SUPPORTING INFORMATION FOR

Bent thorocene complexes with the cyanide, azide and hydride ligands

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Experimental

The complexes described below are moisture sensitive. Syntheses and manipulations of the compounds were conducted under ultra high purity argon atmosphere with rigorous exclusion of air and water, using Schlenk-vessel and vacuum-line techniques or in a glove box.

The solvents, toluene, pentane and tetrahydrofuran were dried over a mixture of sodium-benzophenone and pyridine over potassium and were distilled immediately before use. Deuterated pyridine (Eurisotop) was distilled over K and stored over 3 Å molecular sieves in the glove box. NaCN, NaN_3 (Aldrich) were dried at 80°C under vacuum for 20 h and kept under argon. The oil protecting the commercially available NaH (Aldrich) was eliminated and NaH was washed in toluene. The 18-crown-6 (Aldrich) was dried and stored under argon. $(Cot)_2U$[1] (**1**) and $(Cot)_2Th$[2] (**2**) were synthesis as previously described.

IR samples were prepared as Nujol mulls between KBr round cell windows and the spectra recorded on a Perkin-Elmer FT-IR 1725X spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 23°C on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The $\{^1H\}$ NMR signals of pyridine were referenced at 8.58, 7.42 and 7.0 and in $\{^{13}C\}$ NMR at 150.4, 135.9, 123.9. The $\{^{13}C\}$ NMR signals of THF at referenced at 67.4 and 25.3. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany) or by Medac Ltd at Chobham Surrey (UK). The analyses of the thorium compounds gave systematically a low C content; this has been already noticed and explained by the formation of incombustible thorium carbide species.[3,4]

NBu_4CN : **$^{13}C\{^1H\}$ NMR** (py-d_5): 168.2 (CN), 59.43 (CH_2), 24.85(CH_2), 20.63(CH_2), 14.42 (CH_3). $(Cot)_2Th$: **^1H NMR** (THF-d_8): δ = 6.50 (s, 8 H, Cot). **$^{13}C\{^1H\}$** NMR (THF-d_8): δ = 107.67 (s, 8H, Cot).

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; Natural thorium (primary isotope ^{232}Th) is a weak α-emitter (4.012 MeV) with a half-life of 1.41×10^{10} years; all the manipulations and reactions should be carried out in monitored fume hoods or in glove-box, in a laboratory equipped with α- and β-counting equipment.

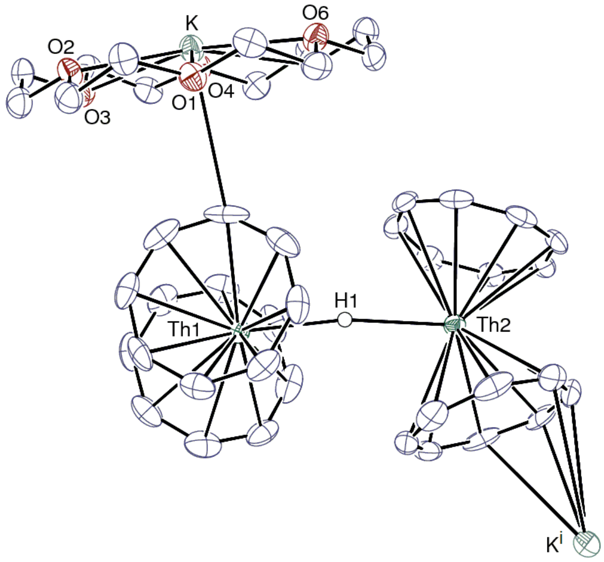
[(Cot)$_2$Th(CN)][Na*] : A 50 mL round bottom flask was charged with **1** (100 mg, 0.23 mmol), NaCN (35.0 mg, 0,71 mmol), 18-crown-6 (60.0 mg, 0,23 mmol) and pyridine (15 mL) was condensed in it. The orange suspension gave an orange solution and after 20 h at room temperature the solvent was evaporated off and the product extracted in THF (20 mL). Evaporation of the solvent, washing of the yellow residue with 15 mL of hot toluene and drying under vacuum for 15h at 20°C afforded pure sample of [(Cot)$_2$Th(CN)][Na*] as a yellow powder (140 mg, 82%). Anal. Calcd. for $C_{29}H_{40}NNaO_6Th$ (753.66): C 46.22, H 5.35, N 1.86, Na 3.05; found : C, 41.40; H, 4.97; N, 2.03; Na, 2.65. **^{1}H NMR** (pyridine-d_5, 23°C): δ = 6.60 (s, 16 H, Cot), 3.22 (s, 24 H, OCH_2). **^{1}H NMR** (THF-d_8, 23°C): δ 6.07 (s, 16 H, Cot), 3.57 (s, 24 H, OCH_2). **^{13}C{^{1}H}** NMR (pyridine-d_5, 23°C): 175.5 (CN), 103.0 (Cot), 70.4 (CH_2O). **^{13}C{^{1}H} NMR** (THF-d_8, 23°C):102.5 (Cot), 70.8 (OCH_2), CN not seen.

Yellow crystals of **[(Cot)$_2$Th(CN)][Na*]** were obtained by slow diffusion of Et_2O in a pyridine solution of the product or by slow cooling to room temperature of a hot THF solution. IR spectrum (KBr/Nujol): ν(CN)= 2108 cm^{-1}

[(Cot)$_2$Th(N$_3$)][Na*] : A flask was charged with (Cot)$_2$Th (100 mg, 0.23 mmol) and NaN_3 (39 mg, 0.60 mmol), 18-crown-6 (59 mg, 0.23 mmol) and pyridine (15 mL) was condensed in it. The reaction mixture was stirred for 24 h at 85 °C giving a brown-orange solution. After evaporation of the solvent and drying under vacuum (3 h at rt), the product was extracted in THF (20 mL) from the excess of NaN_3. The solvent was evaporated off, and the orange powder of [(Cot)$_2$Th(N$_3$)][Na*] was dried under vacuum for 24 h at rt. (123.0 mg, 62%). Anal. Calc. For $C_{28}H_{40}N_3NaO_6Th$ (769.66): C 43.70, H 5.24, N 5.46. Found : C 42.17, H 5.48, N 5.80. Large yellow platelets of [(Cot)$_2$Th(N$_3$)][Na*] were obtained by slow diffusion of pentane in a THF solution of the product. IR spectrum (KBr/Nujol): $\nu_{antisym}(N_3)$= 2075 cm^{-1}, $\nu_{sym}(N_3)$= 1299 cm^{-1}. ^{1}H NMR (pyridine-d_5, 23 °C): δ = 6.56 (s, 8 H, Cot), 3.26 (s, 12 H, CH_2O). ^{1}H NMR (THF-d_8, 23 °C): δ = 6.00 (s, 8 H, Cot), 3.46 (s, 12 H, CH_2O). ^{13}C NMR (pyridine-d_5, 23 °C): δ = 101.9 (s, Cot), 70.2 (s, CH_2O). ^{13}C NMR (THF-d_8, 23 °C): δ = 102.2 (s, Cot), 71.0 (s, CH_2O).

[{(Cot)$_2$Th}$_2$(μ−H)][Na*(THF)] : A 50 mL round bottom flask was charged with **1** (100 mg, 0.23 mmol), NaH (30.0 mg, 1.25 mmol), 18-crown-6 (30.0 mg, 0.11 mmol) and THF (20 mL) was condensed in it. The yellow suspension was sonicated 4 h (in a 1510 Branson utrasonic bath) and stirred for 20 h at room temperature, leading to a pale blue solution with a green-yellow deposit which was separated from the excess of NaH by soxhlet extraction in THF for 3 h. The extracted green solid was then washed with a mixture THF/Et_2O (5 mL/10 mL), and dried under vacuum for 4 h (113 mg, 80%). **[{(Cot)$_2$Th}$_2$(μ−H)][Na*(THF)]** is poorly soluble in toluene, insoluble in diethyl ether and degrades in pyridine. Anal. Calcd. for $C_{48}H_{65}NaO_7Th_2$ (1241.09): C, 46.45; H, 5.28; Na, 1.85. Found : C, 45.31; H, 5.58. **^{1}H NMR** (THF-d_8, 23° C): δ = 13.47 (s, 1 H, Th−H), 6.30 (s, 32 H, Cot), 3.37 (s, 24 H, CH_2O). **^{13}C{^{1}H}** NMR (THF-d_8, 23°C): 104.4 (Cot, broad), 70.9 (CH_2O). ^{1}H NMR (pyridine-d$_5$, 23 °C): δ = 6.53 (s, 16 H, Cot), 6.30 (s, 16 H, Cot), 3.5 (broad s, 4H, THF), 3.21 (s, 12 H, CH_2O), 1.45 (broad s, 4H, THF). Note that the hydride reacts in pyridine, giving two products, one unidentified at 6.53 and another is thorocene. Integration of the Cot:THF shows a ratio of 4:1. IR spectrum (KBr/Nujol): ν(Th−H) not seen or masked by Nujol. Thin green-yellow crystalline platelets of [{(Cot)$_2$Th}$_2$(μ−H)][Na*(THF)$_2$] (**6[Na*(THF)$_2$]**) deposited from a THF solution containing (Cot)$_2$Th (10 mg, 0.022 mmol), NaH (3 mg, 0.125 mmol) and 18-c-6 (3.0 mg, 0.011 mmol), when heated at 90°C for 10 h.

Crystals of [{(Cot)$_2$Th}$_2$(μ−H)][K*] : In an NMR tube containing (Cot)$_2$Th (10 mg, 0.023 mmol), KC_8 (6.1 mg, 0.046 mmol) and 18-crown-6 (6.0 mg, 0.023 mmol), THF was condensed under vacuum at -70°C. The mixture was sonicated and rapidly turned green with a deposit of black carbon graphite. After 15 h at room temperature, numerous pale green microcrystalline platelets of [{(Cot)$_2$Th}$_2$(μ−H)][K*] have deposited along the walls.



View of [{(Cot)$_2$Th}$_2$(μ−H)][K(18-crown-6)] **6[K*]**, with 50% probability displacement ellipsoids. Hydrogen atoms are omitted, except for H1. Symmetry code: i = x, 2 − y, z + 1/2. Selected bond lengths (Å) and angles (°):Th1−H1 2.2633, Th2−H1 2.3381, <Th1−C> 2.79 (3), <Th2−C> 2.78(2), K−C3 3.447(4) Th1···Cg 2.107 and 2.121, Th2···Cg 2.103 and 2.104, Cg···Th1···Cg 148.90, Cg···Th2···Cg 148.65.

Reaction of [{(Cot)$_2$Th}$_2$(μ−H)][Na*(THF)] with HNEt$_3$BPh$_4$

In an NMR tube, HNEt$_3$BPh$_4$ (3.4 mg, 0.008 mmol) was added into a pale green solution of [{(Cot)$_2$Th}$_2$(μ−H)][Na*(THF)] (10 mg, 0.008 mmol) in 0.5 mL of THF. Abundant gaseous evolvement (H$_2$) was immediately observed, with formation of a bright yellow deposit. After evaporation of the solvent and drying under vacuum for 6h, 0.4 mL of THF-d_8 was added. The NMR spectrum shows the presence of (Cot)$_2$Th, Na*BPh$_4$ and traces of Na$_2$Cot (δ 5.6).

Reactions of Uranocene with NaCN, NaN$_3$ or NaH in the presence of 18-crown-6 :

Uranocene with NaCN : An NMR tube was charged with (Cot)$_2$U (10 mg, 0.023 mmol), NaCN (5 mg, 0.1 mmol), 18-crown-6 (5.9 mg, 0.023 mmol) and pyridine-d_5 (0.5 mL). The green suspension was heated at 90°C for 48 h leading to a dark-green solution with the presence of large crystals of unreacted (Cot)$_2$U inside (Checked by X-ray diffraction). As for [(Cot)$_2$U(CN)][NR$_4$], the color of the solution is varying from dark-green to red upon lighting conditions. The ^{1}H NMR spectrum showed the formation of [(Cot)$_2$U(CN)][Na*] and the presence of residual uranocene (δ −37.5).

^{1}H NMR (pyridine-d_5, 23°C): δ = 3.31 (s, 24 H, CH$_2$O), −32.44 (s, 32 H, Cot). **^{13}C{^{1}H} NMR** (pyridine-d_5, 23°C) 133.0 (Cot), 70.49 (CH$_2$O).

In similar conditions, no reaction is observed in THF.

Uranocene with NaH : An NMR tube was charged with (Cot)$_2$U (10 mg, 0.023 mmol), NaH (3.0 mg, 0.12 mmol), 18-crown-6 (5.9 mg, 0.023 mmol) and THF-d_8 (0.5 mL). The ^{1}H NMR registered at 23°C showed two signals at δ 3.48 (s, CH$_2$O) and −37.85 (broad s, Cot). The green suspension was heated at 90°C for 60 h leading to a green solution and crystallization of green platelets of (Cot)$_2$U as checked by X-ray diffraction. The ^{1}H NMR spectrum of the solution showed a small shift of the Cot signal. (THF-d_8, 23°C) δ 3.61 (s, CH$_2$O), −35.8 (broad s, Cot). No U-H signal of a potential hydride could be detected from +360 to −60 ppm.

Note that the ^{1}H NMR spectrum of trivalent uranocene $(Cot)_2UK$ (obtained by reduction of **1** with KC_8 in THF-d_8) is $\delta \approx -32$ (broad s); the above downfield shift of the Cot−U signal may be the mean signal of a U^{III} and U^{IV} uranocenes mixture in rapid equilibrium.

Uranocene with NaN_3 : An NMR tube was charged with $(Cot)_2U$ (10 mg, 0.023 mmol), NaN_3 (7.0 mg, 0.10 mmol), 18-crown-6 (5.9 mg, 0.023 mmol) and THF-d_8 (0.5 mL). The green suspension was heated at 90°C for 24 h leading to a green solution with formation of small dark-green crystals of uranocene as checked by X-ray diffraction. The ^{1}H NMR spectrum showed the presence of the starting materials.

An NMR tube was charged with $(Cot)_2U$ (10 mg, 0.023 mmol), NaN_3 (7.0 mg, 0.10 mmol), 18-crown-6 (5.9 mg, 0.023 mmol) and pyridine-d_5 (0.5 mL). After 24 h at 90°C, dark-green platelets of $(Cot)_2U$ were deposited and the ^{1}H NMR spectrum of the green solution showed only the presence of unreacted uranocene.

Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[5] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to θ = 30° and a minimum redundancy of **4** for 90% of the reflections) were processed with HKL2000.[6] Absorption effects were corrected with SCALEPACK.[6] The structures were solved by direct methods with SHELXS-97, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[7] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydride protons in **6[Na*(THF)$_2$]** and **6[K*]** were found on Fourier-difference maps; in **6[Na*(THF)$_2$]**, the proton positional parameters were refined, but not its isotropic displacement parameter, fixed to 1.2 times that of Th, while no satisfying refinement was possible in **6[K*]**. All the other hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. The drawings were done with ORTEP-3.[8] CCDC-918802–918805 contain the supplementary crystallographic data for compounds **4**,

5, **6[Na*(THF)$_2$]** and **6[K*]**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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