Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION FOR

Nitrite Complexes of Uranium and Thorium

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Experimental details

General considerations

Unless otherwise noted, all reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 120 ºC before use. All NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to solvent impurities. Elemental analyses were performed at Analytische Laboratorien at Lindlar (Germany) and Medac Ltd at Chobham (United Kingdom). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. Celite (Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Tetrahydrofuran (THF), tetrahydrofuran-d_8 (THF-d_8), pentane, diethyl ether and benzene-d_6 were dried over a sodium(0)/benzophenone mixture and distilled before use. Triethylamine, acetonitrile, dichloromethane and dichloromethane-d_2 were dried over CaH_2 and distilled before use.

Caution! Natural thorium (primary isotope ^{232}Th) is a weak α-emitter (4.012 MeV) with a half-life of 1.41×10^{10} years and depleted uranium (primary isotope ^{238}U) is a weak α-emitter

(4.197 MeV) with a half-life of 4.47 x 10^9 years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of [PPh$_4$][NO$_2$]

A 100 mL flask was charged with PPh_4I (4.75 g, 10.2 mmol), $AgNO_2$ (1.57 g, 10.2 mmol) and deionized water (30 mL). A yellow precipitate of AgI immediately formed, and the light yellow suspension, sheltered from light, was further stirred 1h at room temperature. The solution was then filtrated and the water evaporated off at 60 °C to afford an off-white powder which was washed with ethanol (3 x 20 mL) and dried for 15 h at 50°C under reduced pressure to yield pure $[PPh_4][NO_2]$ (3.70 g, 94 %). Translucent crystals of $[PPh_4][NO_2]$·EtOH were recovered by recrystallization from ethanol.

Anal. Calcd for $C_{24}H_{20}NO_2P$: C, 74.80; H, 5.23; N, 3.63; Found; C, 74.28; H, 5.27; N, 3.74; IR (cm^{-1}): σ 1240 (N–O), 1311 (N–O), 1583 (C=C), 2671 (C–H), 2725 (C–H).

Synthesis of [PPh$_4$]$_2$[Th(NO$_2$)$_6$] (1)

A 100 mL round bottom flask was charged with $[PPh_4][NO_2]$ (1.08 g, 2.78 mmol), $AgNO_2$ (861 mg, 5.59 mmol) and CH_3CN (40 mL). After complete dissolution of the solids, the mixture was cooled to -40°C and $ThCl_4(DME)_2$ (775 mg, 1.40 mmol) was slowly added with vigorous stirring yielding a pale yellow solution from which white AgCl precipitated immediately. The suspension was then allowed to warm to room temperature, stirred further for 1 h, and centrifuged for 20 min. The pale yellow supernatant was transferred into a 100 mL flask and the volatiles were removed under reduced pressure to afford pure **1** as an off-white powder (1.43 g, 86 %). X-ray suitable crystals of $[\mathbf{1}]_2$·CH_3CN·Et_2O were obtained by slow diffusion of diethylether in an acetonitrile solution of **1** (type **I** and type **II** isomers), and crystals of **1**·Py were collected after slow diffusion of diethylether in a pyridine solution of **1**

(type **II** isomer).

Anal. Calcd for $C_{48}H_{40}N_6O_{12}P_2Th$: C, 48.58; H, 3.40; N, 7.08; Found: C, 48.56; H, 3.39; N, 6.83; IR (cm^{-1}): σ 1212 (N–O); 1305 (N–O); 1585 (C=C); 2681 (C–H); 2725 (C–H).

Synthesis of $[PPh_4]_2[UO_2(NO_2)_4]$ (2)

(I) From $[UO_2Cl_2(THF)_2]_2$

A 100 mL round bottom flask was charged with $[PPh_4][NO_2]$ (237 mg, 0.614 mmol), $AgNO_2$ (95.0 mg, 0.614 mmol) and pyridine (10 mL). After complete dissolution of the solids, the mixture was cooled to -40°C and $[UO_2Cl_2(THF)_2]_2$ (149 mg, 0.154 mmol) was added by fractions to the stirred yellow solution. The reaction mixture was then allowed to warm to 25 °C and stirred for 1 h. Pyridine was then evaporated off and acetonitrile (10 mL) was condensed in the flask resulting in the precipitation of AgCl as a white solid. After centrifugation, the yellow supernatant was collected and the volatiles removed under reduced pressure to afford **2** as a yellow powder (317 mg, 91 %). Crystals of **2** were obtained by slow diffusion of diethylether in an acetonitrile solution of **2**; crystals of **2**·Py were obtained by diffusion of diethylether in a pyridine solution of **2**.

Anal. Calcd for $C_{48}H_{40}N_4O_{10}P_2U$: C, 50.89; H, 3.56; N, 4.95; Found: C, 50.13; H, 3.49; N, 5.09; IR (cm^{-1}): σ 921 (U=O); 1220 (N–O); 1308 (N–O); 1583 (C=C); 2678 (C–H); 2725 (C–H).

(II) From $UI_4(1,4\text{-dioxane})_2$

A 100 mL round bottom flask was charged with $[PPh_4][NO_2]$ (140 mg, 0.363 mmol), $AgNO_2$ (112 mg, 0.726 mmol) and pyridine (10 mL). The mixture was stirred until complete dissolution of solids and cooled to -40°C. $UI_4(1,4\text{-dioxane})_2$ (167 mg, 0.182 mmol) was then slowly added under stirring, and the solution was degassed several times to eliminate the released NO gas. After 1 h at 25°C, the volatiles were removed under reduced pressure and MeCN (10 mL) was added, to yield a yellow solution with a yellow precipitate of AgI. After

centrifugation for 20 mn, the yellow supernatant was collected and the volatiles were removed under reduced pressure yielding **2** as a yellow powder (185 mg, 90 %).

Detection of NO gas from the reaction between $UI_4(1,4\text{-dioxane})_2$, $AgNO_2$ and $[PPh_4][NO_2]$

NO gas evolution from the reaction between $UI_4(1,4\text{-dioxane})_2$, $AgNO_2$ and $[PPh_4][NO_2]$ was detected using gas chromatography. Data were collected on a Shimadzu GC-2010+ gas chromatograph equipped with a Supelco SLB^{TM}- capillary column carboxen 1006 plot (30 m x 0.53 mm x 0.25 µm). Conditions: T_{inj} = 50°C, T_{col} = 26°C, T_{det} = 230°C, V_{inj} = 250 µL, total flow = 10 mL.min^{-1}, purge flow = 5.8 mL.min^{-1}

$UI_4(dioxane)_2$ (177.9 mg, 0.1930 mmol), silver nitrite (118.8 mg, 0.7720 mmol) and tetraphenylphosphonium nitrite (148.8 mg, 0.3860 mmol) were introduced in a J. Young NMR tube in recirculating mBraun LabMaster DP argon atmosphere drybox. Dry pyridine (400 µL) was then added and the valve was quickly closed. A gas sample of the headspace (250 µL) was analyzed using gas chromatography and compared to a reference sample consisting of a mixture of nitric oxide (Air Liquide) and argon (Figure S1).

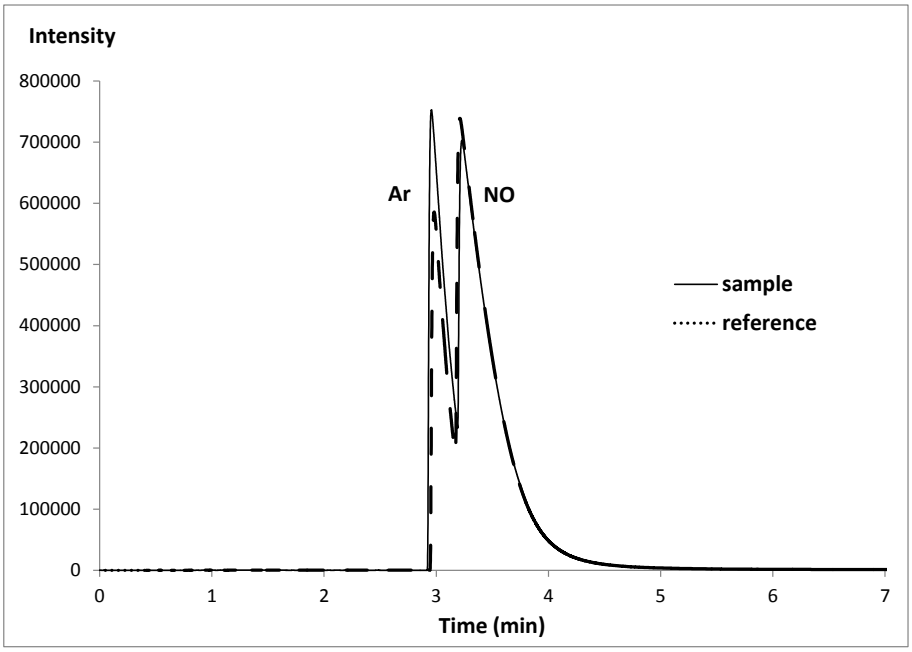

Figure S1. Gas chromatogram

Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[1] 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 with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[2] Absorption effects in the metal-containing compounds were corrected empirically with the program SCALEPACK.[2] The structures were solved by direct methods or Patterson map interpretation with SHELXS-97, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom bound to O3 in $PPh_4NO_2 \cdot EtOH$ was found on a Fourier-difference map, and the carbon-bound hydrogen atoms were introduced at calculated positions in all compounds. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3.[4]

Table 1. Crystal data and structure refinement details

	$PPh_4NO_2 \cdot EtOH$	**1**·py	$[\mathbf{1}]_2 \cdot MeCN \cdot Et_2O$	**2**	**2**·py
Chemical formula	$C_{26}H_{26}NO_3P$	$C_{53}H_{45}N_7O_{12}P_2Th$	$C_{51}H_{46.5}N_{6.5}O_{12.5}P_2Th$	$C_{48}H_{40}N_4O_{10}P_2U$	$C_{53}H_{45}N_5O_{10}P_2U$
M/g mol^{-1}	431.45	1265.94	1244.43	1132.81	1211.91
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic
Space group	$Pca2_1$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	18.7202(5)	17.6259(4)	11.2048(3)	10.0718(2)	19.1742(9)
b/Å	7.6215(2)	13.8559(4)	21.6990(6)	10.7528(2)	13.8266(8)
c/Å	15.8566(5)	23.1389(5)	22.4861(4)	11.7809(3)	38.374(2)
α/°	90	90	78.0104(15)	99.5411(7)	90
β/°	90	110.6431(14)	81.8288(15)	93.7891(7)	99.580(3)
γ/°	90	90	75.3495(13)	114.6103(9)	90
V/Å^3	2262.36(11)	5288.2(2)	5150.7(2)	1130.86(4)	10031.6(9)
Z	4	4	4	1	8
D_{calcd}/g cm^{-3}	1.267	1.590	1.605	1.663	1.605
μ(Mo-Kα)/mm^{-1}	0.149	2.949	3.026	3.723	3.364
F(000)	912	2512	2472	558	4800
Reflections collected	57297	191840	297726	71913	128712
Independent reflections	6561	16114	31356	6903	12907
Observed reflections [$I > 2\sigma(I)$]	5699	12394	22646	6859	8968
R_{int}	0.026	0.038	0.041	0.043	0.084
Parameters refined	282	676	1318	295	640
R_1	0.047	0.032	0.035	0.021	0.049
wR_2	0.135	0.082	0.090	0.051	0.136
S	1.047	1.054	1.066	1.050	1.019
$\Delta\rho_{min}$/e Å^{-3}	–0.39	–1.18	–2.04	–1.14	–1.94
$\Delta\rho_{max}$/e Å^{-3}	0.96	2.72	2.47	0.54	4.76
Flack parameter	0.41(8)	–	–	–	–

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