Supporting Information

A New Tripodal Ligand System with Steric and Electronic Modularity for Uranium Coordination Chemistry

*Suzanne C. Bart, Frank W. Heinemann, Christian Anthon, Christina Hauser, Karsten Meyer**

Department of Chemistry and Pharmacy, Inorganic Chemistry, Friedrich-Alexander University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany

kmeyer@chemie.uni-erlangen.de

Experimental Section

General Considerations. All air- and moisture-sensitive experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. The glovebox is equipped with a -35°C freezer and N_2(l) coldwell for freezing samples in liquid nitrogen. Solvents were purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA) and transferred to the glovebox without exposure to air. NMR solvents were obtained packaged under argon and stored over activated molecular sieves and sodium (where appropriate) prior to use. 2,4-Di-tert-butyl phenol, 2,4,6-tris(bromomethylmesitylene), and $ZnCl_2$ were purchased from Aldrich and used as received. Tris(chloromethyl mesitylene),[1] $U(N(SiMe_3)_2)_3$,[2,3] [(($^{tBu}ArO_3$)tacn)U],[4] and Lidbabh•Et_2O[5] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on JEOL 270 and 400 MHz instruments operating at respective frequencies of 269.714 and 400.178 MHz with a probe temperature of 23 ºC. Chemical shifts were reported relative to the peak for $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard and are reported in ppm. For paramagnetic molecules, the ^{1}H NMR data are reported with the chemical shift, followed by the peak width at half-height in hertz, the integration value, and where possible, the peak assignment.

Electronic absorption spectra were recorded from 200 to 2500 nm (Shimadzu (UV-3101PC)) in the indicated solvent.

Magnetization data of crystalline powdered samples were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe between 5 and 300 K for all samples. Values of the magnetic susceptibility were corrected for underlying diamagnetic contributions (χ_{dia} = -561.8 • 10^{-6} cm^3 mol^{-1} (**1-U**), -679.7 • 10^{-6} cm^3 mol^{-1} (**1-Udbabh**), and -684.2 • 10^{-6} cm^3 mol^{-1} (**2-Udbabh**)) by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition and purity by elemental analysis (C, H, and N) and ^{1}H NMR spectroscopy. Data reproducibility was also carefully checked by obtaining data on 2-3 samples.

Results from elemental analysis were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nurnberg (Erlangen, Germany).

Kohn-Sham DFT analysis and geometry optimization of **1-U** were performed with the ADF package[6-8] employing the BP86 gradient corrected functional in the scalar zeroth–order regular approximation (ZORA[9-13]). The plots were made with gOpenMol.[14,15] A comparison of selected experimental and calculated metric parameters is give below:

Geometry comparison for [((^{tBu}ArO)$_3$mes)U] (1-U)

1-U	Experimental	Calculated
d(U–C) (in Å)	2.738, 2.722, 2.740, 2.745, 2.719, 2.724	2.679, 2.683, 2.685, 2.685, 2.693, 2.698
d(U–O) (in Å)	2.158, 2.166, 2.166	2.145, 2.150, 2.153
∠U–O–C (°)	144.5, 146.4, 149.1	146.1, 147.0, 149.7
U(oop) (in Å)	0.464	0.496

U(oop) is defined as the distance of the uranium ion below the plane of the three aryloxide oxygen atoms.

X-ray crystal structure determinations of 2,4,6-tris(chloromethyl)mesitylene, 1 • CH_3CN, 1-U • $^3/_4C_5H_{12}$ • $^1/_4CH_3C_6H_5$, 1-Udbabh • ½$C_{14}H_{10}$ • C_5H_{12} and 2-Udbabh • 2 C_5H_{12}:

Suitable single crystals were isolated and coated with protective perfluoropolyalkylether oil, mounted on a glass capillary and brought into the cold gas stream of the low temperature device of the diffractometer. Data were collected at 150 K (2,4,6-tris(chloromethyl)mesitylene, **1** • CH_3CN, and **2-Udbabh** • 2 C_5H_{12}) or at 100 K (**1-U** • $^3/_4C_5H_{12}$ • $^1/_4CH_3C_6H_5$ and **1-Udbabh** • ½$C_{14}H_{10}$ • C_5H_{12}) on a Bruker-Nonius KappaCCD diffractometer using Mo*K*α radiation (λ = 0.71073 Å, graphite monochromator).

Preliminary data revealed the crystal system. Intensity data were corrected for Lorentz and polarization effects, absorption was taken into account by a semi-empirical correction based on multiple scans of equivalent reflections (SADABS[16]). All structures were solved by direct methods and refined on F^2 using full-matrix least squares procedures (SHELXTL NT 6.12[17]). All non-hydrogen atoms were refined anisotropically. For **1** • CH_3CN the positions of all hydrogen atoms were derived from a difference fourier synthesis and their coordinates were refined. For all other compounds the hydrogen atoms are in positions calculated for optimized geometry. The isotropic displacement parameters of the hydrogen atoms in all five structure determinations are tied to those of their corresponding carrier atom by a factor of either 1.2 or 1.5. The crystal structure of **1-U** • ¾ C_5H_{12} • ¼ $CH_3C_6H_5$ contains a total of 0.75 n-pentane and 0.25 toluene per formula unit. All of these solvent molecules are disordered and no hydrogen atoms were included for these solvent molecules. One half of an *n*-pentane is situated on a crystallographic inversion center. A molecule of toluene and another *n*-pentane share a common site on a crystallographic inversion center with an occupancy of 50% each. One of the *t*Bu groups of the ligand in **1-U** • ¾ C_5H_{12} • $^1/_4$ $CH_3C_6H_5$ is disordered. Two alternative positions were refined to give occupancies of 47(2) % for C51 – C54 and 53(2) % for C51' – C54'. DFIX, SIMU, and ISOR restraints were used in the refinement of the disordered regions of this crystal structure. The unit cell of **1-Udbabh** • ½ $C_{14}H_{10}$ • C_5H_{12} contains half a molecule of anthracene and more than one *n*-pentane molecules per formula unit. PLATON analysis revealed the presence of a solvent accessible void. Bubbling was observed during the preparation of the crystals and indicated the loss of solvent. While one *n*-pentane molecule could be localized and sufficiently treated during the refinement, the position of a second one could only be identified but not reasonably treated. Application of the SQUEEZE procedure gave no reasonable results, however. Two of the *t*Bu-groups of the ligand are disordered. Two alternative positions have been refined in each case resulting in site occupancies of 74.7(7) and

25.3(7) % for C22 – C24 and C22A – C24A and of 86.9(7) and 13.1(7) % for C52 – C54 and C52A – C54A, respectively. SIMU restraints were applied in the refinement of these *t*Bu groups and the *n*-pentane solvate molecule. Here, additional DFIX restraints were applied. Attempts to account for high anisotropic displacement parameters of another *t*Bu group (C36 - C39) by a disorder model were not successful. For **2-Udbabh** • $2C_5H_{12}$, three of the tbutyl groups are subject to rotational disorder. Two preferred positions were refined in all three cases that are occupied by 56(5) and 44(5)% for atoms C18-C21 and C18'-C21', by 86(2) and 14(2)% for atoms C34-C36 and C34'-C36', and by 76(2) and 24(2)% for atoms C49-C51 and C49'-C51', respectively. The n-pentane molecules are disordered and are situated in part on the crystallographic symmetry elements. The site occupancy of the four determined n-pentane sites has been fixed to 0.5 either from symmetry restraints or from attempts to refine the site occupancy factor. SAME and SIMU and ISOR restraints were used in the refinement of the disordered structure parts. CCDC-673199 (2,4,6-tris(chloromethyl)mesitylene), CCDC-673200 (**1** • CH_3CN), CCDC-673201 (**1-U** • $^3/_4C_5H_{12}$ • $^1/_4CH_3C_6H_5$), CCDC-673202 (**1-Udbabh** • $½C_{14}H_{10}$ • C_5H_{12}) and CCDC-735472 (**2-Udbabh** • $2C_5H_{12}$) contain the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic data, data collection and refinement details of the X-ray crystal structure determinations of 2,4,6-tris(chloromethyl)mesitylene, **1** • CH_3CN, **1-U** • $^3/_4C_5H_{12}$ • $^1/_4CH_3C_6H_5$.

	2,4,6-tris(chloromethyl) mesitylene	**1 • CH_3CN**	**1-U • $^3/_4C_5H_{12}$ • $^1/_4CH_3C_6H_5$**
	CCDC-673199	**CCDC-673200**	**CCDC-673201**
Molecular formula	$C_{12}H_{15}Cl_3$	$C_{56}H_{81}NO_3$	$C_{59.5}H_{86}O_3U$
M_r	265.59	816.22	1087.31
Temperature [K]	150(2)	150(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal description	colorless prism	colorless block	brown needle
Crystal size [mm]	0.35 × 0.32 × 0.18	0.37 × 0.25 × 0.12	0.34 × 0.08 × 0.07
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a [Å]	9.2206(4)	11.7954(4)	41.768(5)
b [Å]	9.3069(8)	14.2154(9)	11.3426(6)
c [Å]	9.3088(5)	17.260(2)	30.362(4)
α [°]	117.915(6)	93.168(5)	90
β [°]	108.127(3)	104.788(4)	132.596(8)
γ [°]	102.038(6)	111.500(4)	90
V [Å^3]	608.3(1)	2567.7(3)	10589(2)
Z	2	2	8
F(000)	276	896	4472
$\rho_{calc.}$ [g cm^{-3}]	1.450	1.056	1.364
μ [mm^{-1}]	0.717	0.063	3.108
Total reflections	10411	55238	110665
Unique reflections	2664	10486	11678
Observed refl. [$I > 2\sigma$(I)]	2024	7119	9554
R(int)	0.0473	0.0577	0.0590
Scan range θ [°]	3.50 to 27.10	3.26 to 26.37	3.31 to 27.10
Completeness to $\theta_{max.}$ [%]	99.8	99.8	99.8
Index ranges	$-11 \le h \le 11$	$-14 \le h \le 14$	$-53 \le h \le 53$
	$-11 \le k \le 11$	$-17 \le k \le 17$	$-14 \le k \le 14$
	$-11 \le l \le 11$	$-21 \le l \le 21$	$-38 \le l \le 38$
Data / restraints / parameters	2664 / 0 / 139	10486 / 0 / 784	11678 / 154 / 683
Goodness-of-fit on F^2	1.007	1.013	1.058
R_1, wR_2 [$I > 2\sigma(I)$]	0.0351, 0.0781	0.0499, 0.1103	0.0249, 0.0495
R_1, wR_2 (all data)	0.0571, 0.0851	0.0873, 0.1276	0.0399, 0.0540
Max./min. el. density [e.Å^{-3}]	0.348, –0.277	0.325, –0.249	1.003, –0.620

Table S2 Crystallographic data, data collection and refinement details of the X-ray crystal structure determinations of **1-Udbabh** • ½$C_{14}H_{10}$ • C_5H_{12} and **2-Udbabh** • 2 C_5H_{12}.

	1-Udbabh • ½$C_{14}H_{10}$ • C_5H_{12}	**2-Udbabh** • 2 C_5H_{12}
	CCDC-673202	**CCDC-735472**
Molecular formula	$C_{80}H_{102}NO_3U$	$C_{75}H_{110}N_4O_3U$
M_r	1363.66	1353.70
Temperature [K]	100(2)	150(2)
Wavelength [Å]	0.71073	0.71073
Crystal description	orange block	yellow block
Crystal size [mm]	0.22 × 0.21 × 0.12	0.27 × 0.25 × 0.14
Crystal system	monoclinic	Tetragonal
Space group	$P2_1/c$ (No. 14)	$I\bar{4}$ (No. 82)
a [Å]	17.072(2)	27.122(4)
b [Å]	15.126(2)	27.122(4)
c [Å]	30.280(2)	21.761(3)
α [°]	90	90
β [°]	93.325(8)	90
γ [°]	90	90
V [Å^3]	7806(2)	16008(4)
Z	4	8
F(000)	2820	5632
$\rho_{calc.}$ [g cm^{-3}]	1.160	1.123
μ [mm^{-1}]	2.121	2.069
Total reflections	81887	150726
Unique reflections	17000	17291
Observed refl. [$I > 2\sigma$(I)]	12926	13929
R(int)	0.0686	0.0610
Scan range θ [°]	3.18 to 27.10	3.24 to 27.10
Completeness to $\theta_{max.}$ [%]	98.6	99.0
Index ranges	$-21 \le h \le 21$	$-34 \le h \le 34$
	$-19 \le k \le 19$	$-34 \le k \le 34$
	$-38 \le l \le 38$	$-27 \le l \le 27$
Data / restraints / parameters	17000 / 235 / 851	17291 / 477 / 920
Goodness-of-fit on F^2	1.101	1.191
R_1, wR_2 [$I > 2\sigma(I)$]	0.0498, 0.1038	0.0418, 0.0938
R_1, wR_2 (all data)	0.0731, 0.1100	0.0731, 0.1127
Max./min. el. density [e.Å^{-3}]	2.124, –2.343	3.137, –1.771

Figure S1 Thermal ellipsoid plot of the molecular structure of 2,4,6-tris(chloromethyl)mesitylene **(**50% probability).

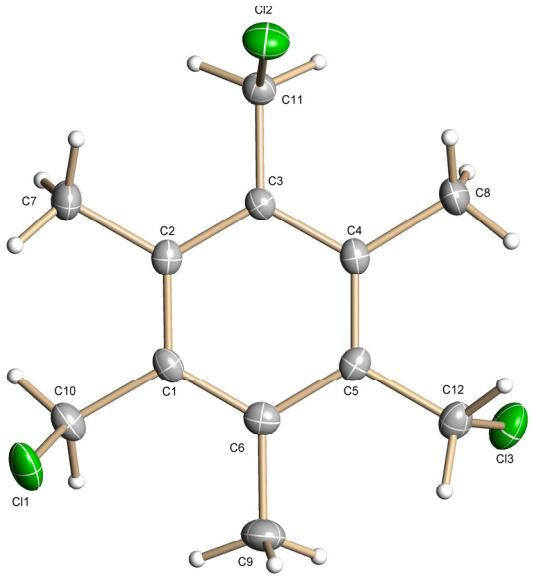

Table S3 Selected bond distances (Å) and bond angles (^{O}) of 2,4,6-tris(chloromethyl)mesitylene**.**

Bond distances		Bond angles	
Cl(1)-C(10)	1.815(2)	C(6)-C(1)-C(2)	120.49(18)
Cl(2)-C(11)	1.815(2)	C(6)-C(1)-C(10)	120.61(18)
Cl(3)-C(12)	1.810(2)	C(2)-C(1)-C(10)	118.91(18)
C(1)-C(6)	1.401(3)	C(3)-C(2)-C(1)	118.88(18)
C(1)-C(2)	1.413(3)	C(3)-C(2)-C(7)	120.52(18)
C(1)-C(10)	1.500(3)	C(1)-C(2)-C(7)	120.60(18)
C(2)-C(3)	1.401(3)	C(2)-C(3)-C(4)	121.13(18)
C(2)-C(7)	1.511(3)	C(2)-C(3)-C(11)	119.22(18)
C(3)-C(4)	1.406(3)	C(4)-C(3)-C(11)	119.65(17)
C(3)-C(11)	1.502(3)	C(5)-C(4)-C(3)	119.11(18)
C(4)-C(5)	1.404(3)	C(5)-C(4)-C(8)	120.91(18)
C(4)-C(8)	1.512(3)	C(3)-C(4)-C(8)	119.96(18)
C(5)-C(6)	1.406(3)	C(4)-C(5)-C(6)	120.48(18)
C(5)-C(12)	1.503(3)	C(4)-C(5)-C(12)	119.61(18)
C(6)-C(9)	1.521(3)	C(6)-C(5)-C(12)	119.89(18)
		C(1)-C(6)-C(5)	119.66(18)
		C(1)-C(6)-C(9)	120.30(18)
		C(5)-C(6)-C(9)	120.04(19)

Figure S2 Thermal ellipsoid plot of the molecular structure of **1** • CH_3CN **(**50% probability, H atoms and solvent molecules omitted for clarity).

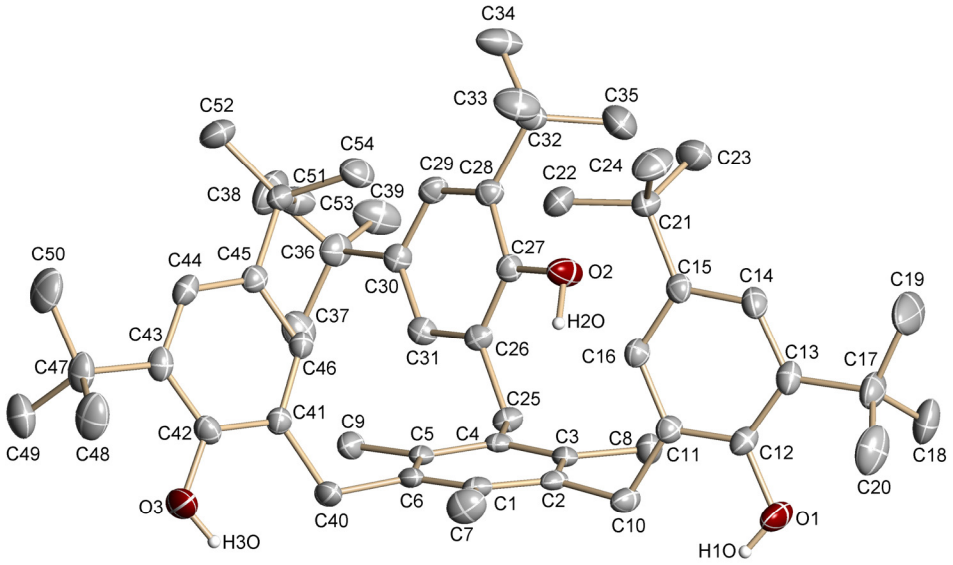

Table S4 Selected bond distances (Å) and bond angles (^{O}) of **1** • CH_3CN.

Bond distances		Bond angles	
O(1)-C(12)	1.384(2)	C(12)-O(1)-H(1O)	114.4(18)
O(1)-H(1O)	0.80(2)	C(27)-O(2)-H(2O)	107.3(14)
O(2)-C(27)	1.388(2)	C(42)-O(3)-H(3O)	114.4(16)
O(2)-H(2O)	0.95(2)	C(2)-C(1)-C(6)	120.05(15)
O(3)-C(42)	1.373(2)	C(2)-C(1)-C(7)	119.61(16)
O(3)-H(3O)	0.86(2)	C(6)-C(1)-C(7)	120.34(16)
C(1)-C(2)	1.403(2)	C(1)-C(2)-C(3)	120.23(15)
C(1)-C(6)	1.404(2)	C(1)-C(2)-C(10)	120.07(15)
C(1)-C(7)	1.511(3)	C(3)-C(2)-C(10)	119.68(15)
C(2)-C(3)	1.406(2)	C(2)-C(3)-C(4)	119.71(14)
C(2)-C(10)	1.519(2)	C(2)-C(3)-C(8)	119.00(15)
C(3)-C(4)	1.407(2)	C(4)-C(3)-C(8)	121.27(15)
C(3)-C(8)	1.521(2)	C(3)-C(4)-C(5)	119.91(15)
C(4)-C(5)	1.415(2)	C(3)-C(4)-C(25)	121.50(14)
C(4)-C(25)	1.522(2)	C(5)-C(4)-C(25)	118.48(15)
C(5)-C(6)	1.404(2)	C(6)-C(5)-C(4)	119.84(15)
C(5)-C(9)	1.512(2)	C(6)-C(5)-C(9)	120.72(15)
C(6)-C(40)	1.526(2)	C(4)-C(5)-C(9)	119.43(15)
		C(5)-C(6)-C(1)	120.01(14)
		C(5)-C(6)-C(40)	120.27(15)
		C(1)-C(6)-C(40)	119.70(15)

Figure S3 Thermal ellipsoid plot of the molecular structure of **1-U** • $^{3}/_{4}C_5H_{12}$ • $^{1}/_{4}CH_3C_6H_5$ **(**50% probability, H atoms, disorder and solvent molecules omitted for clarity).

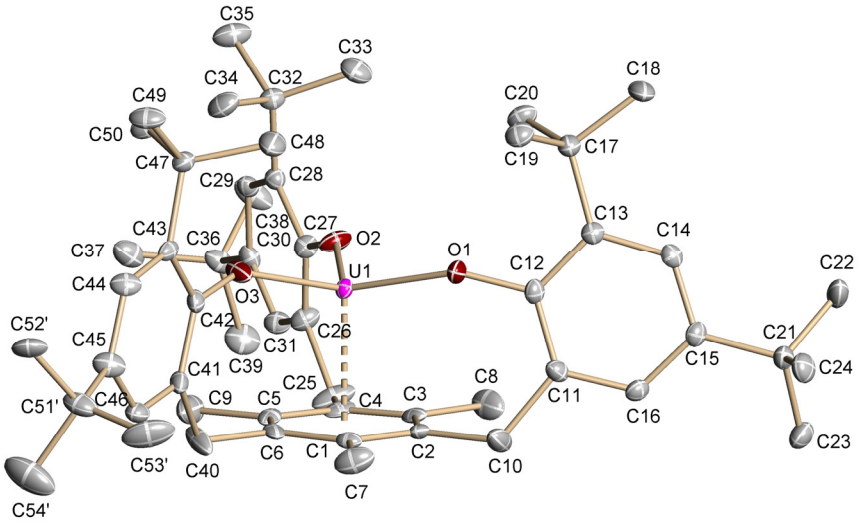

Table S5 Selected bond distances (Å) and bond angles (^{O}) of **1-U** • $^{3}/_{4}C_5H_{12}$ • $^{1}/_{4}CH_3C_6H_5$.

Bond distances		Bond angles	
U(1)-O(2)	2.158(2)	O(2)-U(1)-O(3)	113.59(8)
U(1)-O(3)	2.166(2)	O(2)-U(1)-O(1)	115.72(8)
U(1)-O(1)	2.1666(19)	O(3)-U(1)-O(1)	117.27(8)
U(1)-C(6)	2.719(3)	O(2)-U(1)-C(6)	114.94(9)
U(1)-C(3)	2.722(3)	O(3)-U(1)-C(6)	71.65(8)
U(1)-C(5)	2.723(3)	O(1)-U(1)-C(6)	116.39(8)
U(1)-C(4)	2.737(3)	O(2)-U(1)-C(3)	85.74(8)
U(1)-C(2)	2.740(3)	O(3)-U(1)-C(3)	134.61(8)
U(1)-C(1)	2.745(3)	O(1)-U(1)-C(3)	85.29(8)
O(1)-C(12)	1.357(3)	C(6)-U(1)-C(3)	62.97(8)
O(2)-C(27)	1.358(3)	O(2)-U(1)-C(5)	85.03(9)
O(3)-C(42)	1.356(3)	O(3)-U(1)-C(5)	86.16(8)
C(1)-C(6)	1.419(4)	O(1)-U(1)-C(5)	133.48(8)
C(1)-C(2)	1.424(4)	C(6)-U(1)-C(5)	30.13(9)
C(1)-C(7)	1.516(4)	C(3)-U(1)-C(5)	53.59(9)
C(2)-C(3)	1.418(4)	O(2)-U(1)-C(4)	70.43(8)
C(2)-C(10)	1.513(4)	O(3)-U(1)-C(4)	116.06(9)
C(3)-C(4)	1.421(4)	O(1)-U(1)-C(4)	115.26(8)
C(3)-C(8)	1.510(4)	C(6)-U(1)-C(4)	53.67(9)
C(4)-C(5)	1.420(4)	C(3)-U(1)-C(4)	30.17(9)
C(4)-C(25)	1.518(4)	C(5)-U(1)-C(4)	30.15(9)
C(5)-C(6)	1.414(4)	O(2)-U(1)-C(2)	115.73(8)

C(5)-C(9)	1.514(4)	O(3)-U(1)-C(2)	117.26(8)
C(6)-C(40)	1.521(4)	O(1)-U(1)-C(2)	70.89(8)
		C(6)-U(1)-C(2)	53.78(8)
		C(3)-U(1)-C(2)	30.09(8)
		C(5)-U(1)-C(2)	62.60(8)
		C(4)-U(1)-C(2)	53.46(8)
		O(2)-U(1)-C(1)	132.73(8)
		O(3)-U(1)-C(1)	87.32(8)
		O(1)-U(1)-C(1)	86.44(8)
		C(6)-U(1)-C(1)	30.11(8)
		C(3)-U(1)-C(1)	53.33(8)
		C(5)-U(1)-C(1)	53.16(9)
		C(4)-U(1)-C(1)	62.30(8)
		C(2)-U(1)-C(1)	30.09(8)
		C(12)-O(1)-U(1)	146.37(18)
		C(27)-O(2)-U(1)	149.13(19)
		C(42)-O(3)-U(1)	144.47(18)

Figure S4 Thermal ellipsoid plot of the molecular structure of **1-Udbabh** • ½$C_{14}H_{10}$ • C_5H_{12} **(**50% probability, H atoms, disorder and solvent molecules omitted for clarity).

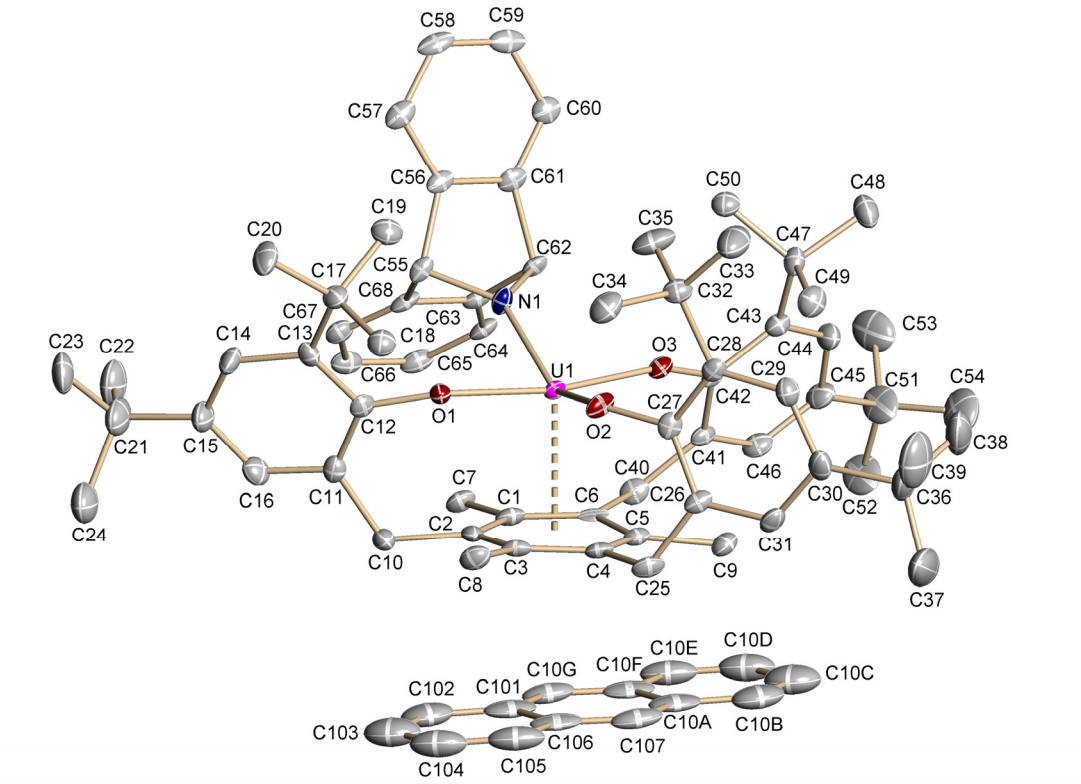

Table S6 Selected bond distances (Å) and bond angles (^{O}) of **1-Udbabh** • ½$C_{14}H_{10}$ • C_5H_{12}.

Bond distances		Bond angles	
U(1)-O(1)	2.138(3)	O(1)-U(1)-O(3)	168.07(12)
U(1)-O(3)	2.158(3)	O(1)-U(1)-O(2)	87.41(13)
U(1)-O(2)	2.182(3)	O(3)-U(1)-O(2)	101.69(13)
U(1)-N(1)	2.247(4)	O(1)-U(1)-N(1)	83.97(14)
U(1)-C(6)	2.852(5)	O(3)-U(1)-N(1)	84.11(14)
U(1)-C(3)	2.869(5)	O(2)-U(1)-N(1)	142.33(14)
U(1)-C(1)	2.872(5)	O(1)-U(1)-C(6)	115.95(13)
U(1)-C(2)	2.879(5)	O(3)-U(1)-C(6)	67.51(13)
U(1)-C(4)	2.912(5)	O(2)-U(1)-C(6)	114.20(13)
U(1)-C(5)	2.940(5)	N(1)-U(1)-C(6)	102.49(14)
O(1)-C(12)	1.358(6)	O(1)-U(1)-C(3)	70.80(13)
O(2)-C(27)	1.349(6)	O(3)-U(1)-C(3)	118.69(13)
O(3)-C(42)	1.357(6)	O(2)-U(1)-C(3)	75.75(14)
N(1)-C(55)	1.495(6)	N(1)-U(1)-C(3)	133.99(15)
N(1)-C(62)	1.506(6)	C(6)-U(1)-C(3)	59.53(14)
C(1)-C(2)	1.414(7)	O(1)-U(1)-C(1)	88.55(14)

C(1)-C(6)	1.418(7)	O(3)-U(1)-C(1)	92.53(14)
C(1)-C(7)	1.509(7)	O(2)-U(1)-C(1)	124.40(13)
C(2)-C(3)	1.424(7)	N(1)-U(1)-C(1)	92.03(14)
C(2)-C(10)	1.521(7)	C(6)-U(1)-C(1)	28.68(14)
C(3)-C(4)	1.414(7)	C(3)-U(1)-C(1)	50.87(14)
C(3)-C(8)	1.514(7)	O(1)-U(1)-C(2)	66.23(13)
C(4)-C(5)	1.405(7)	O(3)-U(1)-C(2)	118.05(13)
C(4)-C(25)	1.521(7)	O(2)-U(1)-C(2)	103.79(14)
C(5)-C(6)	1.420(7)	N(1)-U(1)-C(2)	105.98(15)
C(5)-C(9)	1.513(7)	C(6)-U(1)-C(2)	50.56(14)
C(6)-C(40)	1.513(7)	C(3)-U(1)-C(2)	28.68(14)
		C(1)-U(1)-C(2)	28.47(14)
		O(1)-U(1)-C(4)	97.51(13)
		O(3)-U(1)-C(4)	93.21(13)
		O(2)-U(1)-C(4)	66.89(14)
		N(1)-U(1)-C(4)	150.62(15)
		C(6)-U(1)-C(4)	50.46(14)
		C(3)-U(1)-C(4)	28.31(15)
		C(1)-U(1)-C(4)	58.79(14)
		C(2)-U(1)-C(4)	50.04(14)
		O(1)-U(1)-C(5)	119.83(13)
		O(3)-U(1)-C(5)	69.05(13)
		O(2)-U(1)-C(5)	86.00(13)
		N(1)-U(1)-C(5)	129.71(14)
		C(6)-U(1)-C(5)	28.33(13)
		C(3)-U(1)-C(5)	49.65(14)
		C(1)-U(1)-C(5)	49.80(14)
		C(2)-U(1)-C(5)	57.77(14)
		C(4)-U(1)-C(5)	27.78(14)
		C(12)-O(1)-U(1)	150.1(3)
		C(27)-O(2)-U(1)	134.5(3)
		C(42)-O(3)-U(1)	156.8(3)
		C(55)-N(1)-C(62)	95.2(4)
		C(55)-N(1)-U(1)	134.2(3)
		C(62)-N(1)-U(1)	129.3(3)

Figure S5 Thermal ellipsoid plot of the molecular structure of **2-Udbabh** • 2 C_5H_{12} **(**50% probability, H atoms, disorder and solvent molecules omitted for clarity).

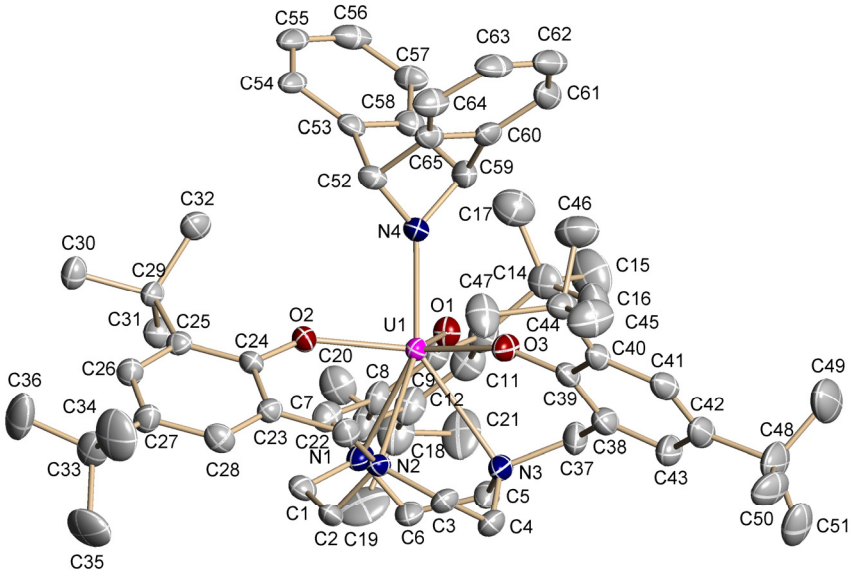

Table S7 Selected bond distances (Å) and bond angles (^{O}) of **2-Udbabh** • 2 C_5H_{12}.

Bond distances		Bond angles	
U(1)-O(3)	2.203(4)	O(3)-U(1)-O(2)	123.00(16)
U(1)-O(2)	2.212(4)	O(3)-U(1)-O(1)	115.00(17)
U(1)-O(1)	2.220(4)	O(2)-U(1)-O(1)	120.12(16)
U(1)-N(4)	2.260(5)	O(3)-U(1)-N(4)	85.78(17)
U(1)-N(2)	2.688(5)	O(2)-U(1)-N(4)	83.46(17)
U(1)-N(1)	2.714(5)	O(1)-U(1)-N(4)	87.22(18)
U(1)-N(3)	2.752(5)	O(3)-U(1)-N(2)	82.69(16)
O(1)-C(9)	1.347(8)	O(2)-U(1)-N(2)	70.67(14)
O(2)-C(24)	1.355(7)	O(1)-U(1)-N(2)	133.08(16)
O(3)-C(39)	1.351(8)	N(4)-U(1)-N(2)	139.05(18)
N(1)-C(1)	1.479(8)	O(3)-U(1)-N(1)	130.73(15)
N(1)-C(6)	1.492(8)	O(2)-U(1)-N(1)	80.73(15)
N(1)-C(7)	1.496(8)	O(1)-U(1)-N(1)	72.46(16)
N(2)-C(3)	1.479(8)	N(4)-U(1)-N(1)	142.92(17)
N(2)-C(2)	1.486(8)	N(2)-U(1)-N(1)	64.29(16)
N(2)-C(22)	1.495(9)	O(3)-U(1)-N(3)	69.90(15)
N(3)-C(4)	1.478(9)	O(2)-U(1)-N(3)	130.90(15)
N(3)-C(5)	1.479(8)	O(1)-U(1)-N(3)	81.00(16)
N(3)-C(37)	1.504(9)	N(4)-U(1)-N(3)	144.87(17)
N(4)-C(52)	1.492(8)	N(2)-U(1)-N(3)	64.23(16)

N(4)-C(59)	1.495(8)	N(1)-U(1)-N(3)	63.25(15)
		C(9)-O(1)-U(1)	145.1(4)
		C(24)-O(2)-U(1)	147.3(4)
		C(39)-O(3)-U(1)	150.0(4)
		C(1)-N(1)-C(6)	111.2(5)
		C(1)-N(1)-C(7)	108.6(5)
		C(6)-N(1)-C(7)	112.2(5)
		C(1)-N(1)-U(1)	105.8(4)
		C(6)-N(1)-U(1)	117.8(4)
		C(7)-N(1)-U(1)	100.3(4)
		C(3)-N(2)-C(2)	110.4(5)
		C(3)-N(2)-C(22)	107.0(5)
		C(2)-N(2)-C(22)	113.2(5)
		C(3)-N(2)-U(1)	107.5(4)
		C(2)-N(2)-U(1)	115.9(4)
		C(22)-N(2)-U(1)	102.1(3)
		C(4)-N(3)-C(5)	110.6(5)
		C(4)-N(3)-C(37)	111.5(5)
		C(5)-N(3)-C(37)	107.5(5)
		C(4)-N(3)-U(1)	115.4(4)
		C(5)-N(3)-U(1)	107.5(4)
		C(37)-N(3)-U(1)	104.0(4)
		C(52)-N(4)-C(59)	94.4(5)
		C(52)-N(4)-U(1)	134.7(4)
		C(59)-N(4)-U(1)	130.8(4)

References:

(1) (a) Tveten, J. L. US 3336402, 1967. (b) Van der Made, A.W.; Van der Made, R.H. *J. Org. Chem.* **1993**, *58*, 1262-1263. (c)Kochansky, J.; Cohen, C. F.; Lusby, W. R. *J. Agric. Food Chem.* **1995**, *43*, 2974.

(2) Clark, D. L.; Sattelberger, A. P.; Andersen, R. A. *Inorg. Synth.* **1997**, *31*, 307.

(3) Stewart, J. L.; Andersen, R. A. *Polyhedron* **1998**, *17*, 953-958.

(4) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2002**, 2764-2765.

(5) Mindiola, D.J.; Cummins, C.C. *Angew. Chem. Int. Ed.* **1998**, *37*, 945.

(6) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(7) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

(8) ADF2007.01, S., Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com

(9) Van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(10) Van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101(11)*, 9783.

(11) Van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.

(12) Perdew, J. P. *Phys. Rev. B* **1986**, *33(12)*, 8822.

(13) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(14) Bergman, D. L.; Laaksonen, L.; Laaksonen, A. *J. Mol. Graphics & Modeling* **1997**, *15*, 301.

(15) Laaksonen, L. *J. Mol. Graphics* **1992**, *10*, 33.

(16) *SADABS*, 2.10, Bruker AXS, Inc., 2002, Madison, WI, USA.

(17) *SHELXTL* NT 6.12, Bruker AXS, Inc., 2002, Madison, WI, USA.