu } K_\alpha$ radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction and correction were carried out by *CrysAlisPro*.²³

The solutions and refinements were performed by *SHELXT*²⁴ and *SHELXL*,²⁵ respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Additional electron density (due to disordered solvent molecules) found in the difference Fourier map of compound **1a**, **2** and **4** was treated by the *SQUEEZE* algorithm of *PLATON*.²⁶ Similarity and rigid bond restraints (SADI, SIMU and RIGU cards) were employed during the last stages of refinement of **2** and **3**, because of the disorder displayed by the two structures. In the case of compound **1a**, the anisotropic behaviour of light atoms was rather unstable; hence adapted restraints were applied to carbons and nitrogens (SIMU and RIGU cards). The crystal structure of **4** displayed unusual atomic parameters for the THF molecules and some restraints were used in order to get acceptable distances, angles and adp's (SIMU, DFIX cards). Constraints were applied to the adp's of O13 and O15 (EADP card).

Table 1. Mean values of selected bond lengths (Å) in the uranium complexes of the ^ttrens ligands.

Compound	U-N _{amido}	U-N _{imino}	U-O _{phenolate}	C-Cl _{ink}	C-N _{amido}	C-N _{imino}
1a , $[\text{U}_2\text{-bis-}^t\text{Bu-trens}]$	2.312(9)	2.56(2)	2.204(18)	1.59(2)	1.493(14)	1.291(1)
2 , $[\text{U}(\text{trens})][\text{OTf}]$	-	2.513(8)	2.26(10)	-	-	1.250(13)
3-py , $[\{\text{K}(\text{py})_3\}_2\text{U}_2(\text{cyclo-trens})]$	2.54(3)	2.581(8)	2.227(13)	1.553(13)	1.49(2)	1.397(4)
4		2.61(7)	2.238(6)	1.59(4)	1.52(4)	1.29(3)

RESULTS AND DISCUSSION

Synthesis of $[\text{U}_2(\text{bis-Rtrens})]$ complexes. The reaction between $\text{K}_3^t\text{Bu-trens}$ and $\text{UCl}_3(\text{THF})_4$ led to the dinuclear uranium(IV) $[\text{U}_2(\text{bis-}^t\text{Bu-trens})]$, complex **1a** (Scheme 3). Two U(III) cations provide one electron each to give a dinuclear uranium(IV) complex in which two imino groups of two ^tBu-trens ligands are coupled.

The molecular structure of **1a** (Figure 1) shows a dinuclear uranium(IV) complex with an inversion center at half length of the C-C bond connecting the two ^tBu-trens units in the bis-^tBu-trens ligand.

Each uranium center is heptacoordinated in a distorted capped trigonal prismatic environment by two imino nitrogen, one amino nitrogen (U-N₂= 2.753(9) Å), one amido nitrogen and three phenoxide oxygen atoms

(average U-O = 2.22(6) Å) of the bis-^tBu-trens ligand. The C-N_{amido} bond distances (C-N_{am} = 1.493(14) Å) of the ligand backbone are much longer than the C-N_{imino} distance in complex **2** (see below) and are in agreement with the presence of two amido groups. The value of the U-N_{amido} distance in **1a** (U-N₃= 2.312(9) Å) falls in the range of values reported for U(IV)-amido compounds²⁷ and is significantly shorter than the value found for the U-N_{imino} distances in **1a** (average U-N = 2.56(2) Å). These distances compare well with the values reported for $\text{Na}_2[\text{U}^{\text{IV}}(\text{bis-salophen})]$ (U-N_{am} (2.387(8) Å) and U-N_{im} (2.624(7) Å).^{2e} The two uranium centers are located in the two pockets of the dinucleating ligand with a U-U distance of 7.311(2) Å. The structural parameters of the complex clearly show that a reduction has occurred on the imino groups of the ligands resulting in the formation of a U(IV) complex of the reduced ligand rather than the formation of a U(III) complex of the ^tBu-trens. Notably, the two electron

reduction of the ligand results in the formation of the C–C bond (C20–C20 = 1.59(2) Å), by intermolecular reductive coupling of the original imino groups. The value of the C–C bond distance falls in the range of the intermolecular and intramolecular C–C bonds of Na₂[U(bis-salophen)] (1.559(7) Å), [U₂(cyclo-salophen)(py)₄] (1.609(5) Å) and [U(μ-bis-^{Me}naphthquinolen)]₂ (1.64(1) Å).^{2e, 8a} Reductive coupling mediated by low valent uranium has also been previously reported for carbonyl compounds,²⁸ heterocycles,^{2c} CO,²⁹ and CS₂.³⁰

The proton NMR of the reaction mixture leading to the isolation of crystals of **1a** shows the presence of the signals assigned to the complex, but also signals of additional species which prevented the isolation of the complex in analytically pure form.

In contrast, ¹H NMR studies (Figure 2) show that the reaction of K₃trensals with U₃(THF)₄ leads to the formation of a single species showing 27 narrow signals assigned to the symmetric dinuclear uranium(IV) [U₂(bis-trensals)], complex **1** (Scheme 1). ESI-MS analysis of complex **1** (see SI) revealed the presence of the dinuclear complex as the only species (1387.5 m/z). Any attempt to obtain X-ray quality crystals of **1** were unsuccessful but the complex was isolated in 66.6% yield.

Scheme 3. Synthesis of [U₂(bis-Rtrensals)], **1**.

Figure 1. Molecular structure of complex **1a**. Hydrogen atoms and methyl groups omitted for clarity. Color cod: uranium (green), nitrogen (blue), oxygen (red), carbon (grey), C–C bond between imine (yellow).

Figure 2. ¹H NMR spectrum of complex **1**.

Reactivity of [U₂(bis-trensals)]. The two electrons stored in the C–C bond of the bis-trensals ligand in complex **1** are readily available for the reduction of strongly oxidizing substrates, similarly to what reported for Na₂[U(bis-salophen)] and [U(μ-bis-^{Me}naphthquinolen)]₂ complexes.^{8a} The reaction of **1** with two equiv. of AgOTf led to the immediate oxidation of complex **1** with immediate cleavage of the C–C bond in the bis-trensals ligand and restoration of the imino groups of the trensal ligand. Thus, the two electrons stored on the bis-trensals ligand react with the Ag⁺ ions to produce Ag and the monocationic U(IV) complex of the trensal ligand [U(trensals)]OTf, **2** (Scheme 4).

Scheme 4. Reaction of **1** with AgOTf

The X-ray crystal structure of **2** (Figure 3) shows the presence of a mononuclear U(IV) complex with the triflate anion in the outer coordination sphere. The U(IV) center in **2** is heptacoordinated, with a distorted capped octahedral geometry, by the three imino nitrogen (U–N1 = 2.513(8) Å), the amino nitrogen (U–N2 = 2.782(13) Å) and the three phenoxide oxygen atoms (average U–O = 2.162(7) Å) of a trensal ligand. The values of the U–N and U–O bond distances fall in the range of those found in the previously reported eight-coordinated U(IV) complex [U(trensals)(py)]I (U–N_{im} = 2.54(1) Å avg, U–N_{am} = 2.855(5) Å and U–O = 2.192(6) Å).^{11a}

Figure 3. Molecular structure of complex **2**. Hydrogen atoms and triflate anion omitted for clarity. Color code: uranium (green), nitrogen (blue), oxygen (red), carbon (grey).

The oxidation and cleavage of **1** by addition of AgOTf, led us to investigate the reactivity with CO₂. In spite of the fact that no reactivity with CO₂ was reported for the Na₂[U(bis-salophen)] and [U(μ -bis-Menaphtquinolen)]₂ complexes, the addition of excess CO₂ (1 atm) to a THF solution of **1** resulted in the slow disappearance of the proton NMR signals of **1** and in the appearance of a new set of 54 signals together with the formation of a pale orange precipitate within 6 days.

Scheme 5. Reactivity of **1** with CO₂.

All the attempts to crystallize the products of the reaction were not successful. The reaction of **1** with CO₂ most probably involves CO₂ insertion into the U–N_{amide} bond. This hypothesis is corroborated by the lack of reactivity with CS₂, less prone to insertion reactions into U–N bonds. The possibility of insertion of CO₂ into the U–O bond cannot be completely ruled out but the isolation of crystals of **4** (see below) is consistent with the insertion occurring in the U–N_{amide} bond. Moreover, CO₂ reduction products such as oxalate or carbonate were not observed in the ¹³C{¹H} NMR spectrum of the crude mixture, in THF or in the spectrum of the reaction mixture after quenching with basic D₂O (pD=12). In contrast the ¹³C{¹H} NMR spectrum in THF of the soluble fraction of the reaction mixture after reaction of ¹³CO₂ with **1** shows only one signal at a chemical shift of 202 ppm (Figure S7) and after quenching with basic D₂O (pD=12) a signal at 162.5 ppm compatible with the presence of a carbamate (Figure S10).

The mass spectrum of the solution shows a peak at 1431.6 m/z, consistent with the presence of the [U₂(bis-trensalsalophen)] species. The insertion of CO₂ into U–N_{amide} bonds has been previously reported for U(III) and U(IV) complexes^{4g, 31} but was not observed for the amido ligands resulting from the reduction of imino groups in uranium Schiff Base complexes. The higher reactivity of **1** with respect to the CO₂ insertion reaction compared to the Na₂[U(bis-salophen)] and [U(μ -bis-Menaphtquinolen)]₂ complexes is probably the result of the higher flexibility of the tripodal trensal framework, although the presence of a more polarized C–N_{amide} bond and of a more nucleophilic nitrogen atom cannot be ruled out.

The orange solid formed (accounting for the 60% of the mass of the **1** compound) upon addition of ¹³CO₂ to **1** is insoluble in THF but can be solubilized in pyridine.

The ¹³C{¹H} NMR spectrum of the resulting pyridine solution after removing all volatiles and quenching the solution with basic D₂O (pD=12) did not show any CO₂ reduction products but only the presence of three carbamate signals in the range 162–164 ppm (Figure S11) suggesting that multiple insertion products may form in the reaction.

Synthesis of [{K(THF)}₃]₂U₂(cyclo-trensalsalophen)], **3-THF.** The reduction of complex **1** with 2 equivalents of KC₈ led to the reductive coupling of two imino groups from two different

trensals units in the bis-trensalsalophen ligand yielding the dinuclear macrocyclic complex [{K(THF)}₃]₂U₂(cyclo-trensalsalophen)], **3-THF** (Scheme 6). The ¹H NMR of the reaction mixture did not show any signals probably due to the presence of fluxional solution species. The ¹H NMR spectrum of **3** remains silent at low temperature (–40 °C) and in pyr-d₅. Single crystals suitable for X-ray diffraction of [{K(Py)}₃]₂U₂(cyclo-trensalsalophen)], **3-py**, were obtained by slow diffusion of hexane into a pyridine solution of **3-THF**. A crystallographic inversion center is located between the two uranium centers and relates the two halves of the macrocyclic complex.

Scheme 6. Reduction of **1** with 2 equiv. KC₈

The structural parameters of **3-py** (Figure 4) point unambiguously to the presence of a U(IV) dimer complexed by the dodecadentate decaanionic amidophenolate macrocyclic ligand *cyclo-trensalsalophen* formed through two reductive C–C coupling reactions between two trensal ligands. The resulting dinuclear *cyclo-trensalsalophen* ligand in **3-py** holds the two uranium atoms in close proximity, at a shorter U–U distance of 3.439(2) Å compared to the previously reported distance in [U₂(cyclo-salophen)(py)₄] complex (U–U = 3.54(1) Å).^{2e}

Each uranium centre in **3-py** is nonacoordinated in a distorted tricapped trigonal prismatic environment by four bridging amido nitrogens (N3 and N1) (mean U–N = 2.54(3) Å), one imino nitrogen (U–N4 = 2.581(8) Å), one amino nitrogen (U–N2 = 2.722(8) Å) and three phenoxide oxygen atoms (mean U–O = 2.34(3) Å). Two of the phenoxide oxygen atoms (O2) coordinate a K⁺ cation, together with three molecules of pyridine.

The C–N3 and C–N1 bond distances (mean C–N_{am} = 1.49(2) Å) of the ligand backbone are much longer than the C–N bond distances found in complex **2** and are in agreement with the presence of four amido groups. Similarly, the values of the U–N_{am} bond distances in **3-py** (mean value U–N_{am} = 2.54(3) Å) are significantly shorter than the U–N_{im} distances in **3-py** (U–N_{im} = 2.581(8) Å) and in **2**. These values compare well with those reported for the macrocyclic amidophenolate complex [U₂(cyclo-salophen)(py)₄] (avg value C–N = 1.473(4) Å, U–N = 2.39–2.60 Å).^{2e}

The value of the C–C bond distances (1.553(13) Å) fall in the range of those found for the intermolecular and intramolecular C–C bonds in Na₂[U(bis-salophen)] (1.559(7) Å), [U₂(cyclo-salophen)(py)₄] (1.609(5) Å) and [U(μ -bis-Menaphtquinolen)]₂ (1.64(1) Å).^{2e, 8a}

Figure 4. Molecular structure of complex **3-py**. Hydrogen atoms and pyridine molecules are omitted for clarity. Color cod: uranium (green), nitrogen (blue), oxygen (red), carbon (grey), C–C bond between imine (yellow)

Reactivity of $[\{K(THF)_3\}_2U_2(cyclo-trensall)]$, **3-THF.** In previous studies we showed that the electrons stored in the two C–C bonds of the *cyclo*-salophen ligand in $[U_2(cyclo-salophen)(py)_4]$ can become available to strong oxidizing agents such as AgOTf and phenanthrenequinone leading to cleavage of the C–C bonds and formation of the original salophen Schiff base ligand. However, complex $[U_2(cyclo-salophen)(py)_4]$ did not react with small molecules such as CS_2 and CO_2 .

1H NMR studies showed that complex **3** also reacts rapidly with 2 equiv. or 4 equiv. of AgOTf resulting in the cleavage of one or the two C–C bonds and formation of $[U_2(bis-trensall)]$, **1** and $[U(trensall)]OTf$, **2** complexes, respectively.

Remarkably complex **3** also reacts with excess $^{13}CS_2$ leading to cleavage of one C–C bond in the cyclo-trensall ligand, formation of the bis-trensall complex **1** and release of $^{13}CS_2$ reduction products. From the $^{13}C\{^1H\}$ NMR of the reaction mixture in $DMSO-d_6$ the presence of CS_3^{2-} and $C_2S_4^{2-}$ and $C_3S_5^{2-}$ (from $C_2S_4^{2-}$ and CS) was identified.²⁰

Scheme 7. Reaction of **3** with $^{13}CS_2$

Complex **3** also reacted with two equivalents of CO_2 and the 1H NMR spectrum of the reaction mixture taken immediately after the addition (Figures S23) showed only the presence of the signals assigned to the THF soluble complex **1** (Scheme 8).

The outcome of the reaction was also investigated by quantitative $^{13}C\{^1H\}$ NMR in basic D_2O (pD=12). After quenching the reaction mixture in basic D_2O (pD=12) quantitative $^{13}C\{^1H\}$ NMR showed the presence of $^{13}CO_3^{2-}$ in 80% yield (calculated with respect to the value expected if only two molecules of CO_2 react with **3** as shown in Scheme 8).

The presence of carbonate indicated that the electrons stored in the two C–C bonds in complex **3** can become

available for the reduction of CO_2 . Notably, formation of CO_3^{2-} is the result of the reductive disproportionation of CO_2 by the highly reducing complex **3**. In contrast, no formation of carbonate was observed after reaction of complex **1** with CO_2 .

The reductive disproportionation of carbon dioxide to afford carbonate and CO was reported for U(III) complexes but never reported for U(IV) compounds.^{4a, 32}

The addition of higher amounts of CO_2 (4 equiv., see supporting information) did not lead to an increase in carbonate (78.2%) suggesting that only two out of the four electrons stored in the two bonds in **3** effects the reductive disproportionation of CO_2 with concomitant formation of **1**. The addition of 4 equiv. of CO_2 however also leads to formation of insertion products detected by 1H NMR of the reaction mixture recorded in $THF-d_8$ after several days.

Scheme 8. Redox reaction of **3** with two equivalents of CO_2

When complex **3** is exposed to a large excess of CO_2 (100 equiv or 1 atm) in THF the immediate formation of a solid is observed. The 1H NMR of the solid dissolved in $DMSO-d_6$ showed the presence of multiple species. The $^{13}C\{^1H\}$ NMR of the reaction mixture (after addition of 100 equiv. $^{13}CO_2$) quenched in basic D_2O (pD=12) showed the presence of $^{13}CO_3^{2-}$ in 90% yield (calculated with respect to the value expected if only two molecules of CO_2 react with **3** as shown in Scheme 8). The $^{13}C\{^1H\}$ NMR also shows also the presence of an additional signal assigned to insertion products (162.5 ppm).

Scheme 9. Structure of complex **4**, a minor product isolated from the reaction of **3** with excess CO_2

Recrystallization of the solid isolated from pyridine, after addition of 1 atm CO_2 to **3**, by slow diffusion of hexane in the resulting pyridine solution afforded after long time a few single crystals suitable for X ray diffraction. The

formation of the crystals was not reproducible but allowed to identify a notable product of reactivity, complex **4**, $[\{K(THF)_3\}_2U_2(\mu-O)(CO_2-CO-cyclo-trens al)(U(trens al))]$ (Scheme 9).

The molecular structure of **4** (Figure 5) shows a trinuclear U(IV) complex resulting from three different types of reactivity. The insertion of a CO_2 molecule into one out of the four U–N_{amido} bonds of **3** is observed and provides additional evidence for the formation of a $[U_2(bis-trens alCO_2)]$ species in the reaction of **1** with CO_2 . A second molecule of CO_2 is cleaved leading to a bridging oxide and CO addition to two U–N_{amido} bonds followed by the formation of a cycloimidazolidinone five membered heterocycle. The CO_2 cleavage is probably promoted by the cooperative interaction of two uranium centers and of the nucleophilic amido groups of the *cyclo-trens al* ligand (Figure 5, b).

Finally, a third process must have occurred in the reaction with CO_2 since in the molecular structure, a $[U(trens al)]^+$ cation is found, suggesting that two C–C bonds of the *cyclo-trens al* ligand have been cleaved to restore the original imino groups, through transfer of four electrons to the CO_2 substrate affording carbonate and CO. The fact that free CO is not observed by $^{13}C\{^1H\}$ NMR spectroscopy can be explained by its insertion into the U–N_{amido} bonds. Insertion of CO into U–N_{amido} bonds is reported in literature.³³

The molecular structure of **4** shows a trimeric U(IV) complex. Two uranium centres, U1 and U2, are bound by the $CO_2-CO-cyclo-trens al$ ligand resulting from the insertion of one CO and one CO_2 molecule in the *cyclo-trens al* framework (Figure 5a). The U1 and U2 centers are held together in close proximity at a distance of 3.7266(7) Å, slightly longer than the U–U distance found in **3**. The two centres are bridged by a μ -oxo ligand, the μ -amido nitrogen and μ -k₂(kO:kN) carbamate from the $CO_2-CO-cyclo-trens al$ ligand. U1 is octacoordinated and its coordination sphere is completed by one amino nitrogen (U1–N3 = 2.694(14) Å), one imino nitrogen (U1–N2 = 2.648(14) Å), and three phenoxide oxygens (mean U1–O = 2.31(3) Å). The carbamate moiety is formed upon insertion of a CO_2 molecule in a U–N_{amido} bond. U2 is also octacoordinated and its coordination sphere is completed by one amino nitrogen (U2–N6 = 2.698(14) Å), one imino nitrogen (U2–N7 = 2.570(12) Å), one amido nitrogen (U2–N8 = 2.649(14) Å), two phenoxide oxygen (mean U–O = 2.297(7) Å), and one oxygen from the cycloimidazolidinone fragment in the $CO_2-CO-cyclo-trens al$ ligand.

The structural parameters of the five member heterocycle formed from the addition of CO to the *cyclo-trens al* ligand (C30–O5 distance = 1.302(19) Å, C30–N5 distance = 1.32(2) Å and C30–N4 distance = 1.36(2) Å) are similar to those reported values for free *cyclo-imidazolidinones*.³⁴ A K^+ cation is hexacoordinated by the two phenoxide coordinated to U1, an oxygen from the inserted CO_2 molecule and 3 THF oxygens. One appended phenoxide ligand (O13) of the $CO_2-CO-cyclo-trens al$ ligand, binds the U3 atom of a $[U(trens al)]^+$ moiety.

The unusual structure of **4** consisting of two different components, the macrocyclic dinuclear anionic complex $[K(THF)_3U_2(\mu-O)(CO_2-CO-cyclo-trens al)]^-$ and the cationic $[U(trens al)]^+$ complex is probably at the origin of the lack

of reproducibility in crystal isolation. However, the structure of **4** gives a clear indication of the multiple processes occurring when complex **3** is reacted with a large excess of CO_2 .

Figure 5 a) structure of **4** after removing the $[U(trens al)]^+$ arm b) Detail of the structure showing the inserted and cleaved CO_2 molecules. Hydrogen atoms and methyl groups were omitted for clarity. Color code: uranium (green), nitrogen (blue), oxygen (red), carbon (grey), C–C bond between imine (yellow).

Electrochemistry.

In contrast with what observed previously with the $[U_2(cyclo-salophen)(py)_4]$ the electrons stored on the *trens al* ligand via the formation of C–C bonds can become available for the reduction of CO_2 to carbonate. In order to understand the origins of the higher reactivity of the C–C bond in the $[\{K(THF)_3\}_2U_2(cyclo-trens al)]$, **3-THF** complex we performed electrochemistry studies of the complexes **1** and **2**.

Cyclic voltammetry data were measured for complexes **1** and **2** in ~0.1 M pyridine solution of $[Bu_4N][PF_6]$ and are presented in Figure 6. All redox potentials are referenced against the $[(C_5H_5)_2Fe]^{+/0}$ redox couple. The voltammogram of complex **1** shows in the first scan only one distinct irreversible reduction event at $E_{pc} = -2.53$ V associated with two irreversible redox processes at -0.43

V and -0.07V. The same peak is present in the cyclic voltammogram of **2** measured in the same conditions, at $E_{pc} = -2.50$. In the latter a first irreversible reduction event is occurring at $E_{pc} = -2.03$ V, which is also observed in the second scan of the voltammogram of **1** after oxidation. This event is associated with one irreversible oxidation processes occurring at $E_{pa} = -1.48$ V which is not observed in the voltammogram of **1** when the voltammogram is swept initially from -0.91 V towards the positive direction but is always present in the voltammogram of **2**. These data indicate the presence of a system with a limited degree of chemical reversibility as previously observed for the reduction of U(IV) Schiff base complexes leading to the formation of C-C bonds after ligand reduction. Since only one irreversible reduction process was observed for complex **1** the redox process at $E_{pc} = -2.50$ is assigned to the ligand reduction leading to the formation of complex **3** while the redox event at $E_{pc} = -2.03$ V is assigned to the formation of complex **1**. The assignment of the event at $E_{pc} = -2.50$ to the formation of complex **3** was confirmed by the cyclic voltammogram of **3** measured after addition of cryptand which did not show any reduction event in the first scan.

The oxidation event at -1.48 V is associated to the two-electron ligand oxidation in **3** while the oxidation event at -0.55 V is associated to the second successive two-electrons ligand oxidation leading from **1** to **2**. The irreversibility of the ligand-based processes arises from the fact that the electrochemical reduction and oxidation is followed by a rapid chemical transformation involving the formation or cleavage of the C-C bond between two reduced imino groups.

The pseudo-reversible redox event observed in the voltammograms of both **1** and **2**, with $E_{pa} = 0.37$ V and $E_{pc} = 0.21$ V is assigned to the U(IV)/U(V) metal centered redox event. This fits with the range of values of redox potentials reported for other U(IV)/U(V) reversible systems in the range (-1.81 to 0.12 V vs. Fc^+/Fc).³⁵ The ligand based irreversible oxidation events at -1.13 V and -0.13 present in the voltammograms of **1** and **2** are also observed in the voltammogram of the K_3 trensal ligand^{11a} and they could be due to oxidation of the phenol groups.

Electrochemistry studies reported for the U(IV) complex $[U_2(M^e\text{naphtquinolen})_2]^{8a}$ containing two tridentate Schiff base ligands showed a series of ligand -based and metal-based redox processes. Ligand based reduction was reported to occur in the -1.49- -1.70 V range. Ligand based reduction were found at lower potential in the range -2.17 to -2.25 V for the mononuclear U(IV) complexes $M[U(\text{bis-}^R\text{salophen})]$ ($M, R = \text{Na, H; K, Me; K, }^t\text{Bu}$) formed from intramolecular reduction of the salophen Schiff base (Scheme 1, bottom).³⁶

The ability of complex **3** to reduce CO_2 is probably due to its lower reduction potential ($E_{pc} = -2.50$ V) compared to the $[U_2(M^e\text{naphtquinolen})_2]$ $M[U(\text{bis-}^R\text{salophen})]$ complexes and associated to a higher accessibility to the metal center compared to the bis- $M^e\text{naphtquinolen}$ and bis-salophen complexes.

Figure 6. Room temperature cyclic voltammetry of complexes 4 mM pyridine solutions of **1** (blue), **2** (orange) and **3** in presence of cryptand (grey) in ~0.1 M

$[\text{Bu}_4\text{N}][\text{PF}_6]$ at a 100 mV/sec scan rate versus Fc , using a Pt^0 disk as working electrode (arrows indicate scan direction).

SUMMARY

Here we have prepared and characterized a new example of dinuclear U(IV) complex (**1**) resulting from the reductive coupling of the imino groups of the tripodal heptadentate *trensal* Schiff base by U(III). Complex **1** was further reduced to afford the diuranium(IV) complex (**3**) of the dodecadentate decaanionic amidophenolate macrocyclic ligand *cyclo-trensal* formed from the reductive C-C coupling of two imino groups of two *trensal* ligands. The electrons stored in the C-C bonds in complex **1** and **3** can become available to strong oxidizing agents such as AgOTf restoring the original imino functions of the *trensal* ligand. Complex **1** also reacts with CO_2 but only insertion reactions into the U-N_{amido} bonds are observed.

In contrast the electrons stored in the C-C bonds in the complex **3** are also available for the CO_2 reduction to carbonate which is the major product for a **3**: CO_2 stoichiometry of 1:2.

Parallel reactions leading to modification of the ligand structure through insertion reactions into the U-N_{amido} bonds of CO_2 and CO occur in the presence of excess CO_2 .

The higher reactivity of the reduced complex of *cyclo-trensal* compared to the previously reported U(IV) complexes of reduced Schiff bases is ascribed to more negative redox potential and to the higher flexibility of the *trensal* scaffold.

Future work will be directed to identify Schiff bases that allow to favor the reduction compared to the insertion reaction.

ASSOCIATED CONTENT

Supporting Information.

Selected ^1H NMR and ^{13}C NMR spectra, Selected cyclovoltammograms, X-ray crystallographic data and files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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