Catalytic one-electron reduction of uranyl(VI) to Group 1 uranyl(V) complexes *via* Al(III) coordination

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1. Experimental details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or an MBraun Unilab glovebox. Deuterated pyridine and deuterated benzene were boiled over potassium, distilled and freeze-pump-thaw degassed three times prior to use. All other solvents were purged with nitrogen and dried using Vacuum Atmospheres drying towers. Pyridine was degassed and distilled from potassium. ^{1}H-NMR spectra were recorded on a Bruker ava400 spectrometer at 298 K operating at 399.90 MHz. ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ava500 spectrometer operating at 125.76 MHz. Chemical shifts are given in parts per million (ppm) and referenced to residual resonances of the respective solvent. IR spectra were recorded in the range of 400-4000 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer as nujol mulls between NaCl disks. Elemental analyses were carried out by Mr. Stephen Boyer, London Metropolitan University, Analytische Laboratorien Germany and Medac Ltd UK. Cyclic voltammograms were recorded using an Autolab 302 potentiostat and the data processed using GPES Manager version 4.9. Experiments were undertaken at room temperature in a glovebox in a 15 mL glass vial as the cell with a platinum wire embedded in glass as the working electrode, a platinum gauze as the counter electrode and a silver wire as the pseudo-reference electrode. The solution employed was a 5.0 mM (**2**) and 3.2 mM (**6**) tetrahydrofuran solution, respectively, with 0.2 M (**2**) and 0.1 M (**6**) $[NBu_4][PF_6]$ as the supporting electrolyte and scan rates between 100–1000 mVs^{-1}. All potentials were referenced against $[Cp_2Fe]^{0/+}$ (i.e. Fc/Fc$^+$ = 0.0 V).

1.1 Synthetic Procedures

$[(UO_2)(py)(H_2L)]$[1] and Tebbe's reagent[2] were synthesized according to literature procedures. Titanocene dichloride (Merck Schuchardt), trimethylaluminium (Acros Organics) and di-(*iso*-butyl)-aluminum hydride, 1 M in hexane (Acros Organics) were used as received.

[(py)(Me$_2$AlOUO)(py)(H$_2$L)] 1

A brown suspension of $[(UO_2)(py)(H_2L)]$ **A** (150 mg, 0.1035 mmol) in C_6D_6 (1.0 mL plus 0.1 ml pyridine) was combined with $Cp_2TiCH_2ClAlMe_2$ **(**0.15 ml, 0.1035 mmol) (Tebbe's reagent) at room temperature to form a dark brown solution. The solvent was reduced to *ca.* 0.5 mL under vacuum to afford $[(py)(Me_2AlOUO)(py)(H_2L)]$ **1** as yellow crystals. The product was isolated by filtration and washed with cold toluene (3 x 0.5 mL, -35 ºC). Recrystallization of **1** from toluene at -35 °C afforded yellow crystals suitable for X-ray diffraction. Yield: 79 mg (67%).

^{1}H-NMR (C_6D_6): δ_H -5.11 (s, 3H, C*H*$_3$), -4.96 (s, 3H, C*H*$_3$), -2.04 (s, 2H), -1.35 (s, 6H, Ph-C*H*$_3$), 0.12 (s, 2H), 0.29 (s, 6H, Ph-C*H*$_3$), 0.85 (s, 2H), 0.87 (s, 2H), 3.02 (s, 2H), 7.19 (s, 2H), 8.10 (s, 3H, C*H*$_3$), 10.21 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 12.18 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 14.51 (s, 6H, Al-C*H*$_3$), 21.25 (s, 3H, C*H*$_3$), 68.65 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_6D_6): δ_C 15.74, 15.92, 16.34, 16.90, 17.56, 18.69, 21.04, 21.76, 34.10, 52.23, 77.29, 101.99, 108.06, 109.35, 112.11, 115.90, 119.93, 120.40, 122.79, 126.03, 126.33, 126.77, 128.90, 129.66, 138.22, 145.22, 148.97, 162.64; Analysis. Found: C, 56.58; H, 4.99; N, 12.17 % $C_{54}H_{60}AlN_{10}O_2U$ requires: C, 56.59; H, 5.28; N, 12.22 %; FTIR (nujol, cm^{-1}): ν 3585 (w, NH), 2927 (s, nujol), 2854 (s, nujol), 1581 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1285 (m, L), 1261 (m, L), 1084 (w, L), 1044 (m, L), 1019 (m, L), 893 (s, asymm. UO stretch), 865 (w, L), 800 (s, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

[(py){(*i*-Bu)$_2$AlOUO}(py)(H$_2$L)] 2

A solution of di(*iso*-butyl)aluminium hydride in hexane (1.0 M, 3.5 mL, 3.53 mmol) was added to a stirred brown solution of **A** (2.30 g, 1.77 mmol) in toluene (40 mL) in a Teflon-tapped ampoule and the resulting mixture heated to 70 °C for 24 h. The pale brown reaction mixture was filtered hot, concentrated to a volume of 20 mL and cooled to -35 °C upon which a dark-yellow solid of [(py){(*i*-Bu)$_2$AlOUO}(py)(H$_2$L)] **2** precipitated. The product was isolated by filtration and washed with cold toluene (3 x 0.5 ml, -35 ºC). Recrystallization of **2** from benzene-THF at -35 °C yielded yellow needles suitable for X-ray diffraction. Yield: 1.10 g (51%).

^{1}H-NMR (C_6D_6): δ_H -5.29 (s, 3H, CH_3), -5.22 (s, 3H, CH_3), -2.50 (s, 2H), -0.01 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 0.16 (s, 6H, Ph-CH_3), 0.67 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 1.09 (s, 2H), 2.42 (s, 2H), 6.08 (d, 6H, Al-CH$_2$CH(CH_3)$_2$, $^3J_{H-H}$ = 8 Hz), 6.66 (d, 6H, Al-CH(CH_3)$_2$, $^3J_{H-H}$ = 8 Hz), 7.43 (s, 2H), 8.05 (d, 4H, $^3J_{H-H}$ = 4 Hz), 8.61 (m, 2H), 10.33 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 11.29 (br, 2H, Al-CH$_2$CH(CH$_3$)$_2$), 12.23 (d, 2H, pyrrole, $^3J_{H-H}$ = 4 Hz), 16.30 (d, 2H, Al-CH_2CH(CH$_3$)$_2$, $^3J_{H-H}$ = 8 Hz), 16.78 (d, 2H, Al-CH_2CH(CH$_3$)$_2$, $^3J_{H-H}$ = 8 Hz), 20.71 (s, 3H, CH_3), 22.35 (s, 2H), 69.12 (br, 2H, NH); ^{13}C{^{1}H}-NMR (C_6D_6): δ_C 1.75, 2.98, 15.72, 16.73, 20.71, 25.17, 30.55, 36.41, 39.25, 52.12, 76.27, 101.97, 107.83, 109.51, 111.58, 113.65, 115.88, 118.70, 120.49, 122.93, 123.27, 126.02, 127.19, 130.67, 142.91, 145.53, 149.59, 162.74; Analysis. Found: C, 58.57; H, 5.85; N, 11.26 % $C_{60}H_{70}AlN_{10}O_2U$ requires: C, 58.67; H, 5.74, N, 11.40 %; FTIR (nujol, cm^{-1}): ν 3364 (w, NH), 2924 (s, nujol), 2853 (s, nujol), 1581 (w, imine), 1461 (s, L), 1377 (s, nujol), 1284 (m, L), 1262 (m, L), 1217 (m, L), 1070 (m, L), 1043 (m, L), 1019 (m, L), 892 (s, asymm. UO stretch), 867 (w, L), 796 (s, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand; CV: $i_{p/c}$ = -1.65 V; $i_{p/a}$ = -1.31 V; $E_{1/2}$ = -1.42 V uranium(IV)/uranyl(V).

[{(UO$_2$)Li(py)(H$_2$L)}$_2$] 3

With MeLi (1eq): A solution of MeLi in Et$_2$O (0.23 mL, 0.036 mmol, 0.16 mM) was added by micro-syringe to a yellow solution of [(py){(*i*-Bu)$_2$AlOUO}(py)(H$_2$L)] **2** (45.0 mg, 0.036 mmol) in C_6D_6 (0.5 mL) in a Teflon-tapped NMR tube. The resulting brown solution was separated from a small amount of precipitate by centrifugation (4500 rpm/10 min). This clear brown solution afforded red-brown crystals of [{(UO$_2$)Li(py)(H$_2$L)}$_2$] **3** suitable for X-ray structural analysis. The solvent was decanted off and the product dried under vacuum. Yield: 7.4 mg (40 %).

With MeLi (2eq): A solution of MeLi in Et_2O (0.46 mL, 0.072 mmol, 0.16 mM) was added by micro-syringe to a yellow solution of $[(py)\{(i\text{-}Bu)_2AlOUO\}(py)(H_2L)]$ **2** (45.0 mg, 0.036 mmol) in C_6D_6 (0.5 mL) in a Teflon-tapped NMR tube. The resulting brown solution was separated from a small amount of precipitate by centrifugation (4500 rpm/10 min). The brown solution afforded a red-brown precipitate of $[\{(UO_2)Li(py)(H_2L)\}_2]$ **3**. The supernatant was decanted off and dried under vacuum. Yield: 8.3 mg (45 %).

With $LiCH_2(TMS)$: Solid $LiCH_2(TMS)$ (1.6 mg, 0.016 mmol) was added to a yellow solution of **2** (20.0 mg, 0.016 mmol) in C_6D_6 (0.5 mL) in a Teflon-tapped NMR tube and the mixture heated at 50 °C for 12 h. The resulting brown solution afforded dark red crystals of **3** suitable for an X-ray crystallographic cell check. The product was decanted and dried under vacuum. Yield: 3.3 mg (40 %).

With $LiCH(TMS)_2$: Solid $LiCH(TMS)_2$ (2.7 mg, 0.016 mmol) was added to a yellow solution of **2** (20.0 mg, 0.016 mmol) in C_6D_6 (0.5 mL) in a Teflon-tapped NMR tube and the mixture left to react at room temperature for 48 h. The resulting brown solution afforded dark red crystals of **3** suitable for an X-ray crystallographic cell check. The product was decanted and dried under vacuum. Yield: 3.6 mg (44%).

^{1}H-NMR (C_6D_6): δ_H -4.50 (s, 3H, CH_3), -1.07 (s, 3H, CH_3), -1.03 (s, 3H, CH_3), -0.75 (s, 6H, Ph-CH_3), -0.35 (s, 2H), 1.77 (s, 6H, Ph-CH_3), 2.12 (s, 2H), 7.44 (s, 2H), 7.60 (s, 2H), 9.89 (s, 2H), 10.69 (s, 2H), 11.24 (s, 2H), 11.92 (s, 2H), 10.09 (s, 3H, CH_3), 19.56 (br, 2H, N*H*); $^{13}C\{^1H\}$-NMR (C_5D_5N): δ_C 1.48, 3.42, 15.38, 16.54, 17.94, 25.90, 38.70, 67.93, 106.00, 107.24, 107.38, 109.41, 111.42, 115.73, 120.42, 149.18; Analysis. Found: C, 55.80; H, 4.46; N, 12.57% $C_{94}H_{94}Li_2N_{18}O_4U_2$ requires: C, 55.62; H, 4.67, N, 12.42 %; FTIR (nujol, cm^{-1}): ν 2952 (s, nujol), 2854 (s, nujol), 1578 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1279 (m, L), 1262 (m, L), 1047 (m, L), 1019 (w), 894 (s, asymm. UO stretch), 796 (w, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

*Rearrangement of **3** to **4**:* Solid **3** (7 mg, 3.5 μmol) was dissolved in C_5D_5N at room temperature and the ^{1}H NMR spectrum was recorded. The spectrum shows resonances that support the formation of complex **4**.

$[(py)_3(LiOUO)(py)(\{Li(py)\}_2L)]$ B

An excess of solid LiH (2.0 mg, 0.251 mmol) was added to an orange solution of **2** (6.0 mg, 4.79 μmol) in C_5D_5N (0.5 mL) in a Teflon-tapped NMR tube and the resulting dark red mixture was heated at 40 °C for 12 h. The reaction mixture was then centrifuged (7000 rpm/1 min) to remove any unreacted LiH. The resulting clear red solution afforded orange crystals of $[(py)_3(LiOUO)(py)(\{Li(py)\}_2L)]$ **B** suitable for X-ray diffraction. The crystals were decanted and dried under vacuum. Yield: 2.3 mg (34%).

^{1}H-NMR (C_5D_5N): δ_H -8.34 (s, 2H), -4.92 (s, 3H, C*H*$_3$), -2.40 (s, 2H), -2.31 (s, 2H), -1.87 (s, 6H, Ph-C*H*$_3$), -1.19 (s, 2H), 0.33 (s, 6H, Ph-C*H*$_3$), 1.10 (s, 2H), 1.33 (s, 3H, C*H*$_3$), 7.10 (s, 2H), 7.90 (s, 3H, C*H*$_3$), 9.60 (s, 2H), 11.30 (s, 2H), 20.98 (s, 3H, C*H*$_3$); Analysis. Found: C, 60.63; H, 5.02; N, 13.67 % $C_{72}H_{70}Li_3N_{14}O_2U$ requires: C, 60.80; H, 4.96, N, 13.79 %; FTIR (nujol, cm^{-1}): ν 1594 (w, imine), 1463 (s, nujol), 1376 (s, nujol), 1305 (m, L), 1261 (m, L), 1089 (m, L), 1041 (m, L), 968 (w), 894 (s, asymm. UO stretch), 804 (w, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

$[(py)_3(LiOUO)(py)(H_2L)]$ 4

A solution of DIBAL (0.1 M, 0.05 mL, 5.4 μmol) in hexane was added to a mixture of **A** (60.0 mg, 54.0 μmol) and LiH (2.1 mg, 0.27 mmol) in toluene (3 mL) at room temperature. The suspension was stirred at 65 °C for 72 h after which an orange suspension had formed. All volatiles were removed under vacuum and the residues were dissolved in C_5D_5N (0.5 mL) to give a red solution. This solution was centrifuged (7000 rpm/min) to remove excess LiH. Analysis of the ^{1}H-NMR and ^{7}Li-NMR spectra showed the sole formation of **4**. On standing at room temperature, crystalline **4** formed and was isolated by decanting the supernatant and drying under vacuum. Isolated yield: 16 mg (24%).

^{1}H-NMR (C_5D_5N): δ_H -8.57 (s, 2H), -6.90 (s, 2H), -6.44 (s, 2H), -3.55 (s, 2H), -2.33 (s, 6H, Ph-C*H*$_3$), -1.79 (s, 2H), -0.47 (s, 3H, C*H*$_3$), 0.52 (s, 6H, Ph-C*H*$_3$), 1.75 (s, 3H, C*H*$_3$), 5.70 (s, 2H), 9.10 (s, 2H), 13.87 (s, 2H), 26.35 (s, 3H, C*H*$_3$), 32.13 (s, 3H, C*H*$_3$), 85.48 (br, 2H, N*H*); ^{7}Li-NMR (C_5D_5N): δ_{Li} 88.48; ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 15.27, 16.95, 18.27, 18.67, 35.12, 37.40, 93.93, 95.86, 106.43, 106.65, 107.34, 107.78, 110.86, 111.41, 112.32, 115.50, 117.81, 118.87, 120.11, 120.97, 122.92, 125.96, 126.95, 129.17, 144.13, 146.46, 146.99, 153.86, 167.64, 174.28; Analysis. Found: C, 59.51; H, 4.86; N, 13.46 % $C_{62}H_{62}LiN_{12}O_2U$ requires: C, 59.47; H, 4.99, N, 13.42 %; FTIR (nujol, cm^{-1}): ν 3586 (w, NH), 2923 (s, nujol), 2854 (s, nujol), 1580 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1287 (m, L), 1215 (w, L), 1181 (w, L), 1040 (m, L), 969 (s), 891 (s, asymm. UO stretch), 823 (w, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

$[(py)_3(NaOUO)(py)(H_2L)]$ 5

Solid NaH (1.0 mg, 0.040 mmol) was added to an orange solution of **2** (50.0 mg, 0.040 mmol) in C_5D_5N (0.4 mL) in a Teflon-tapped NMR tube and the mixture was left to react at room temperature for 1 h. The resulting dark red solution was left to crystallize for two weeks, affording dark red crystals of $[(py)_3(NaOUO)(py)(H_2L)]$ **5** suitable for X-ray structural analysis. The product was decanted and dried under vacuum. Yield: 20.0 mg (40%).

^{1}H-NMR (C_5D_5N): δ_H -7.59 (s, 3H, C*H*$_3$), -7.44 (s, 3H, C*H*$_3$), -3.44 (s, 2H), -2.62 (s, 6H, Ph-C*H*$_3$), -2.07 (s, 2H), -1.87 (s, 3H, C*H*$_3$), 0.45 (s, 6H, Ph-C*H*$_3$), 0.72 (s, 2H), 0.74 (s, 2H), 5.78 (s, 2H), 10.83 (s, 2H), 11.01 (s, 2H), 14.18 (s, 2H), 31.79 (s, 3H, C*H*$_3$), 91.11 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 15.20, 16.80, 19.60, 19.73, 19.94, 24.98, 25.15, 27.11, 28.58, 29.04, 35.22, 36.51, 40.45, 41.71, 106.29, 109.61, 112.72, 114.95, 119.49, 121.32, 132.83, 134.00, 135.53, 141.11, 144.64, 145.40, 149.49, 159.67, 165.07; Analysis. Found: C, 57.82; H, 6.32; N, 12.97 % $C_{62}H_{42}D_{20}N_{12}NaO_2U$ requires: C, 57.80; H, 6.41, N, 13.05 %; FTIR (nujol, cm^{-1}): ν 2928 (s, nujol), 2854 (s, nujol), 1579 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1289 (m, L), 1214 (w, L), 1181 (w, L), 1041 (m, L), 967 (s), 891 (s, asymm. UO stretch), 823 (w, L), 761 (m, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand.

[(py)$_3$(KOUO)(py)(H$_2$L)] 6

Solid KH (0.8 mg, 0.020 mmol) was added to an orange solution of **2** (25.0 mg, 0.020 mmol) in C_5D_5N (0.4 mL) in a Teflon-tapped NMR tube and the mixture was left to react at room temperature for 2 h. The resulting dark red solution was stored at room temperature for three days to afford block-shaped red crystals of [(UO$_2$)(py)(K)(py)$_3$(H$_2$L)] **6** suitable for X-ray diffraction. The crystals were decanted and dried under vacuum. Yield: 34.0 mg (34%).

^{1}H-NMR (C_5D_5N): δ_H -7.53 (s, 3H, C*H*$_3$), -6.57 (s, 3H, C*H*$_3$), -3.59 (s, 2H), -2.71 (s, 6H, Ph-C*H*$_3$), -2.45 (s, 2H), -1.09 (s, 3H, C*H*$_3$), 0.11 (s, 2H), 0.71 (s, 6H, Ph-C*H*$_3$), 4.80 (s, 2H), 5.51 (s, 2H), 11.07 (s, 2H), 11.13 (s, 2H), 14.39 (s, 2H), 32.73 (s, 3H, C*H*$_3$), 93.06 (br, 2H, N*H*); ^{13}C{^{1}H}-NMR (C_5D_5N): δ_C 14.88, 16.56, 19.27, 91.53, 106.05, 109.08, 110.02, 112.35, 114.76, 115.22, 118.59, 118.86, 120.71, 122.03, 123.28, 125.88, 128.76, 129.51, 146.44, 146.70, 148.44, 159.28, 161.10, 161.52; Analysis. Found: C, 52.93; H, 4.82; N, 11.40 % $C_{42}H_{42}KN_8O_2U$ requires: C, 52.11; H, 4.37, N, 11.58 %; FTIR (nujol, cm^{-1}): ν 3366 (w, NH), 2927 (s, nujol), 2854 (s, nujol), 1581 (w, imine), 1462 (s, nujol), 1377 (s, nujol), 1283 (m, L), 1214 (w, L), 1042 (m, L), 1018 (w, L), 907 (s), 894 (s, asymm. UO stretch), 771 (m, L), 722 (m, nujol). L = stretches attributed to the Pacman ligand; CV: $i_{p/c}$ = -1.44 V (at 500 mV/s), -1.41 V (at 100 mV/s); $i_{p/a}$ = -1.17 V (at 500 mV/s), -1.22 V (at 100 mV/s); $E_{1/2}$ = -1.31 V uranyl(V)/uranyl(VI).

1.2 Catalytic synthesis of 5 and 6

Table 1. Formation of [(py)$_3$(KOUO)(py)(H$_2$L)] 6 using catalytic quantities of HAl(*i*-Bu)$_2$

entry	**A**	HAl(*i*-Bu)$_2$	Mol% HAl(*i*-Bu)$_2$	Time/h	Ratio **6**/**A**
1	10.0 mg, 9.00 µmol	45.0 µL, 0.01 M, 0.45 µmol	5	24	20/80
2	10.0 mg, 9.00 µmol	45.0 µL, 0.01 M 0.45 µmol	5	60	20/80
3	100.0 mg, 90.00 µmol	90.0 µL, 0.1 M, 9.00 µmol	10	96	100/0
4	11.0 mg, 10.0 µmol	---	0	96	50/50
5	11.0 mg, 10.0 µmol	---	0	240	80/20

Reaction conditions: 70 °C, toluene, 5 equivalents KH

General procedures:

Small scale reactions (entries 1, 2, 5, 6):

A solution of DIBAL (see Table 1 for quantities) was added to a suspension of $[(UO_2)(py)(H_2L)]$ **A** (see table) and KH in C_6D_6 (0.5 mL) and heated to 70 ˚C. After a certain time period (Table 1), the mixture was filtered, the filtrate evaporated to dryness under reduced pressure, and the residues dissolved in C_5D_5N and analyzed by ^{1}H-NMR spectroscopy.

Large scale reactions

Catalytic synthesis of 5:

A solution of DIBAL (0.01 M, 0.90 mL, 9.00 μmol) in hexane was added to a mixture of **A** (89.6 mg, 90.0 μmol) and NaH (10.7 mg, 0.45 mmol) in toluene (3 mL) at room temperature. The suspension was stirred at 70 °C for 72 h after which an orange precipitate had formed. All volatiles were removed under vacuum and the residues were dissolved in C_5D_5N (0.5 mL) to give a red solution. This solution was centrifuged (7000 rpm/ min) to remove excess NaH. Analysis of the ^{1}H-NMR spectrum showed the sole formation of **5**. On standing at room temperature, crystalline **5** formed and was isolated by decanting the supernatant and drying under vacuum. Yield: 70 mg (62%).

Catalytic synthesis of 6 (entry 3):

A solution of DIBAL in hexane (0.01 M, 90.0 μL, 9.00 μmol) was added to a suspension of $[(UO_2)(py)(H_2L)]$ **A** (100 mg, 90.00 μmol) and KH (18.0 mg, 0.45 mmol) in toluene (15 mL) at room temperature and stirred at 70 °C for 96 h. The mixture was filtered and the filtrate dried under reduced pressure and redissolved in C_5D_5N. Analysis of the ^{1}H-NMR spectrum showed the sole formation of **6**. On standing, crystals of **6** formed, and were isolated by decanting the supernatant liquors and drying under vacuum. Yield: 60 mg (52%).

2. Crystallographic information

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova instrument at 120 K fitted with a CCD area detector using CuKα radiation (λ = 1.5418 Å) (compound **1**) and MoKα radiation (λ = 0.7107 Å) (compound **2**) or an Eos Excalibur instrument at 170 K using MoKα radiation (compounds **3**, **5** and **6**) and *CrysAlis PRO* from Agilent Technologies. The solution and refinement of the data were carried out using WinGX and SHELXL97[3] with SHELXS97 (**1** and **5**), SHELXL97 (**2** and **5**) and SIR92[4] (**3**).

Crystallographic Data Summary Tables

	Crystal data		
Compound	**[(py)(Me$_2$AlOUO)(py)(H$_2$L)] 1**	**[(py){(*i*-Bu)$_2$AlOUO}(thf)(H$_2$L)] 2**	**[{(UO$_2$)Li(py)(H$_2$L)}$_2$] 3**
Local code	PO2015	PO3002	P12124
Chemical formula	$C_{93}H_{97}AlN_{10}O_2U$	$C_{74}H_{88}AlN_9O_3U$	$C_{124}H_{124}Li_2N_{18}O_4U_2$
MW	1651.82	1416.54	2420.35
Crystal system, space group	monoclinic, $P\ 2_1/c$	monoclinic, $P2_1/n$	triclinic, P-1
Temperature (K)	120	120	170
a, b, c (Å)	21.6483(2), 15.4318(2), 24.4807(2)	12.5004 (2), 40.0423 (6), 14.2199 (2)	11.963(5), 14.243(5), 17.926(5)
α, β, γ (º)	90.00, 98.4807, 90.00	90.00, 105.173 (2), 90.00	99.705(5), 90.311(5), 114.231
V (Å^3)	8086.50(14)	6869.57 (18)	2736.0(17)
Z	4	4	1
Radiation type	CuK\α	MoK\α	MoK\α
μ (mm^{-1})	6.182	2.43	3.019
Crystal size (mm)	0.1794 × 0.0864 × 0.167	0.30 × 0.12 × 0.09	0.3746 × 0.1856 × 0.1567
	Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos
Absorption correction	Gaussian	Gaussian	multi-scan
T_{min}, T_{max}	0.481, 0.895	0.648, 0.826	0.851, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	96487, 16582, 13507	140222, 17029, 14619	21299, 21299, 16404
R_{int}	0.0700	0.079	0.0637
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.630	0.667	0.650
	Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.103, 1.03	0.046, 0.109, 0.95	0.040, 0.096, 1.05
No. of reflections	16582	17029	21299
No. of parameters	980	812	661
No. of restraints	0	87	0
H-atom treatment	mixed	mixed	constrained

$\Delta\rho_{max}$,$\Delta\rho_{min}$(e Å^{-3})	2.17, -2.92	1.96, −2.22	4.26, -2.06

	Crystal data		
Compound	**[(py)$_3$(LiOUO)(py)(H$_2$L)] 4**	**[(py)$_3$(NaOUO)(py)(H$_2$L)] 5**	**[(py)$_3$(KOUO)(py)(H$_2$L)] 6**
Local code	p14024	exp13043	p12134
Chemical formula	$C_{84.39}H_{84.39}Li_{0.87}N_{16.48}O_2U$	$C_{62}H_{62}N_{12}NaO_2U$	$C_{77}H_{77}KN_{15}O_2U$
MW	1606.79	1268.26	1521.67
Crystal system, space group	monoclinic, *Cc*	monoclinic, *Cc*	orthorhombic, $P\ 2_1\ 2_1\ 2_1$
Temperature (K)	170	170	170
a, b, c (Å)	14.7282 (5), 24.4176 (6), 22.8717 (7)	14.427 (5), 24.602 (5), 23.182 (5)	13.6930(3), 21.7419(5), 24.2382(4)
α, β, γ (º)	90.00, 90.634 (3), 90.00	90.00, 90.881 (5), 90.00	90.00, 90.00, 90.00
V (Å^3)	7973.5(4)	8227 (4)	7216.0(3)
Z	4	4	4
Radiation type	MoK\α	MoK\α	MoK\α
μ (mm^{-1})	2.09	2.02	2.364
Crystal size (mm)	0.92 × 0.58 × 0.35	0.93 × 0.40 × 0.23	1.2244 × 0.6915 × 0.4865
	Data collection		
Diffractometer	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	multi-scan	multi-scan	multi-scan
T_{min}, T_{max}	0.464, 1.000	0.530, 1.000	0.571, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	41408, 18020, 14162	37697, 17997, 13051	46333, 16376, 14702
R_{int}	0.058	0.048	0.036
$(sin\ \theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649	0.649
	Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.103, 1.00	0.065, 0.170, 0.96	0.032, 0.076, 0.72
No. of reflections	18020	17997	16376
No. of parameters	960	581	874
No. of restraints	76	8	48
H-atom treatment	constrained	mixed	constrained

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.25, -0.68	4.51, −0.92	1.04, -0.95

3. Electrochemistry

3.1 Cyclic voltammogram of [(py)^{i}Bu$_2$AlOUO(py)(H$_2$L)] 2

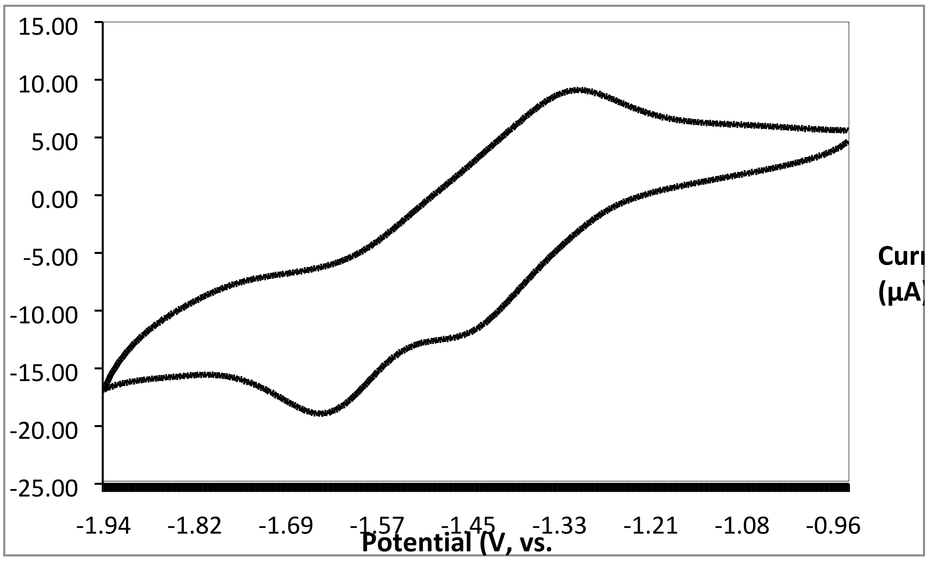

Figure S1: Room temperature cyclic voltammogram of **2** (5 mM) in THF at 500 mV/s (*vs*. Fc/Fc$^+$, 0.1 M [NBu$_4$][PF$_6$] as supporting electrolyte)

$i_{p/c}$ = -1.65 V; $i_{p/a}$ = -1.31 V; $E_{1/2}$ = -1.42 V

3.2 Cyclic voltammogram of [(py)$_3$(KOUO)(py)(H$_2$L)] 6

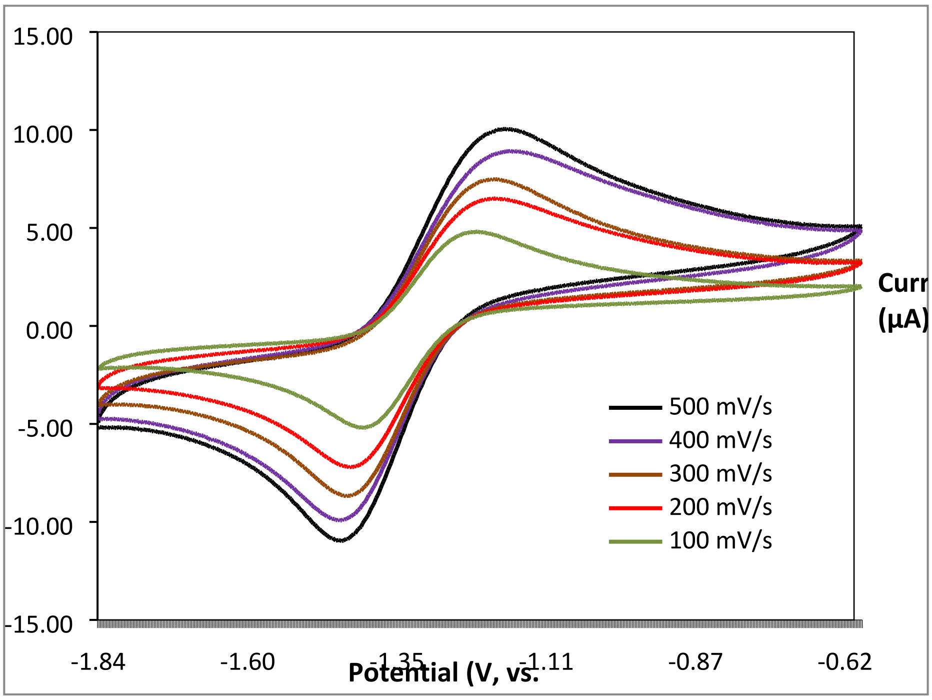

Figure S2 Room temperature cyclic voltammogram of **6** (3.2 mM) in THF at scan rates from 500 to 100 mV/s (*vs*. Fc/Fc$^+$, 0.1 M [NBu$_4$][PF$_6$] as supporting electrolyte)

$i_{p/c}$ = -1.44 V (at 500 mV/s), -1.41 V (at 100 mV/s); $i_{p/a}$ = -1.17 V (at 500 mV/s), -1.22 V (at 100 mV/s); $E_{1/2}$ = -1.31 V

4. 2D COSY of 2

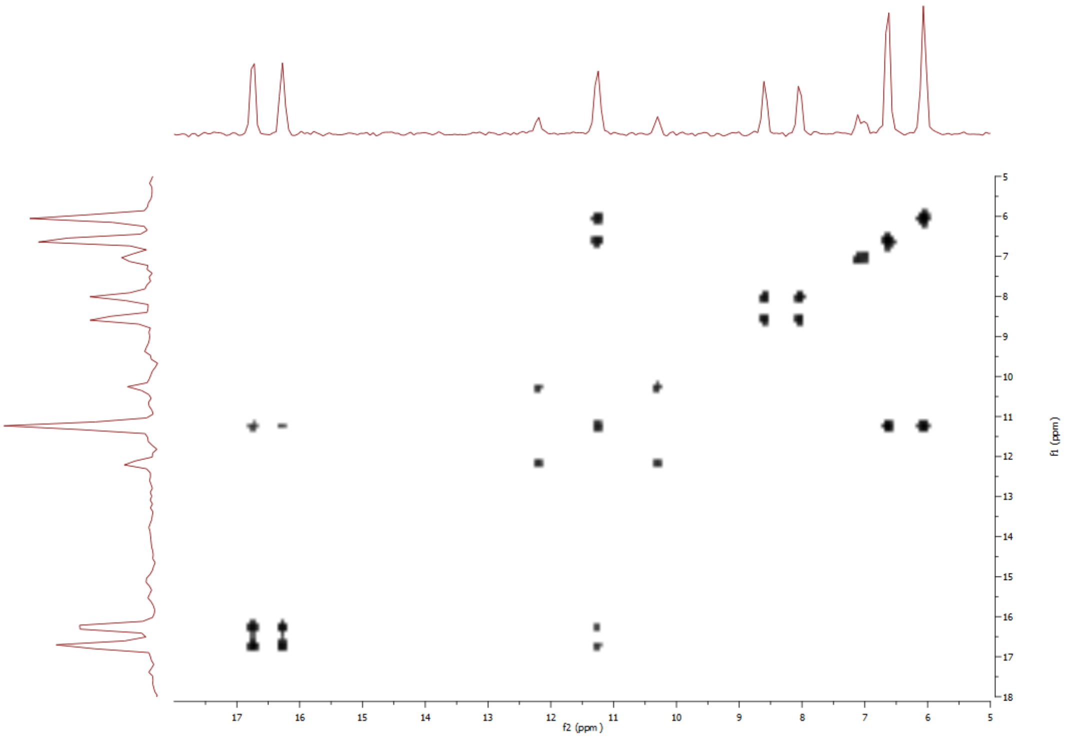

Figure S3: ^{1}H-COSY NMR spectrum of **2** in C_6D_6 covering the range of 18 ppm to 5 ppm showing the coupling of the *iso*-butyl groups.

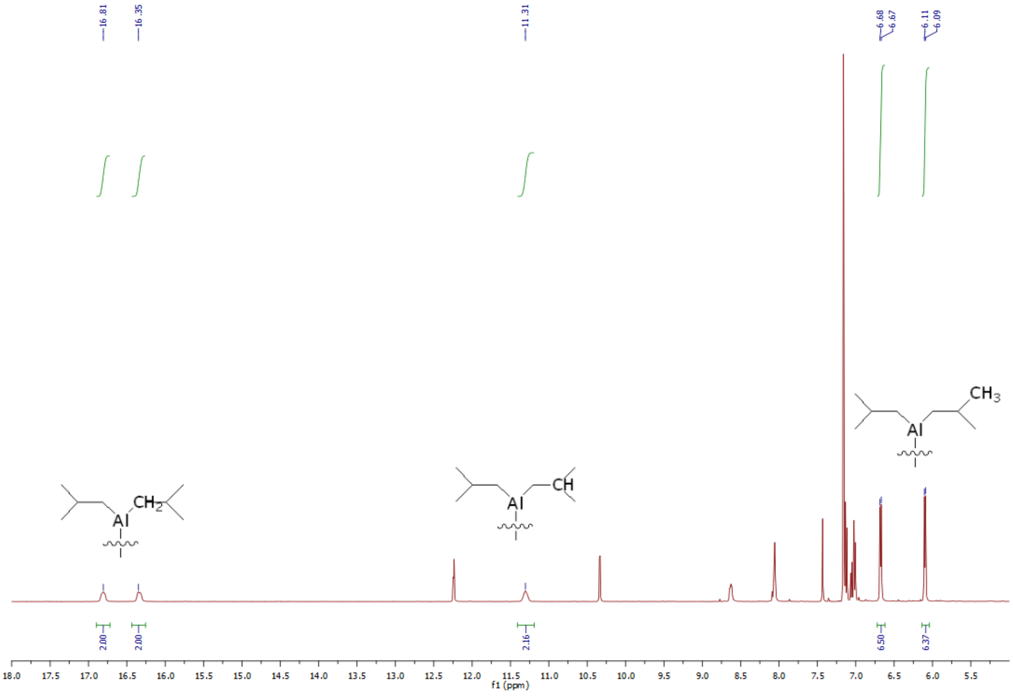

Figure S4: ^{1}H-NMR spectrum of **2** in C_6D_6 covering the range of 18 ppm to 5 ppm showing the coupling of the *iso*-butyl groups.

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