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The first mixed cyclooctatetraenyl-phospholyl metal complexes. Crystal structure of $[U(\eta\text{-}C_8H_8)(\eta\text{-}C_4Me_4P)(BH_4)(OC_4H_8)]$

Sophie M. Cendrowski-Guillaume *, Martine Nierlich, Michel Ephritikhine *

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, Bat. 125, CEA Saclay, 91191 Gif-sur-Yvette, France

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Abstract

Treatment of $[U(COT)(BH_4)_2(THF)]$ (**1**) or $[U(COT)(BH_4)(THF)_2][BPh_4]$ (**2**) ($COT = \eta\text{-}C_8H_8$) with Ktmp (tmp, $\eta\text{-}C_4Me_4P$) gave $[U(COT)(tmp)(BH_4)(THF)]$ (**4**), the crystal structure of which was determined. Further reaction of Ktmp with **4** afforded the 'ate' addition derivative $K[U(COT)(tmp)_2(BH_4)(THF)_x]$. Complex **4** was transformed into $[U(COT)(tmp)(OEt)]$ (**5**) in the presence of NaOEt. The cationic compound $[U(COT)(tmp)(HMPA)_2][BPh_4]$ (**6**) (HMPA, hexamethylphosphoramide) was isolated from the reaction of $[U(COT)(HMPA)_3][BPh_4]_2$ (**3**) with Ktmp. The cationic complexes **2** and **3** were recovered upon protonation of **4** and **6** with NEt_3HBPh_4. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phospholyl; Cyclooctatetraenyl; Borohydride; Uranium

1. Introduction

Mathey et al. discovered in the mid 1970s the first phosphametallocenes, phosphaferrocenes [1] and phosphacymantrenes [2] in which a η^5-phospholyl ligand was used as a substitute for the isoelectronic cyclopentadienyl ligand. Since then, a large variety of phospholyl complexes of the main group, d-transition metals and also lanthanides have been synthesized [3]; these exhibit unique structural and chemical features, which result from the aromaticity of the heterocyclic ligand and the accessibility of the phosphorous lone pair.

In collaboration with the group of F. Mathey, we have prepared the first phospholyl actinide compounds, i.e. the bis(tetramethylphospholyl) uranium borohydrides $[U(tmp)_2(BH_4)_2]$ and $[\{U(tmp)_2(BH_4)\}_2]$ (tmp, 2,3,4,5-tetramethylphospholyl) [4]. This family was then extended to a number of complexes of general formula $[U(tmp)_{4-n}X_n]$ ($n = 1$–3; $X = BH_4$, Cl, alkyl or alkoxide) [5–7]; the $[U(tmp)_3UX]$ derivatives are unique examples of tris(phospholyl) metal complexes [7]. Comparison of these compounds with their pentamethylcyclopentadienyl analogues showed that the tmp ligand has a lower electron-donating capacity than Cp*; in particular, the phospholyl complexes were reduced more easily into the corresponding uranium(III) anions. The tmp ligand was also useful for the synthesis of polynuclear complexes in which uranium and nickel atoms are associated via phospholyl bridges in the $\mu\text{-}\eta^1,\eta^5$ coordination mode [8].

In this paper, we present a new class of phospholyl uranium(IV) compounds with $[U(COT)(tmp)(BH_4)(THF)]$ (COT, $\eta\text{-}C_8H_8$; THF, tetrahydrofuran) and its derivatives. Mixed-ring organoactinide complexes are rather uncommon [9] and those reported here are the first ones in which cyclooctatetraenyl and phospholyl ligands are combined on a single metal center.

2. Results and discussion

Recently, we described the protonolysis reaction of $[U(COT)(BH_4)_2(THF)]$ (**1**) [10] with NEt_3HBPh_4, which gave successively the mono- and dication $[U(COT)(BH_4)(THF)_2][BPh_4]$ (**2**) and $[U(COT)(HMPA)_3][BPh_4]_2$ (**3**) (HMPA, hexamethylphosphoramide) [11]; these represent the first cationic organometallic borohydride and the first organometallic dication of an

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* Corresponding authors. Present address: LCPO, CNRS UMR 5629, ENSCP Bordeaux, 16 Avenue Pey Berland, 33607 Pessac Cedex, France. Tel.: +33-5-56848488; fax: +33-5-56848487 (S.M.C.-G.); tel.: +33-1-69-086436; fax: +33-1-69-086640 (M.E.).

E-mail addresses: guillaume@enscpb.u-bordeaux.fr (S.M. Cendrowski-Guillaume), ephri@drecam.cea.fr (M. Ephritikhine).

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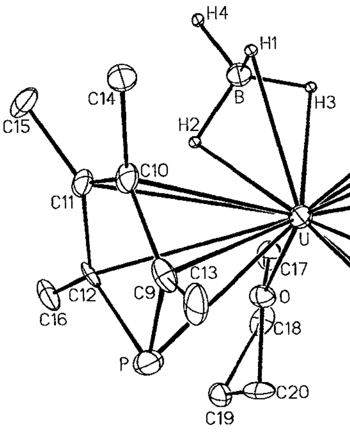

Fig. 1. X-ray crystal structure of **4**.

f-element, respectively. Complexes **1**–**3** are valuable precursors for the preparation of new derivatives by reaction with alkali metal salts of anionic ligands.

Treatment of **1** with one equivalent of Ktmp in THF afforded readily the mixed-ring complex [U(COT)(tmp)(BH$_4$)(THF)] (**4**) according to Eq. (1). After filtration, the

$$\underset{\mathbf{1}}{[\mathrm{U(COT)(BH_4)_2(THF)}]} + \mathrm{Ktmp} \xrightarrow{\mathrm{THF}} \underset{\mathbf{4}}{[\mathrm{U(COT)(tmp)(BH_4)(THF)}]} + \mathrm{KBH_4} \qquad (1)$$

solution was evaporated under vacuum, leaving the brown powder of [U(COT)(tmp)(BH$_4$)] in 89% yield. Crystals of **4** were obtained from THF. Complex **4** was synthesized alternatively in almost quantitative yield by reaction of **2** with Ktmp (Eq. (2)).

$$\underset{\mathbf{2}}{[\mathrm{U(COT)(BH_4)(THF)_2][BPh_4]}} + \mathrm{Ktmp} \xrightarrow{\mathrm{THF}} \underset{\mathbf{4}}{[\mathrm{U(COT)(tmp)(BH_4)(THF)}]} + \mathrm{KBPh_4} \qquad (2)$$

The ^{1}H-NMR spectrum of **4** in THF-d_8 exhibits, in addition to the resonances assigned to the BH$_4$ and COT ligands, two signals of equal intensities which correspond to the α- and β-methyl groups of the tmp ligand. The equivalence of the 2 and 5 positions, as well as the 3 and 4 positions of the heterocycle likely resulted from the facile permutation of the THF and BH$_4$ ligands in the tetrahedral structure of **4** (vide infra) in relation with the rapid exchange between free and coordinated THF molecules. This process was slowed down at low temperature, but the slow-limit spectrum was not observed. A similar fluxionality was encountered previously with the bis(phospholyl) compounds [U(tmp)$_2$(BH$_4$)(THF)] [5]. In the IR spectrum of **4**, the strong singlet at 2417 cm^{-1} and the broad bands at 2125 and 2074 cm^{-1} are characteristic of a tridentate BH$_4$ group [12]. The structure of **4** was confirmed by X-ray crystallography; a view of the molecule is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The uranium atom is found at the center of a distorted tetrahedron defined by the O and B atoms and two rings centroids. The U–B distance of 2.67(1) Å is intermediate between those of typical tridentate and bidentate borohydride ligands, which are 2.55 and 2.80 Å, respectively [12]. The BH$_4$ ligand is in fact not symmetrically oriented, i.e. one of the three bridging hydrogen atoms is farther from the uranium center (U–H(3) 2.772(5) Å) than the other two (2.36(5) and 2.47(5) Å) and the U–B–H(4) angle is 167(2)°. A similar distortion of the tridentate borohydride ligand was also found in [U(BH$_4$)$_4$] and some of its Lewis base adducts [13]. The COT ring is planar within ±0.027(5) Å; the U–C bond distances are ranging from 2.688(9) to 2.740(9) Å and the average value of 2.72(3) Å is at the upper limit of the range of those found in cyclooctatetraenyl uranium(IV) compounds, which vary from 2.62 Å in [U(COT)(S^{i}Pr)$_2$]$_2$ [14] and 2.71 Å in [U(COT)(NEt$_2$)(THF)$_3$][BPh$_4$] [15]. The phospholyl ligand is pentahapto-bonded to uranium, the tmp ring being planar within ±0.015(5) Å with the carbon atoms of the methyl groups lying out of this plane by an average distance of 0.2(1) Å. The U–P bond length is 2.970(8) Å and the mean U–C(ring) distance is 2.93(3) Å; these values are similar to those of 2.927(4) and 2.90(7) Å, determined in [U(tmp)$_3$Cl] [7].

Table 1
Selected bond distances (Å) and bond angles (°) in **4**

Bond distances					
U–C(1)	2.740(9)	U–C(2)	2.724(9)	U–C(3)	2.711(9)
U–C(4)	2.704(9)	U–C(5)	2.688(9)	U–C(6)	2.732(8)
U–C(7)	2.726(8)	U–C(8)	2.730(8)	U–C(9)	2.923(9)
U–C(10)	2.892(8)	U–C(11)	2.937(8)	U–C(12)	2.904(8)
U–P	2.970(8)	U–O	2.528(6)	U–H(1)	2.47(5)
U–H(2)	2.36(5)	U–H(3)	2.772(5)	U–B	2.672(10)
U–COT [a]	2.013(8)	U–tmp [a]	2.610(8)		
Bond angles					
O–U–B	82.2(3)	O–U–COT	112.8(3)	O–U–tmp	96.8(3)
B–U–COT	119.4(3)	B–U–tmp	96.6(3)	COT–U–tmp	135.6(3)

[a] COT and tmp are the centroids of the COT and tmp rings, respectively.

Attempts to prepare new derivatives from **4** have met a moderate success. Reaction of **4** with Ktmp in THF did not afford the substitution product [U(COT)(tmp)$_2$] but gave, as frequently observed in f-element chemistry [16], the 'ate' addition complex K[U(COT)(tmp)$_2$(BH$_4$)(THF)$_x$]. This latter was not stable in solution, being slowly decomposed into unidentified species, and was characterized only by its ^{1}H-NMR spectra. The signals of the phospholyl rings were not visible at 20 °C revealing, as in the case of **4**, the facile intramolecular rearrangement of the ligands; however, the slow-limit spectrum showing eight singlets corresponding to the inequivalent methyl groups of the tmp ligands was observed at low temperature. The alkoxide compound [U(COT)(tmp)(OEt)] (**5**) was isolated as an orange powder in 69% yield from the reaction of **4** with NaOEt in THF. However, similar treatment of **4** with NaS^{t}Bu led to the formation of Na[U(COT)(S^{t}Bu)$_3$] [14] as the only product identified.

While protonation of borohydride ligands proved to be an efficient route to cationic compounds [11,17], reaction of **4** with NEt$_3$HBPh$_4$ did not afford the cationic phospholyl derivative [U(COT)(tmp)(THF)$_x$]$^+$, but gave instead the cationic borohydride **2**, according to Eq. (3).

$$\underset{\mathbf{4}}{[\mathrm{U(COT)(tmp)(BH_4)(THF)}]} + \mathrm{NEt_3HBPh_4} \xrightarrow{\mathrm{THF}} \underset{\mathbf{2}}{[\mathrm{U(COT)(BH_4)(THF)_2}][\mathrm{BPh_4}]} + \mathrm{NEt_3} + \text{'tmpH'} \quad (3)$$

The cationic mixed cyclooctatetraenyl-phospholyl compound [U(COT)(tmp)(HMPA)$_2$][BPh$_4$] (**6**) was, however, synthesized by treating the dication **3** with one equivalent of Ktmp in THF, as depicted by Eq. (4). After 3 h at 20 °C, the solution

$$\underset{\mathbf{3}}{[\mathrm{U(COT)(HMPA)_3[BPh_4]_2}]} + \mathrm{Ktmp} \xrightarrow{\mathrm{THF}} \underset{\mathbf{6}}{[\mathrm{U(COT)(tmp)(HMPA)_2}][\mathrm{BPh_4}]} + \mathrm{KBPh_4} \quad (4)$$

was filtered and evaporated, and the brown powder of **6** was recovered in 81% yield after crystallization from THF–pentane. Similar to reaction (Eq. (3)), treatment of **6** with NEt$_3$HBPh$_4$ gave back the dication **3** (65% yield by NMR) with other unidentified products. Such formation of cationic complexes by protonation of phospholyl precursors is, to our knowledge, unprecedented.

3. Conclusion

The first mixed cyclooctatetraenyl-phospholyl metal compounds [U(COT)(tmp)(BH$_4$)(THF)] (**4**) and [U(COT)(tmp)(HMPA)$_2$][BPh$_4$] (**6**) were synthesized by addition of Ktmp to the cationic precursors [U(COT)(BH$_4$)(THF)$_2$][BPh$_4$] (**2**) and [U(COT)(HMPA)$_3$][BPh$_4$]$_2$ (**3**), respectively. The new reaction of the phospholyl ligands of **4** and **6** with the proton acidic reagent NEt$_3$HBPh$_4$ was found to give back the cationic complexes **2** and **3**.

Further studies will focus on the reduction of **4** and **6**, which would be facilitated by the electron-accepting properties of the phospholyl ligand. The expected uranium(III) complexes and the corresponding mixed COT–Cp* derivatives will be compared with their neodymium counterparts [18] in order to get further information about the differentiation of analogous trivalent lanthanide and actinide compounds.

4. Experimental

4.1. General procedures

All reactions were carried out under argon using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were dried and deoxygenated by standard methods and distilled before use. Deuterated solvents were dried over Na–K alloy. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^{1}H-NMR spectra were recorded on a Bruker DPX-200 instrument and were referenced internally using the residual protio solvent resonances relative to Me$_4$Si (δ 0). IR spectra were obtained on a Perkin–Elmer 1725X spectrometer. The salt NEt$_3$HBPh$_4$ precipitated by mixing NEt$_3$HCl and NaBPh$_4$ in water; Ktmp [5], [U(COT)(BH$_4$)$_2$(THF)] [10], [U(COT)(BH$_4$)(THF)$_2$][BPh$_4$] and [U(COT)(HMPA)$_3$][BPh$_4$]$_2$ [11] were prepared as described previously.

4.2. Synthesis of [U(COT)(tmp)(BH$_4$)(THF)] (4)

4.2.1. From 1

A flask was charged with **1** (466 mg, 1.05 mmol) and Ktmp (187 mg, 1.05 mmol) and THF (40 ml) was condensed in. After stirring for 3 h at 20 °C, the dark brown solution was filtered and the solvent evaporated off. The brown powder of [U(COT)(tmp)(BH$_4$)] was obtained after drying under dynamic vacuum overnight (464 mg, 89%). Anal. Found: C, 38.69; H, 4.84; P, 6.21. Calc. for C$_{16}$H$_{24}$BPU: C, 38.71; H, 4.84; P, 6.25%. ^{1}H-NMR (THF-d_8, 20 °C): δ 39.7 (4 H, q, $J = 85$ Hz, BH$_4$), 11.40 (6 H, s, Me), 8.00 (6 H, s, Me), -33.27 (8 H, s, COT). Coalescence of the signals corresponding to the methyl groups of the tmp ligand occurred at -45 °C but the slow-limit spectrum was not observed. IR (Nujol): 2417 (s), 2125, 2074 (br) cm^{-1}. Crystals of **4** suitable for XRD analysis were obtained from a THF solution.

4.2.2. From 2

An NMR tube was charged with **2** (5.7 mg, 6.96 μmol) and Ktmp (1.5 mg, 8.42 μml) in THF-d_8 (0.3 ml).

The spectrum showed the immediate and quantitative formation of **4**.

4.3. Reaction of **4** with Ktmp

An NMR tube was charged with **4** (7.1 mg, 12.4 μmol) and Ktmp (2.2 mg, 12.4 μml) in THF-d_8 (0.3 ml). After a few minutes at 20 °C, the color of the solution changed from dark brown to dark orange and the spectrum showed the formation of K[U(COT)(tmp)$_2$(BH$_4$)(THF)]: δ (20 °C) 26.3 (4 H, br, $w_{1/2} = 300$ Hz, BH$_4$), −33.96 (8 H, s, COT); δ (−93 °C) 9.8 (4 H, br, $w_{1/2} = 500$ Hz, BH$_4$), −53.27 (8 H, s, COT), 76.75, 35.22, −1.79, −4.61, −30.18, −34.38, −37.08, −38.69 (8 × 3 H, s, Me). This compound, which was also obtained by treating **1** or **2** with two equivalents of Ktmp, was not stable in solution. Encapsulating the potassium cation into 18-crown-6 ether did not improve the stability of the complex.

4.4. Synthesis of [U(COT)(tmp)(OEt)] (**5**)

A flask was charged with **4** (215.8 mg, 0.38 mmol) and NaOEt (26.5 mg, 0.39 mmol) and THF (40 ml) was condensed in. The mixture was stirred for 3 h at 20 °C; the dark orange solution was filtered and the solvent evaporated off. The residue was extracted with toluene (20 ml) and the red–orange powder of **5** was obtained after evaporation and drying under vacuum (141 mg, 69%). Anal. Found: C, 41.22; H, 4.97; P, 5.93. Calc. for $C_{18}H_{25}OPU$: C, 41.06; H, 4.75; P, 5.89%. ^{1}H-NMR (THF-d_8, 20 °C): δ 131.5 (2 H, s, CH$_2$), 45.88 (3 H, s, Me), 14.98 (6 H, s, Me), −12.44 (6 H, s, Me), −33.14 (8 H, s, COT).

4.5. Reaction of **4** with NaS^{t}Bu

An NMR tube was charged with **4** (4.4 mg, 7.8 μmol) and NaS^{t}Bu (10.8 mg, 9.7 μml) in THF-d_8 (0.3 ml). After 30 min at 20 °C, the spectrum of the orange solution showed the formation of Na[U(COT)(S^{t}Bu)$_3$] [14] (ca. 25% yield) with other unidentified products.

4.6. Reaction of **4** with NEt$_3$HBPh$_4$

An NMR tube was charged with **4** (6.1 mg, 10.7 μmol) and NEt$_3$HBPh$_4$ (4.5 mg, 10.7 μml) in THF-d_8 (0.3 ml). After 1 h at 20 °C, the spectrum of the orange solution showed the formation of **2** (65%) along with **4** (23%) and **1** (12%).

4.7. Synthesis of [U(COT)(tmp)(HMPA)$_2$][BPh$_4$] (**6**)

A flask was charged with **3** (811.7 mg, 0.53 mmol) and Ktmp (93.0 mg, 0.52 mmol) and THF (40 ml) was condensed in. The mixture was stirred for 3 h at 20 °C; the brown solution was filtered and evaporated to dryness. The brown powder of **6** was crystallized from THF–pentane, filtered off and dried under vacuum (504 mg, 81%). Anal. Found: C, 54.10; H, 6.49; P, 7.84. Calc. for $C_{52}H_{76}BN_6O_2P_3U$: C, 53.89; H, 6.56; P, 8.03%. ^{1}H-NMR (THF-d_8, 20 °C): δ 6.96 (8 H, br, *o*-Ph), 6.63 (8 H, t, $J = 7$ Hz, *m*-Ph), 6.56 (4 H, t, $J = 7$ Hz, *p*-Ph), −1.24 (36 H, d, $J = 9$ Hz, HMPA), −5.82 (6 H, s, Me), −8.54 (6 H, d, $J = 6$ Hz, Me), −32.60 (8 H, s, COT).

4.8. Reaction of **6** with NEt$_3$HBPh$_4$

An NMR tube was charged with **6** (7.1 mg, 6.1 μmol) and NEt$_3$HBPh$_4$ (2.6 mg, 6.1 μmol) in THF-d_8 (0.3 ml). After 1.5 h at 20 °C, an orange precipitate was obtained and the spectrum of the brown solution showed the formation of unidentified products. The precipitate was identified as **3** by its ^{1}H-NMR spectrum in pyridine-d_5 (65% yield).

4.9. X-ray crystal structure of **4**

Selected single crystals were introduced into thin-walled Lindemann glass tubes in the glove box. Data were recorded on a Nonius Kappa-CCD area-detector diffractometer using graphite-monochromatized Mo–K$_\alpha$ radiation. The crystal-to-detector distance was set to 28 mm and the unit cell was determined from all the reflections measured on ten frames with Φ-rotation steps of 2°. A 180° Φ-range was scanned during data recording (90 frames, Φ-rotation = 2°, exposure time = 30 s by frame). The data were corrected for Lorentz polarization and absorption [19] effects and processed with the HKL package [20]. The structure was solved by the heavy atom method with SHELXS-86 [21] and refined on F^2 with SHELXTL [22] with anisotropic thermal parameters for all non-H atoms. H atoms of the BH$_4$ ligand were found in the last Fourier difference map and refined with constrained B–H and H–H distances and isotropic displacement parameter equal to 1.2 times that of the B atom. The other H atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH$_2$) times that of the parent atom.

Crystal data for **4**: formula $C_{20}H_{32}BOPU$, crystal dimensions 0.20 × 0.20 × 0.20 mm, monoclinic, space group $P2_1/n$, $a = 8.668(2)$, $b = 20.501(4)$, $c = 11.955(2)$ Å, $\beta = 109.27(3)°$, $V = 2005.4(7)$ Å^3, $Z = 4$, $\rho_{\text{calc.}} = 1.882$ g cm^{-3}, $6.2 < 2\theta < 41.6°$, μ(Mo–K$_\alpha$) = 8.178 cm^{-1}, $F(000) = 1088$, $T = 123$ K. Reflections (19 225) collected, 2045 unique, 1584 with $I > 2\sigma(I)$, $R = 0.028$, $wR = 0.058$. Difference Fourier analysis showed no peaks beyond 0.571 or −0.955 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 164913. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336022; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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