Single metal four-electron reduction by U(II) and masked "U(II)" compounds

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Supporting Information

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Experimental Details

General considerations

All manipulations were carried out under inert atmospheres using an MBraun glovebox equipped with a purifier unit and Schlenk line techniques. The water and oxygen levels were always kept at less than 1 ppm. Anhydrous solvents were purchased from Sigma Aldrich and vacuum distilled under potassium/benzophenone (THF, toluene) or sodium sand/benzophenone (hexane). Depleted uranium turnings were purchased from IBILABS, Florida (USA). Azobenzene and diphenylacetylene were purchased from Sigma Aldrich and dried under vacuum.

$[U\{N(SiMe_3)_2\}_3]$[1], KC_8[2], $[K(2.2.2\text{-cryptand}][\{((Me_3Si)_2N)_3U\}_2(\mu\text{-}O)]$[3] (complex **1**) and $[K(2.2.2\text{-cryptand})][U\{N(SiMe_3)_2)_3]$[4] (complex **2**) were synthesized according to their respective literature procedures. Elemental analyses were performed under nitrogen by the "Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH" in Lindlar, Germany and with a Thermo Scientific Flash 2000 Organic Elemental Analyzer at EPFL.

^{1}H NMR experiments were carried out using NMR tubes adapted with J. Young valves. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and the chemical shifts are reported in ppm with residual proteo-solvent signals used as an internal reference.

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. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α- and β-counting equipment.*

Synthesis $[K(2.2.2\text{-cryptand})][U(\eta^2\text{-}C_2Ph_2)\{N(SiMe_3)_2\}_3]$, 3.

From complex 1 NMR scale. A cold (−80 °C) solution of diphenylacetylene (1.2 mg, 6.7 µmol, 1.0 eq) in THF-d_8 (0.5 mL) was added to cold (−80 °C) purple crystals of **1** (15.1 mg, 6.60 µmol, 1.0 eq), resulting in a brown solution. The ^{1}H-NMR spectrum at −80 °C immediately showed full conversion of complex **1** and the appearance of signals corresponding to $[K(2.2.2\text{-cryptand}][U(O)\{N(SiMe_3)_2\}_3]$. At 0 °C and 25 °C additional paramagnetic signals were observed, assigned to complex **3**. TMS_2O (1.5 µL, 6.7 µmol, 1.0 eq) was added and used as internal standard to determine a conversion of 66%.

From complex 1 preparatory scale. A cold (−80 °C) solution of diphenylacetylene (4.0 mg, 22.4 µmol, 1.0 eq) in THF (1 mL) was added to cold (−80 °C) purple crystals of **1** (49.9 mg, 21.8 µmol, 1.0 eq), resulting in a brown solution, which was left to react for 15 min at −80 °C. Slow diffusion of hexane into the THF reaction mixture at −40 °C gave a mixture of X-ray quality copper and pink colored crystals, consisting of complex **3** and $[K(2.2.2\text{-cryptand}][U(O)\{N(SiMe_3)_2\}_3]$. The crystals were washed with toluene until $[K(2.2.2\text{-cryptand}][U(O)\{N(SiMe_3)_2\}_3]$ was fully removed. This resulted in significant loss of complex **3**. The final pure, copper-colored residue of **3** was dried and collected (7.3 mg, 25%).

Anal. Calcd. for $C_{50}H_{100}KN_5O_6Si_6U$: C, 45.74; H, 7.68; N, 5.33. Found: C, 44.29; H, 7.45; N, 4.97.

From in situ complex 2 preparatory scale. A cold (−80 °C) solution of [U{N(SiMe$_3$)$_2$}$_3$] (50.0 mg, 69.5 µmol, 1.0 eq) and 2.2.2-cryptand (26.2 mg, 69.6 µmol, 1.0 eq) in THF (0.5 mL) was added to KC_8 (9.4 mg, 70 µmol, 1.0 eq). After a few minutes, the black mixture was filtered and added to cold (−80 °C) diphenylacetylene (12.4 mg, 69.6 µmol, 1.0 eq), resulting in a brown solution, which was left to react for 15 min at −80 °C. Slow diffusion of hexane into the THF reaction mixture at −40 °C gave X-ray quality copper-colored crystals (33.9 mg, 37%).
Crystals of **3** decompose in a room temperature THF-d_8 solution to form the bis metallacyclic complex, [K(2.2.2-cryptand)][{((Me$_3$Si)$_3$N}U{κ^2-C,N-CH$_2$SiMe$_2$N(SiMe$_3$)}$_2$][5], among other products. After 3 h, approximately 60% remains, after 12 h approximately 25% remains and after 40 h nearly all **3** was consumed.
Anal. Calcd. for $C_{50}H_{100}KN_5O_6Si_6U$: C, 45.74; H, 7.68; N, 5.33. Found: C, 44.82; H, 7.56; N, 5.29. The elemental analyses were reproduced several times in different places and conditions always giving low values of carbon probably due to combustion issues that could not be solved.
^{1}H-NMR (400 MHz, THF-d_8, 233K): δ 29.3 (s, 4H, C*Ph*), 17.1 (s, 4H, C*Ph*), 11.6 (s, 2H, C*Ph-p*), 3.9 (s, 12H, 2.2.2-cryptand), 3.8 (s, 12H, 2.2.2-cryptand), 2.8 (s, 12H, 2.2.2-cryptand), –12.3 (s, 54H, NSi*Me$_3$*). ^{1}H-NMR (400 MHz, THF-d_8, 298K): δ 29.3 (s, 4H, C*Ph*), 17.1 (s, 4H, C*Ph*), 11.6 (s, 2H, C*Ph-p*), 3.9 (s, 12H, 2.2.2-cryptand), 3.8 (s, 12H, 2.2.2-cryptand), 2.8 (s, 12H, 2.2.2-cryptand), –12.3 (s, 54H, NSi*Me$_3$*).

Synthesis [K(2.2.2-cryptand)][U(NPh)$_2${N(SiMe$_3$)$_2$}$_3$], 4.

From complex 1 NMR scale. A cold (−80 °C) solution of azobenzene (1.3 mg, 7.1 µmol, 1.1 eq) in THF-d_8 (0.5 mL) was added to cold (−80 °C) purple crystals of **1** (15.0 mg, 6.56 µmol, 1.0 eq), resulting in a red/brown solution. The ^{1}H-NMR spectrum at −80 °C immediately showed full conversion of complex **1** and the appearance of signals corresponding to [K(2.2.2-cryptand][U(O){N(SiMe$_3$)$_2$}$_3$]. At −40 °C an additional paramagnetic signal was observed that was later assigned to complex **5**. Upon warming up to room temperature, complex **5** immediately starts to transform into complex **4** and the color slowly changed to yellow/brown. After 2h at room temperature, the paramagnetic signals assigned to **5** had completely disappeared and a set of diamagnetic signals assigned to complex **4** was observed in the ^{1}H-NMR spectrum of the solution.
From complex 1 preparatory scale. A cold (−80 °C) solution of azobenzene (4.0 mg, 22 µmol, 1.0 eq) in THF (1 mL) was added to cold (−80 °C) purple crystals of **1** (50.0 mg, 21.9 µmol, 1.0 eq), resulting in a red/brown solution. It was left at low temperature for 5 min and then stirred at room temperature for 2h, causing the color to change to yellow/brown. Slow diffusion of hexane into the THF reaction mixture at −40 °C gave a mixture of X-ray quality brown and pink crystals, consisting of complex **4** and the terminal oxo complex [K(2.2.2-cryptand][U(O){N(SiMe$_3$)$_2$}$_3$]. Washing with toluene (6 x 0.5 mL) removed [K(2.2.2-cryptand][U(O){N(SiMe$_3$)$_2$}$_3$]. The final pure, brown residue of **4** was dried and collected (19.8 mg, 69%).
Anal. Calcd for $C_{48}H_{100}KN_7O_6Si_6U$: C, 43.78; H, 7.65; N, 7.44. Found: C, 43.27; H, 7.61; N, 7.51.

From complex 2 NMR scale. A cold (−80°C) solution of [U{N(SiMe$_3$)$_2$}$_3$] (10.0 mg, 13.9 µmol, 1.0 eq) and 2.2.2-cryptand (5.3 mg, 14 µmol, 1.0 eq) in THF-d_8 (0.5 mL) was added to KC_8 (1.9 mg, 14 µmol, 1.0 eq). After a few minutes, the black mixture was filtered and added to cold (−80°C) azobenzene (2.6 mg, 14 µmol, 1.0 eq), resulting in a red/brown solution. At −40 °C an additional paramagnetic signal was observed that was later assigned to complex **5**. Upon warming up to room temperature, complex **5** immediately starts to transform into complex **4** and the color slowly changed to yellow/brown. After 2h at room temperature, the paramagnetic signals assigned to **5** had completely disappeared and a set of diamagnetic signals assigned to complex **4** was observed in the ^{1}H-NMR spectrum of the solution.

From complex 2 preparatory scale. A cold (−80°C) solution of [U{N(SiMe$_3$)$_2$}$_3$] (50.0 mg, 69.5 µmol, 1.0 eq) and 2.2.2-cryptand (26.3 mg, 69.9 µmol, 1.0 eq) in THF-d_8 (0.5 mL) was added to KC_8 (9.4 mg, 70 µmol, 1.0 eq). After a few minutes, the black mixture was filtered and added to cold (−80 °C) azobenzene (12.7 mg, 69.9 µmol, 1.0 eq), resulting in a red/brown solution. It was left at low temperature for 5 min and then stirred at room temperature for 2h, causing the color to change to yellow/brown. Slow diffusion of hexane into the THF reaction mixture at −40 °C gave X-ray quality brown crystals consisting of **4** (33.8 mg, 37%).

Anal. Calcd for $C_{48}H_{100}KN_7O_6Si_6U$: C, 43.78; H, 7.65; N, 7.44. Found: C, 43.11; H, 7.66; N, 7.45. The elemental analyses were reproduced several times in different places and conditions always giving low values of carbon probably due to combustion issues and/or the formation of silicon carbides that could not be solved.

^{1}H-NMR (400 MHz, THF-d_8, 298K): δ 6.97 (dd, 4H, NPh-*o*), 5.52 (m, 4H, NPh-*m*), 5.44 (dd, 2H, NPh-*p*), 3.57 (s, 12H, 2.2.2-cryptand), 3.53 (t, 12H, 2.2.2-cryptand), 2.54 (t, 12H, 2.2.2-cryptand), 0.45 (s, 54H, NSi*Me$_3$*). IR (Nujol mull): 1579 (m), 1464 (br s), 1377 (s), 1362 (m), 1355 (m), 1298 (m), 1245 (br s), 1164 (w), 1133 (m), 1104 (s), 1079 (m), 1059 (w), 1022 (w), 996 (s), 939 (s), 852 (m), 843 (br s), 773 (w), 753 (m), 722 (m), 695 (m), 665 (m), 600 (m), 565 (w), 522 (w).

Isolation of [K(2.2.2-cryptand)][U(N$_2$Ph$_2$){N(SiMe$_3$)$_2$}$_3$], 5.

From complex 1. A cold (−80 °C) solution of azobenzene (1.3 mg, 7.1 µmol, 1.1 eq) in THF-d_8 (0.5 mL) was added to cold (−80 °C) purple crystals of **1** (15.1 mg, 6.6 µmol, 1.0 eq), resulting in a red/brown solution. Slow diffusion of cold hexane into the reaction mixture at −40 °C resulted in a mixture of pink and dark red crystals, characterized as [K(2.2.2-cryptand][U(O){N(SiMe$_3$)$_2$}$_3$] by NMR and complex **5** by X-ray crystallography, respectively. Complex **5** has a similar solubility as [K(2.2.2-cryptand][U(O){N(SiMe$_3$)$_2$}$_3$], and is temperature sensitive rendering separation impossible .

From complex 2. A cold (−80 °C) solution of [U{N(SiMe$_3$)$_2$}$_3$] (25.0 mg, 34.8 µmol, 1.0 eq) and 2.2.2-cryptand (13.1 mg, 34.8 µmol, 1.0 eq) in THF (0.5 mL) was added to KC_8 (4.7 mg, 35 µmol, 1.0 eq). After a few minutes, the black mixture was filtered and added to cold (−80 °C) azobenzene (6.4 mg, 35 µmol, 1.0 eq), resulting in a red/brown solution, which was left to react for 15 min at −80 °C. Slow diffusion of hexane into the THF reaction mixture at −40 °C

allowed to isolate a few crystals of complex **5**. Upon warming up a THF solution of complex **5** to room temperature, it immediately starts to transform into complex **4**.
^{1}H-NMR (400 MHz, THF-d_8, 233K): δ 28.5 (s, 2H, N*Ph*), 19.2 (s, 2H, N*Ph*), 17.8 (s, 2H, N*Ph*), 10.2 (s, 2H, N*Ph*), 3.8 (s, 12H, 2.2.2-cryptand), 3.7 (s, 12H, 2.2.2-cryptand), 2.8 (s, 12H, 2.2.2-cryptand), –14 (br s, 54H, NSi*Me*$_3$). ^{1}H-NMR (400 MHz, THF-d_8, 273K): δ 38.7 (s, 2H, N*Ph*), 23.8 (s, 2H, N*Ph*), 16.1 (s, 4H, N*Ph*), 9.1 (s, 2H, N*Ph*), 3.7 (s, 12H, 2.2.2-cryptand), 3.6 (s, 12H, 2.2.2-cryptand), 2.7 (s, 12H, 2.2.2-cryptand), –12.0 (s, 54H, NSi*Me*$_3$). ^{1}H-NMR (400 MHz, THF-d_8, 298K): δ 15.1 (s, 4H, N*Ph*), 8.6 (s, 2H, N*Ph*), 3.6 (s, 12H, 2.2.2-cryptand), 3.5 (s, 12H, 2.2.2-cryptand), 2.6 (s, 12H, 2.2.2-cryptand), –10.7 (s, 54H, NSi*Me*$_3$).

NMR Spectroscopy

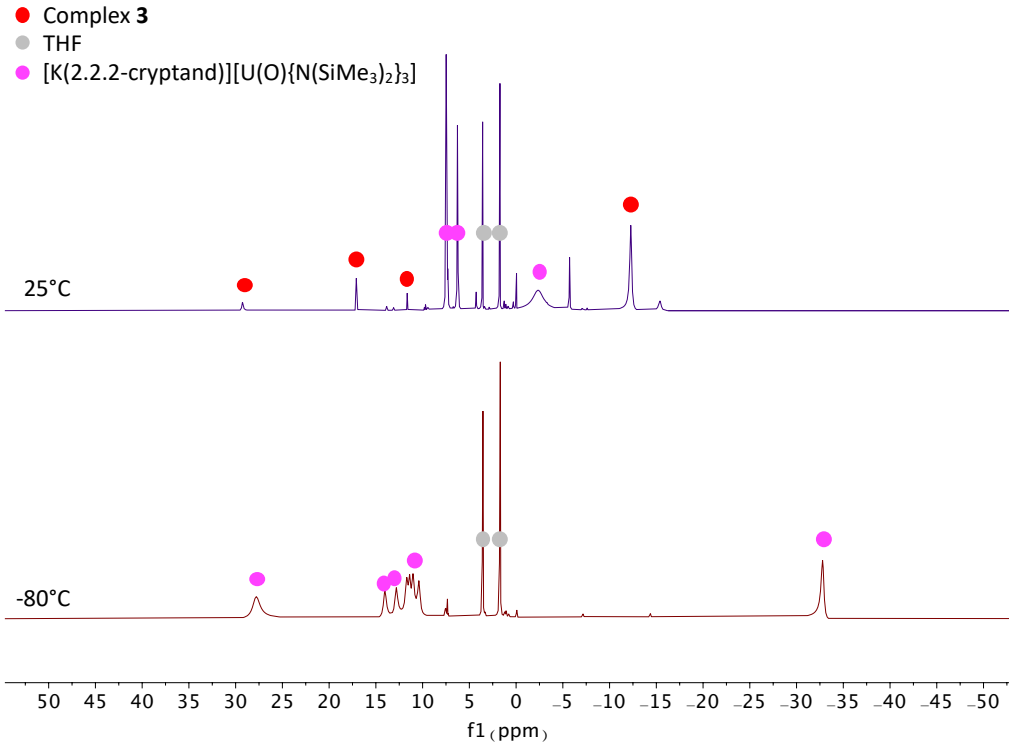


Figure S1 Variable temperature ^{1}H-NMR spectra of the reaction mixture of **1** and diphenylacetylene in 1:1 ratio in THF-d_8.

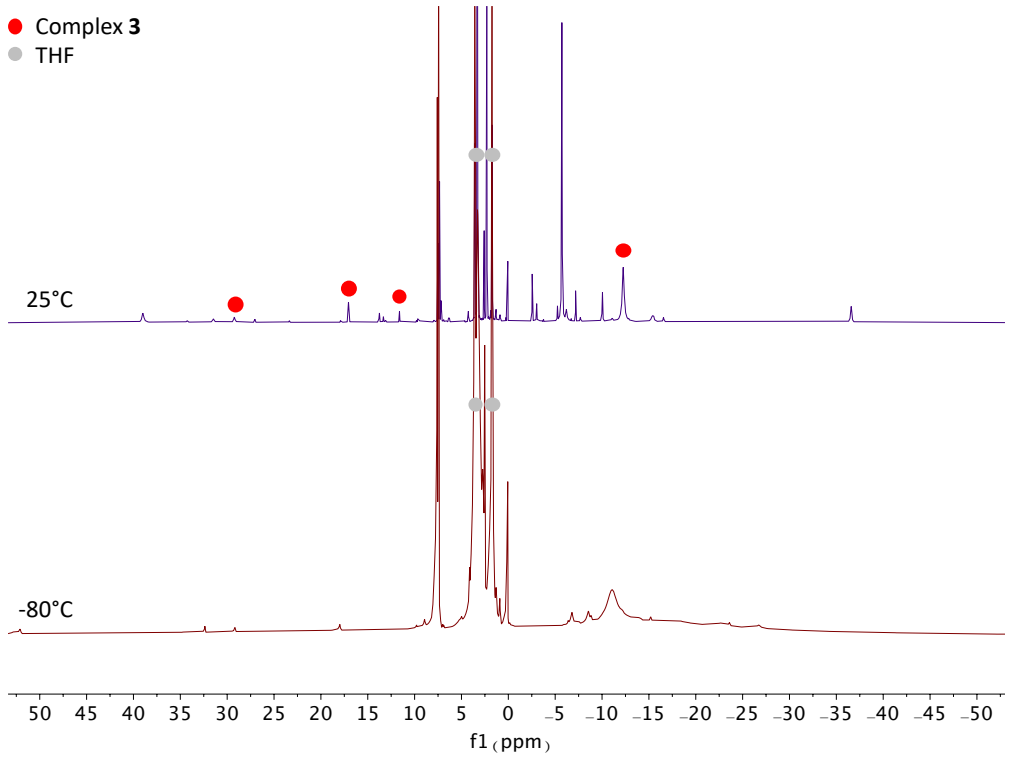


Figure S2 Variable temperature ^{1}H-NMR spectra of the reaction mixture of **2** and diphenylacetylene in 1:1 ratio in THF-d_8.

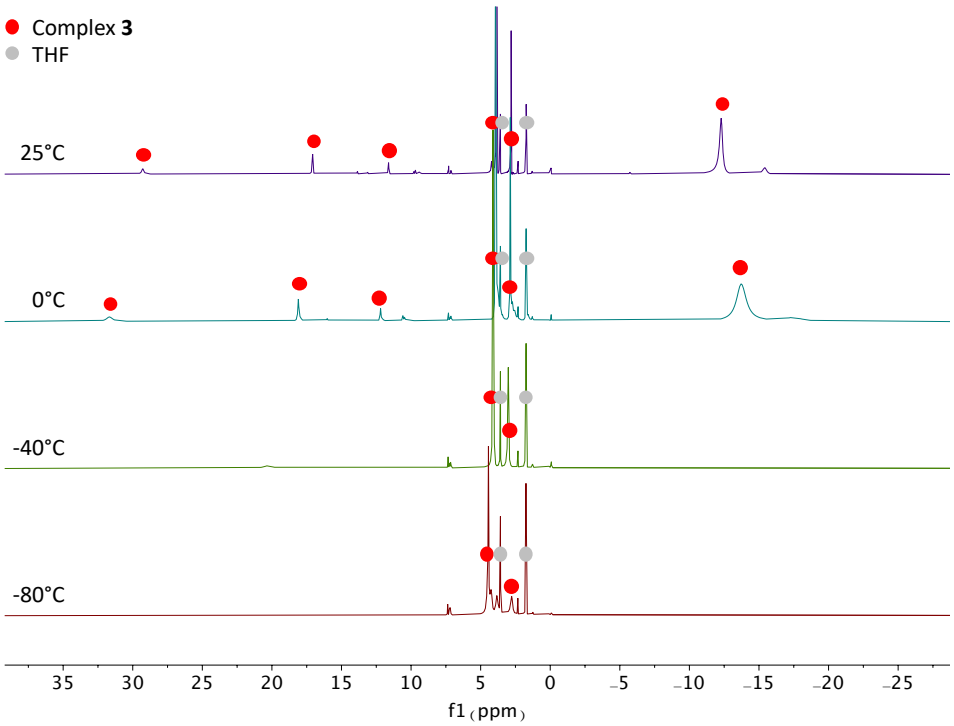


Figure S3 Variable temperature ^{1}H-NMR spectra of complex **3** in THF-d_8.

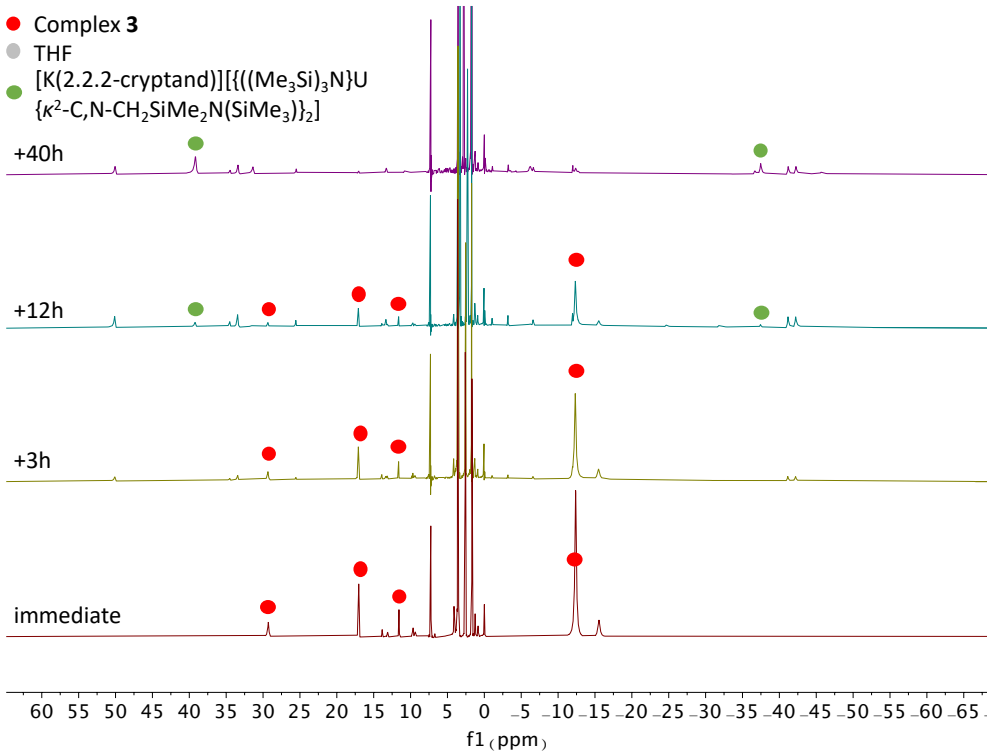


Figure S4 ^{1}H-NMR spectra of complex **3** at room temperature in THF-d_8 over time.

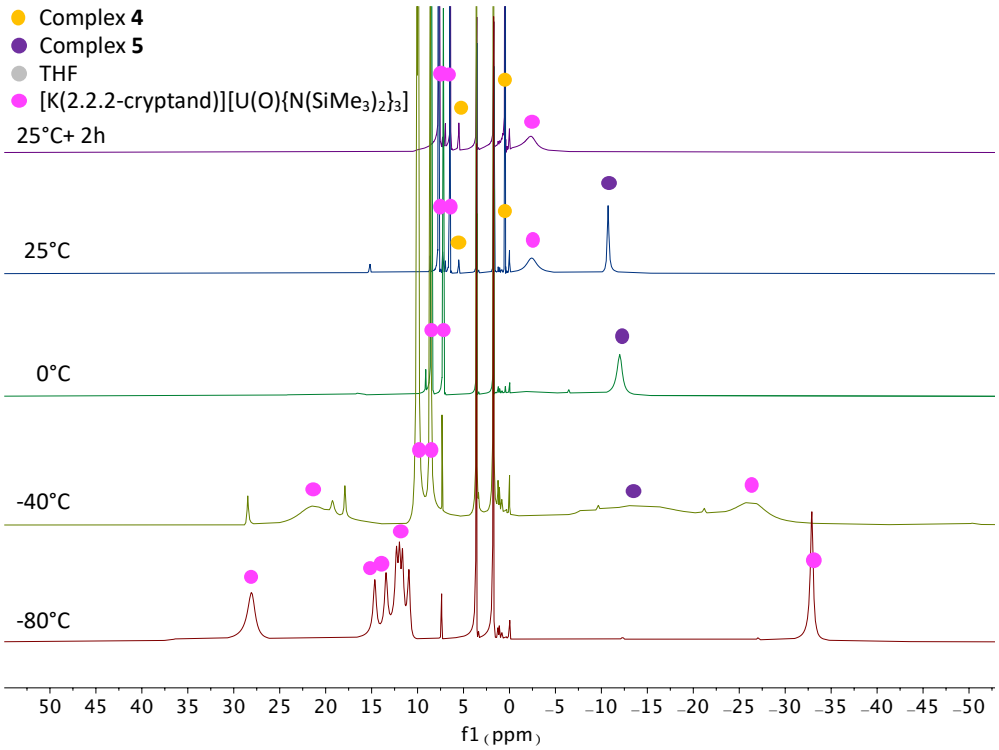


Figure S5 Variable temperature ^{1}H-NMR spectra of the reaction mixture of **1** and azobenzene in 1:1 ratio in THF-d_8.

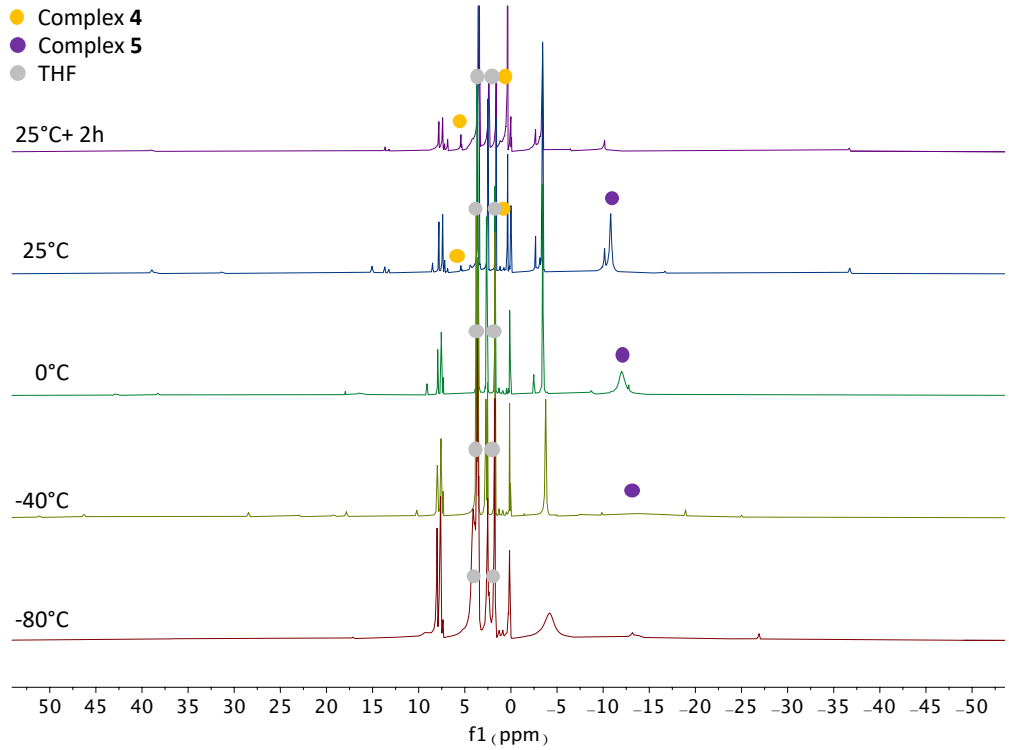


Figure S6 Variable temperature ^{1}H-NMR spectra of the reaction mixture of [K(2.2.2-cryptand)][U{N(SiMe$_3$)$_2$}$_3$] and azobenzene in 1:1 ratio in THF-d_8.

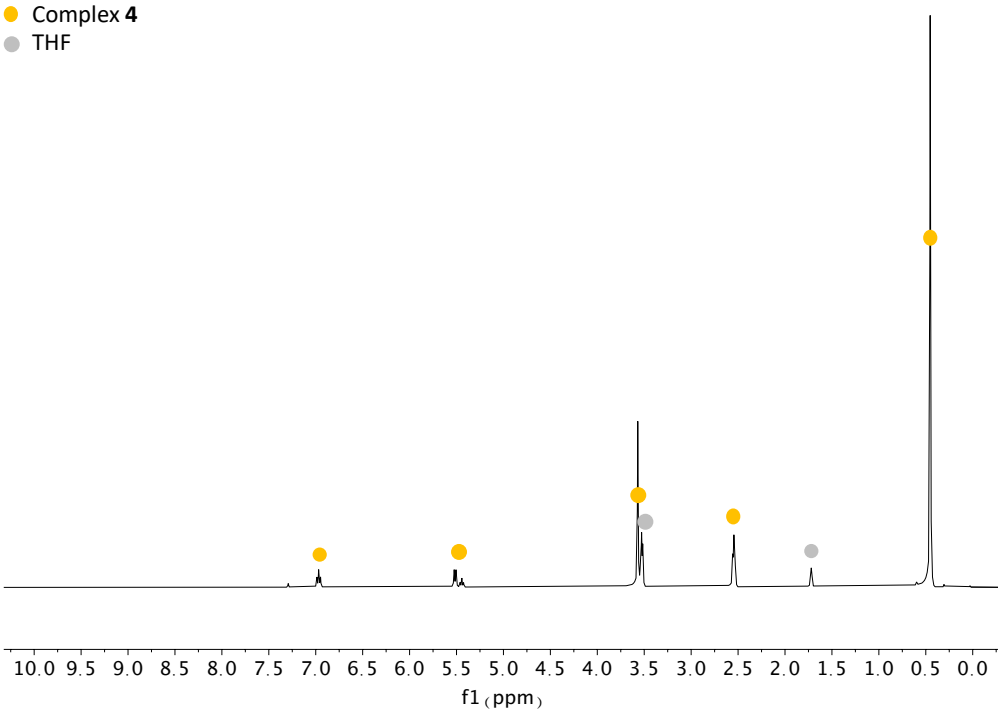


Figure S7 ^{1}H-NMR spectrum of complex **4** in THF-d_8 at room temperature.

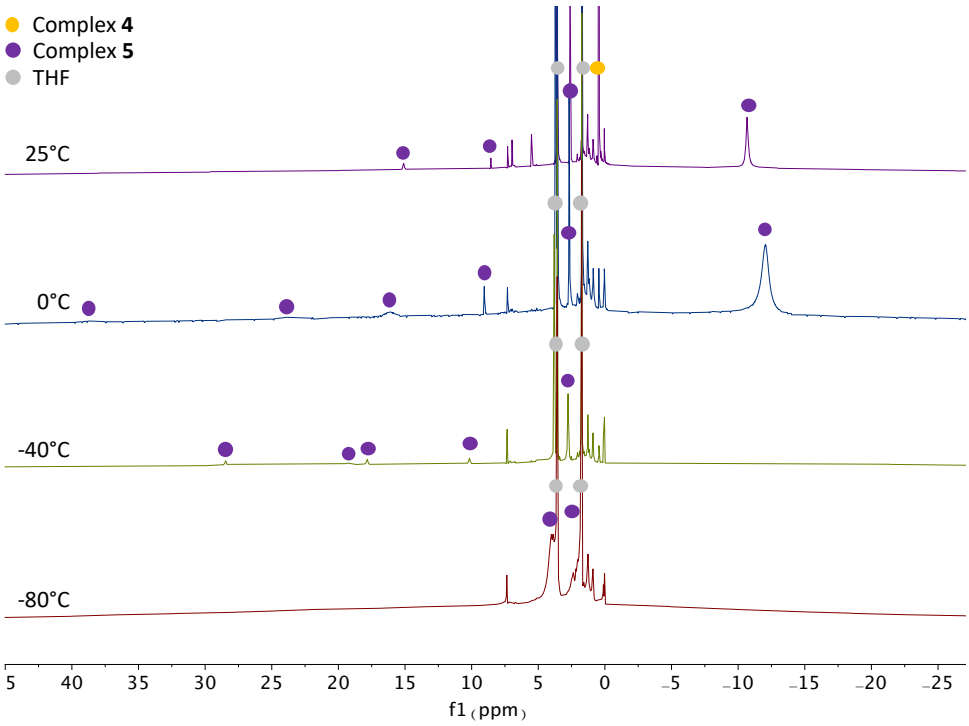


Figure S8 Variable temperature ^{1}H-NMR spectra of complex **5** in THF-d_8.

IR spectroscopy

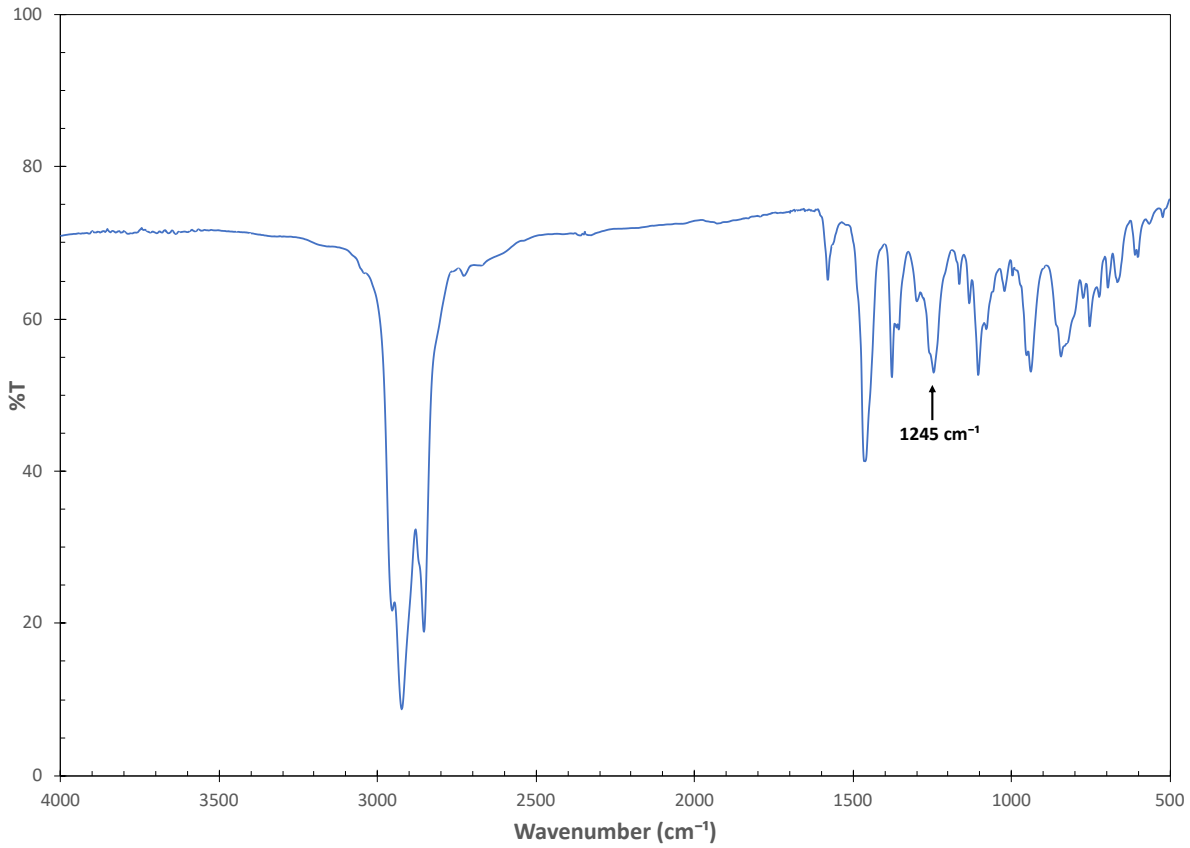


Figure S9 IR spectrum (Nujol mull) of complex **4**.

The imido substituents in **4** show a band at 1245 cm^{-1} in the infrared spectrum, consistent with a U=N-C moiety. The energy of this absorption is similar to that found in previously reported uranium(VI) imido complexes.[6]

X-ray Structure and Refinement Details

The diffraction data for the analysed crystal structures were collected at low temperature using Cu K_α radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction and correction were carried out by *CrysAlis*^{Pro}.[7]

The solutions and refinements were performed by *SHELXT*[8] and *SHELXL*[9], respectively. The crystal structures were refined using full-matrix least-squares based on F^2 with all non-H atoms defined in anisotropic manner. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

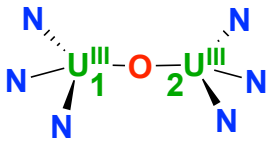
The refinement of the crystal structure of compound **3** was quite straightforward, although the anisotropic behaviour of the $[K(2.2.2\text{-cryptand})]^+$ was far from being ideal and some restraints were needed (SIMU card) to get reasonable ADPS. The raw data of the crystal structure of **4** were treated for twinning (2 major domains were found) and the refinement was completed by using the HKLF 5 format (MERG 0, BASF = 0.192(2)).

The crystal structure of compound **5** displayed several problems; the data were treated for twinning (2 major domains were observed) and the final model showed disordered solvent (1 THF per ionic pair). The solvent was removed by using the *SQUEEZE* algorithm of *PLATON*[10] and the refinement was completed by employing the HKLF 5 format (MERG 0, BASF = 0.342(2)). Some geometries and ADPS were corrected by restraints (SADI and RIGU cards, respectively).

Compound	**3**	**4**	**5**
Formula	$C_{50}H_{100}KN_5O_6Si_6U$	$C_{48}H_{100}KN_7O_6Si_6U$	$C_{48}H_{100}KN_7O_6Si_6U$
$D_{calc.}$/ g cm^{-3}	1.321	1.351	1.264
μ/mm^{-1}	8.875	9.057	8.476
Formula Weight	1313.01	1317.01	1317.01
Colour	clear intense orange	lustrous intense black	clear dark brown
Shape	plate	needle	prism
Size/mm^3	0.20×0.20×0.04	0.14×0.09×0.04	0.28×0.18×0.11
T/K	140.00(10)	139.9(6)	140.00(10)
Crystal System	monoclinic	monoclinic	triclinic
Space Group	$P2_1/c$	$I2/a$	$P\bar{1}$
a/Å	15.66789(14)	22.6297(5)	11.4770(3)
b/Å	17.47136(16)	23.9733(5)	16.6790(8)
c/Å	24.16489(19)	23.9063(5)	19.0067(8)
α/°	90	90	103.478(4)
β/°	93.6596(8)	92.9909(18)	101.463(3)
γ/°	90	90	90.908(3)
V/Å^3	6601.39(10)	12951.7(5)	3460.2(3)
Z	4	8	2
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	3.123	3.688	3.938
Θ_{max}/°	72.677	72.788	72.725
Measured Refl's.	33861	14444	14136
Ind't Refl's	12806	14444	14136
Refl's with I > 2σ(I)	11775	7639	13270
R_{int}	0.0210	.	.
Parameters	640	642	617
Restraints	162	0	934
Largest Peak	1.943	4.553	5.937
Deepest Hole	-1.067	-1.422	-5.122
GooF	1.040	0.841	1.147
wR_2 (all data)	0.0665	0.1328	0.2818
wR_2	0.0648	0.1186	0.2799
R_1 (all data)	0.0306	0.0934	0.1104
R_1	0.0273	0.0502	0.1069

Computational details

All calculations were performed using the Becke's 3-parameter hybrid functional[11] combined with the non-local correlation functional provided by Perdew/Wang[12] using Gaussian09 suite of programs.[13] The U and Si atoms were represented with a small-core Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set. [14-16] Additionally, the Si basis set was augmented by a d-polarization function ($\alpha = 0.284$)[17] to represent the valence orbitals. All the other atoms C, H, O and N were described with a 6-31G (d,p), double –ζ quality basis set.[18] The nature of the extrema (minimum) was established with analytical frequencies calculations and geometry optimizations were computed without any symmetry constraints. Intrinsic Reaction Paths (IRPs)[19] were traced from the various transition structures to obtain the connected intermediates and the enthalpy energies were computed at T = 298 K in the gas phase.



Spin density
U1 = 3.129196
U2 = 3.128229

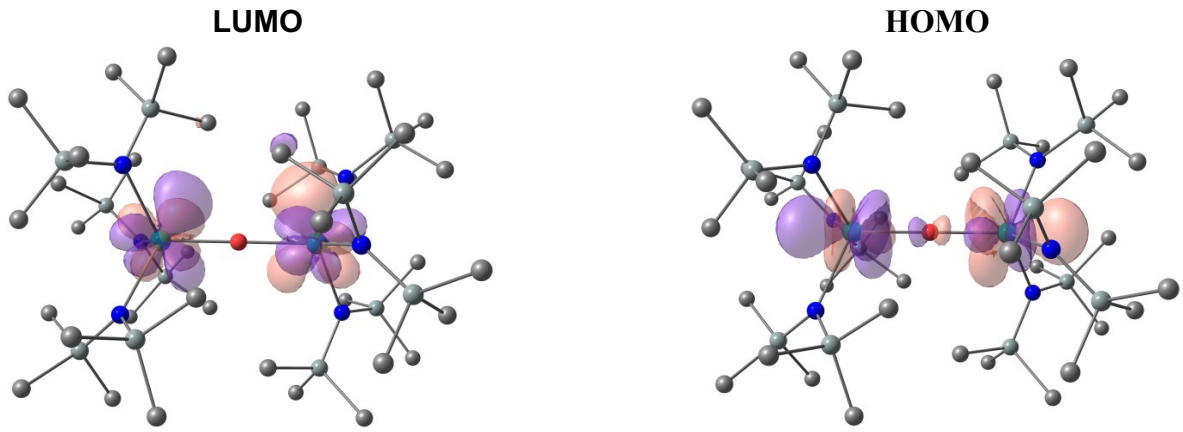
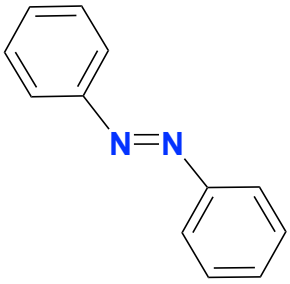


Figure S10 Frontier molecular orbitals of complex **1.**



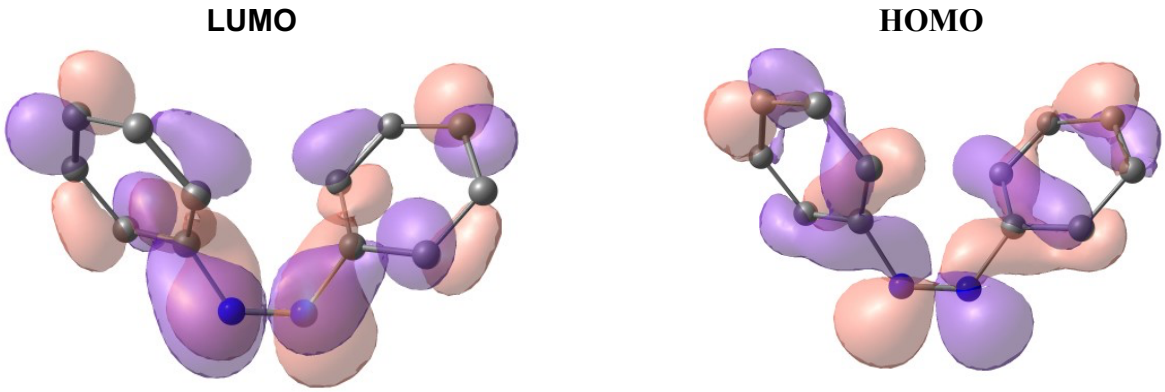
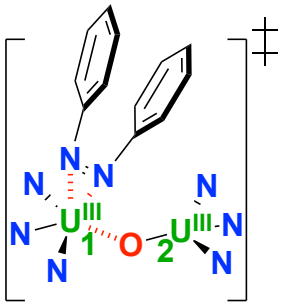


Figure S11 Frontier molecular orbitals of azobenzene**.**



Spin Density
U1 = 2.393774
U2 = 2.954623
N-N = 0.79449

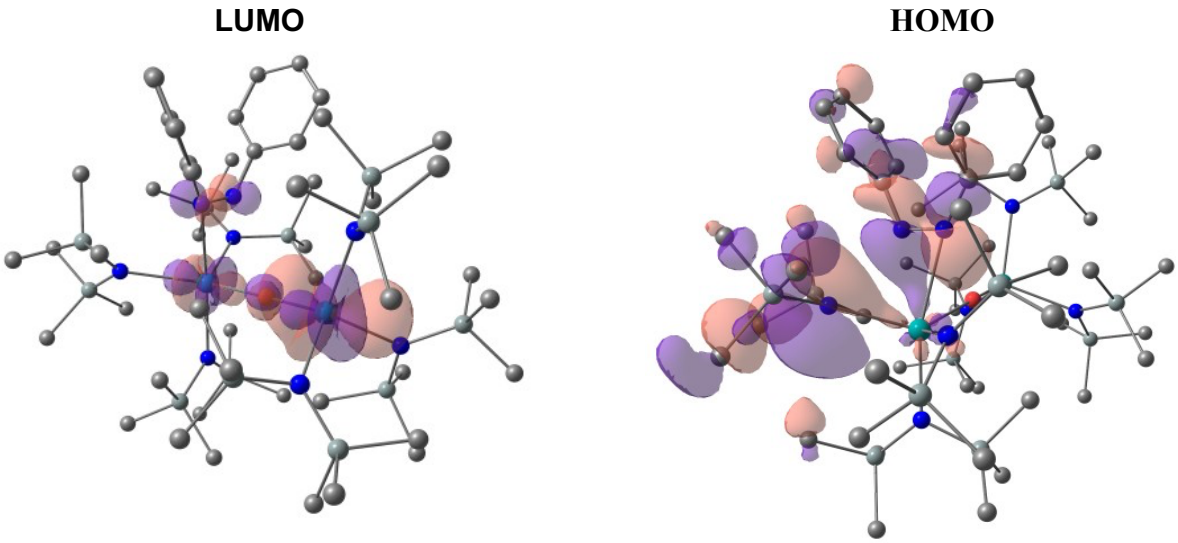
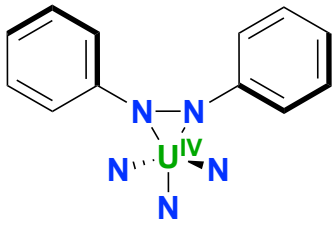


Figure S12 Frontier molecular orbitals of the transition state **TS1** in the reaction of complex **1** with azobenzene.



Spin Density
U1 = 2.196227

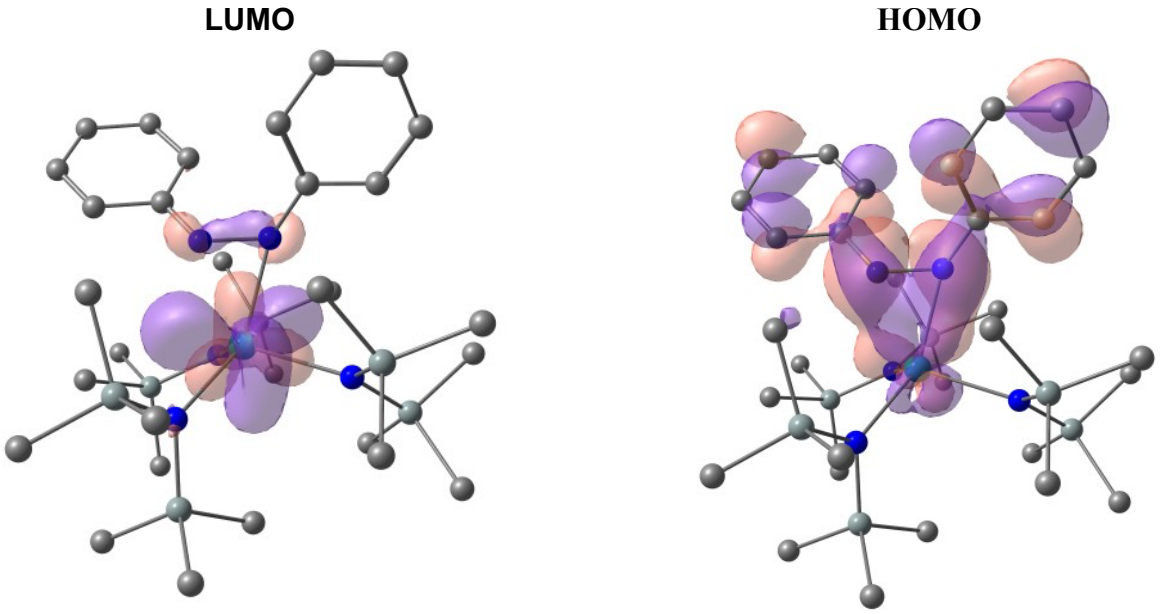
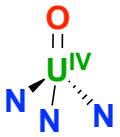


Figure S13 Frontier molecular orbitals of complex **5**.



Spin Density
U1 = 2.158650

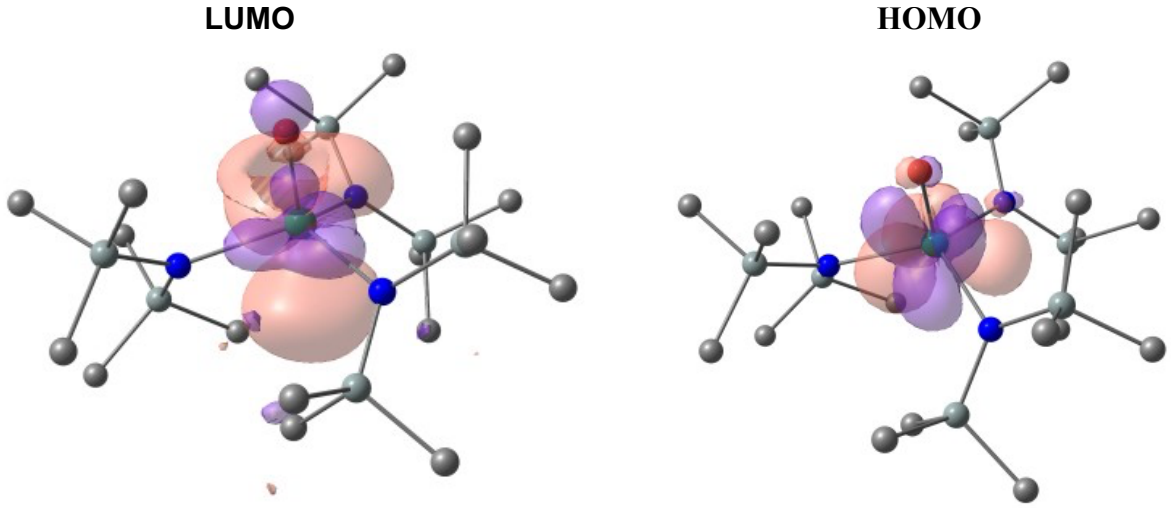
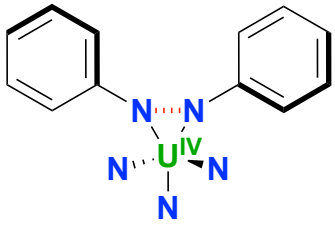


Figure S14 Frontier molecular orbitals of [K(2.2.2-cryptand)][U(O){N(SiMe$_3$)$_2$}$_3$].



Spin Density
U1 = 1.448966
N-N = 0.395456

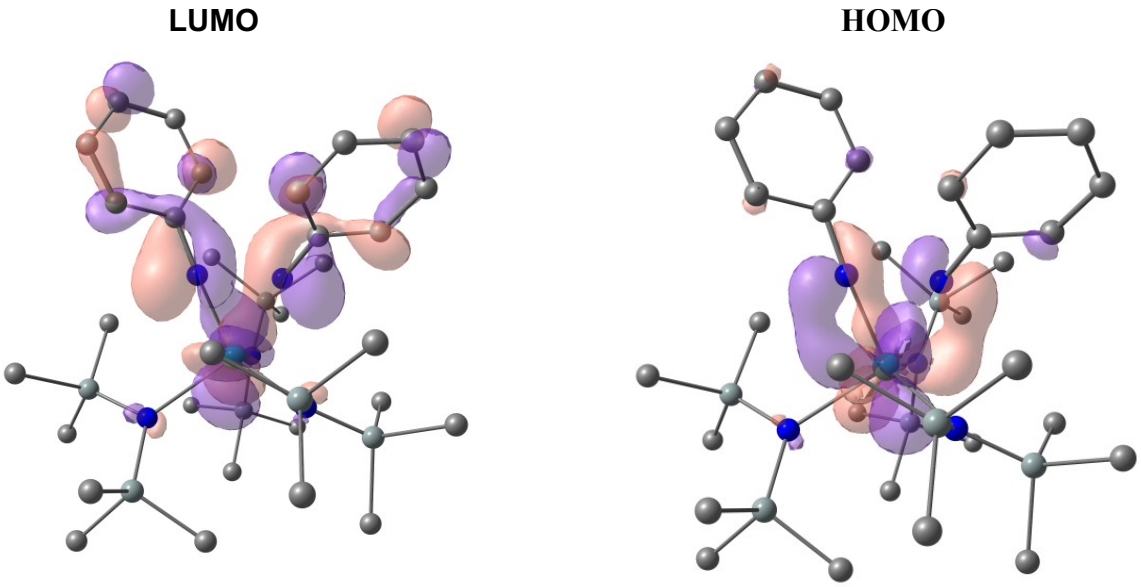
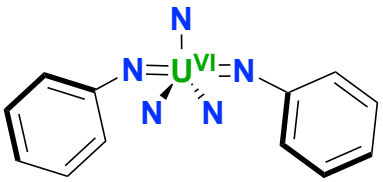


Figure S15 Frontier molecular orbitals of the transition state **TS2** in the reaction of complex **1** or **2** with azobenzene.



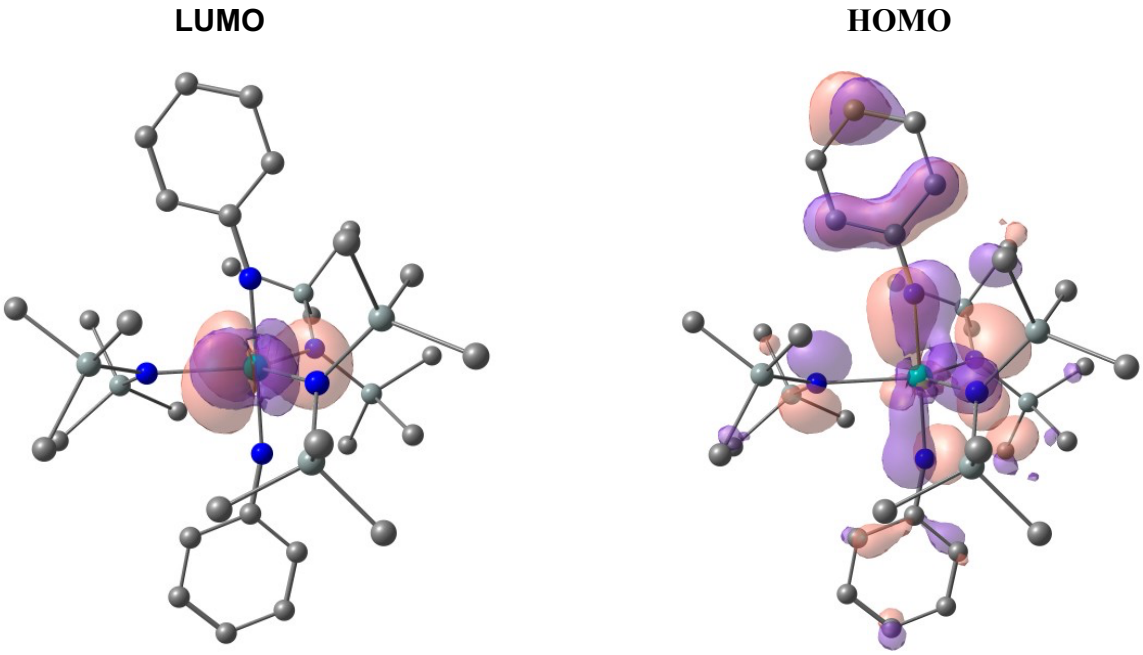


Figure S16 Frontier molecular orbitals of complex **4.**

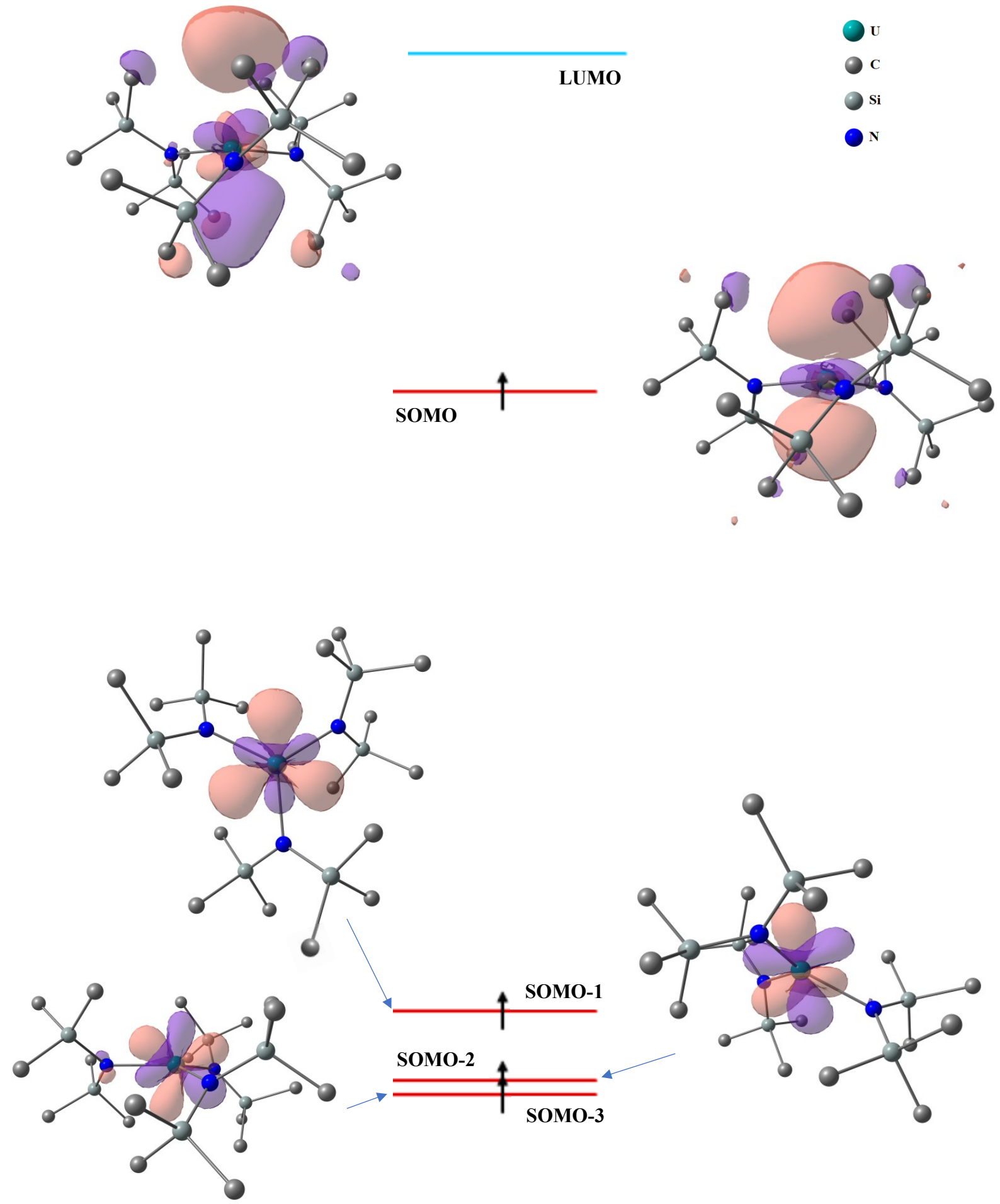


Figure S17 Molecular orbital diagram of complex **2**.

Spin density U(II)

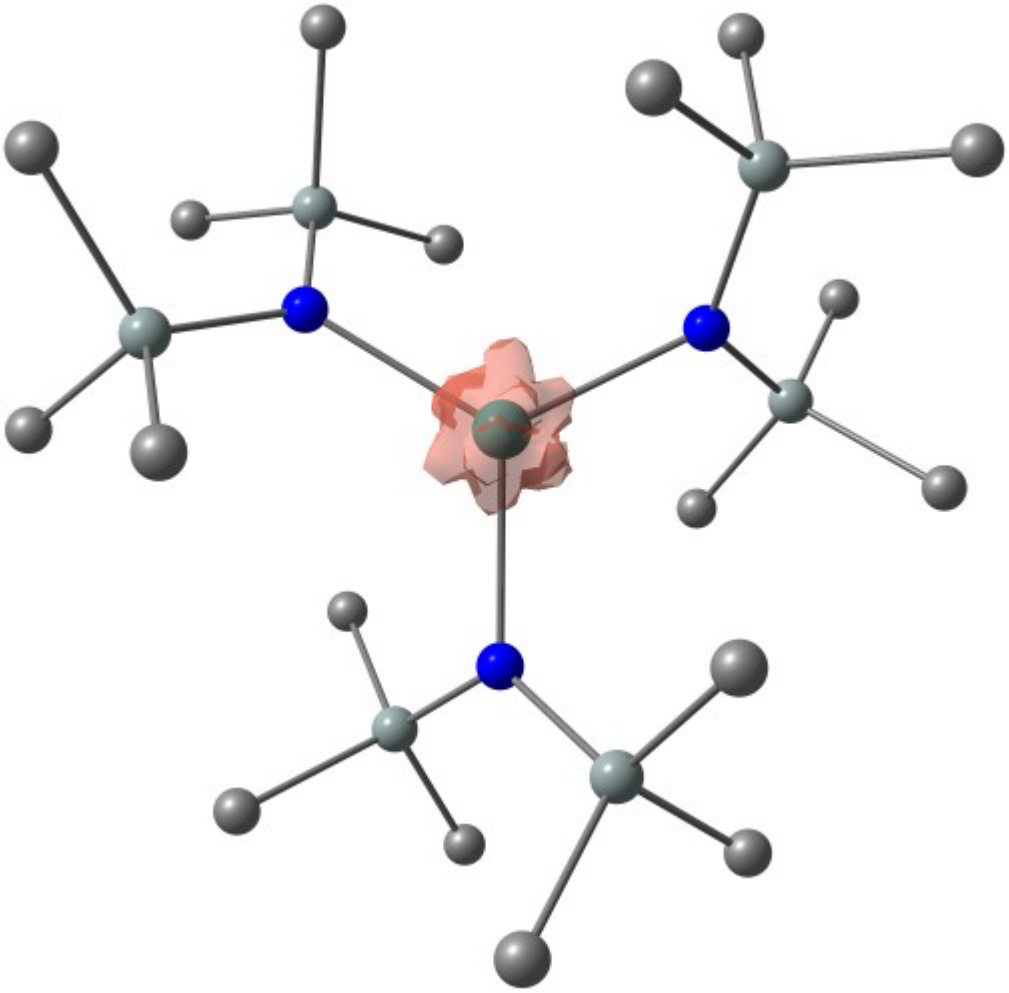


Figure S18 Unpaired spin density plot of complex **2** showing spin density centered on the uranium: U = 4.10.

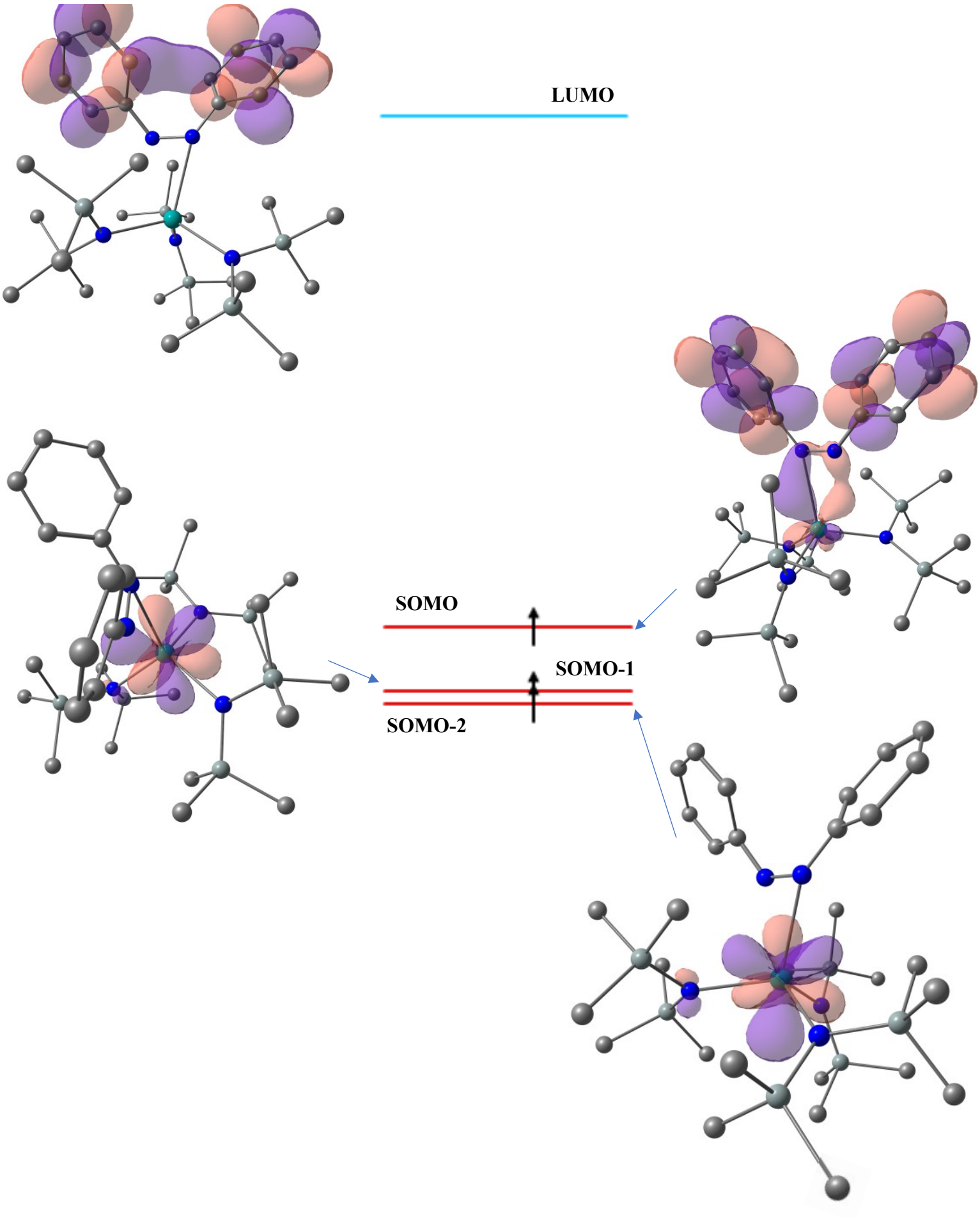


Figure S19 Molecular orbital diagram of the transition state **TS1** in the reaction of complex **2** with azobenzene.

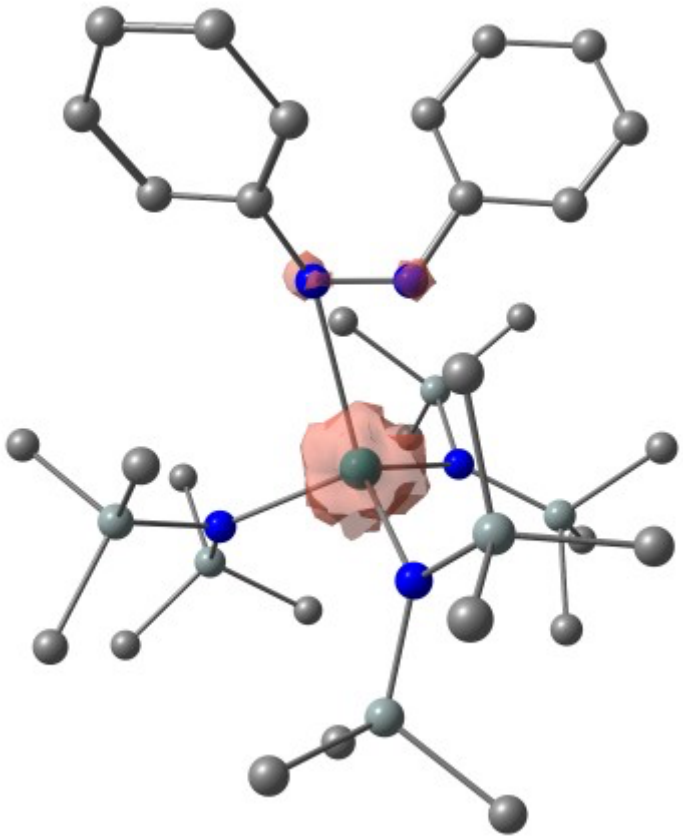


Figure S20 Unpaired spin density plot of the transition state **TS1** in the reaction of complex **2** with azobenzene, showing spin density shared between the uranium and the nitrogen: U1 = 3.10, N-N=0.70.

Cartesian coordinates of all optimized structures

```
165
Complex U-O-U
C       10.053322000     14.994433000      1.204168000
Si      10.194999000     13.507342000      2.403679000
C       10.062687000     11.972837000      1.270273000
N        9.078062000     13.531901000      3.751316000
U        9.976519000     13.860897000      6.005537000
O       11.625026000     12.495802000      6.422622000
U       13.269898000     11.127162000      6.857563000
N       14.137411000     11.434268000      9.133345000
Si      15.837659000     11.644321000      9.500265000
C       16.362390000     13.480830000      9.537389000
C       11.987865000     13.558371000      3.015035000
Si       7.386825000     13.256469000      3.389122000
C        6.237012000     14.125285000      4.626075000
C        6.783376000     13.917296000      1.689958000
C        6.938966000     11.400678000      3.359741000
N        8.127437000     13.515441000      7.597062000
Si       7.357627000     14.798166000      8.506670000
C        7.374298000     16.455695000      7.579739000
N       10.668905000     16.205552000      6.215312000
Si      11.613270000     16.705594000      7.603790000
C       13.222591000     17.643617000      7.166425000
C        5.492885000     14.535507000      8.885007000
C        8.156487000     15.080423000     10.218878000
Si       7.570695000     11.887852000      7.928951000
C        7.475430000     11.430501000      9.785309000
C        8.705949000     10.604639000      7.122353000
C        5.824467000     11.458919000      7.263143000
Si      10.336351000     17.432024000      5.009605000
C       11.747176000     17.630573000      3.735573000
C        8.733518000     17.086299000      4.050437000
C       10.065667000     19.208394000      5.687288000
N       15.120291000     11.442906000      5.282645000
Si      15.693555000     13.068839000      4.977562000
C       17.449473000     13.463846000      5.637240000
N       12.545329000      8.786671000      6.651976000
Si      12.820251000      7.565406000      7.875160000
C       11.379423000      7.415236000      9.121591000
C       14.406166000      7.882433000      8.871223000
C       13.067916000      5.778665000      7.215627000
Si      15.884483000     10.153959000      4.375685000
C       15.847253000      8.499596000      5.307496000
C       17.751273000     10.405825000      4.003474000
C       15.092898000      9.883531000      2.658718000
Si      11.621584000      8.295793000      5.246853000
C        9.990519000      7.378510000      5.644461000
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C       12.531203000      7.114188000      4.042299000
C       12.115924000     15.219900000      8.667130000
C       10.712953000     17.875506000      8.826145000
C       16.966018000     10.747847000      8.263298000
C       16.412663000     10.949422000     11.195868000
C       15.774911000     13.552619000      3.128357000
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C	13.083509000	10.056328000	11.694710000
C	11.226759000	11.609411000	9.905629000
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H       16.063465000     14.606801000      3.031897000

24
Complex Azobenzene
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N        7.191644000      7.593712000     10.697297000
C        5.949329000      6.910581000     10.876823000
C        5.061792000      6.935228000      9.794928000
C        5.683625000      6.089825000     11.980656000
C        3.880362000      6.202695000      9.848587000
H        5.313124000      7.537016000      8.926447000
C        4.518235000      5.330001000     12.007474000
H        6.392939000      6.039404000     12.800218000
C        3.606286000      5.395410000     10.953276000
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H        4.319898000      4.685014000     12.859035000
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C        7.095883000      8.672406000     12.796822000
C        7.886533000      8.632060000     13.951025000
C        5.816823000      9.241970000     12.845067000
C        7.374054000      9.089312000     15.160812000
H        8.894787000      8.234563000     13.879988000
C        5.328425000      9.733233000     14.051804000
H        5.220656000      9.310101000     11.940926000
C        6.095069000      9.644621000     15.214496000
H        7.982367000      9.032884000     16.059172000
H        4.340981000     10.185322000     14.084645000
H        5.703610000     10.022501000     16.154585000

189
TS U-O-U-Azo
U       10.091145364     13.723010080      5.904935245
U       13.507500000     10.766400000      7.307600000
Si      13.716100000      6.953400000      7.761100000
Si      15.775300000     13.011000000      5.699500000
Si      11.441271790     16.651469945      7.584732535
Si       7.366198830     15.058115609      8.146487810
Si      16.786350941     10.364158607      9.139045216
Si      10.939420837     13.108059813      2.451994697
Si      15.622500000     10.512900000      4.100300000
Si      14.765779250     11.584751753     10.857444151
Si       6.726362513     12.462793442      7.002138161
Si       7.979696870     13.106786635      2.813205261
Si      10.846990057     17.219971906      4.717062944
Si      11.810100000      8.048400000      5.759400000
O       11.522300000     12.449600000      6.700800000
N       15.083200000     11.404200000      5.513500000
N       15.123471423     10.929568149      9.262517550
N        7.932110260     13.716937825      7.178216430
N        9.567500864     13.301126861      3.512436535
N       10.817820440     16.090550973      6.053485653
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N       11.303912737      9.701582261      8.781503476
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C       12.475400000      5.514300000      8.053200000
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C	13.224182280	17.340844407	7.505632947
C	10.426862964	18.021156924	8.462396264
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C	10.986441535	11.455876684	1.489387651
C	11.149938312	14.439422623	1.086210911
C	12.519687096	13.250685861	3.476174207
C	13.983078389	10.303154060	12.034267981
C	16.245727226	12.285115348	11.869166724
C	11.438400000	9.627100000	4.789100000
C	10.154700000	7.411900000	6.473000000
C	17.438900000	10.838300000	3.565600000
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C	6.146572353	11.645094174	8.637186986
C	8.118398604	13.436057355	0.924655550
C	6.841128663	14.489722603	3.445611654
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C	13.651110096	13.118130346	10.824114465
C	5.111940050	13.001686403	6.120139274
C	7.311591402	11.328630452	3.038642908
C	10.585529118	19.063430939	5.191568563
C	12.264700000	6.738700000	4.435500000
C	10.202178212	9.038405455	9.389772989
C	8.899452380	9.354126677	9.002845634
C	10.427541560	8.016027530	10.311427952
C	7.822320398	8.648052039	9.538081245
C	9.350180256	7.308861661	10.846128189
C	8.047784366	7.624755331	10.459660616
C	11.003600000	11.004300000	10.548700000
C	10.898700000	10.048200000	11.559300000
C	10.446500000	12.270700000	10.726100000
C	10.236400000	10.358300000	12.746900000
C	9.784700000	12.581300000	11.914500000
C	9.679500000	11.625400000	12.924700000
H	16.197900000	15.109900000	4.435700000
H	17.909300000	13.945800000	6.625000000
H	18.009500000	12.180600000	6.615700000
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H	18.438890070	8.942450714	10.352282515

H	17.237107561	9.514587025	11.513815598
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H	16.717584134	13.129194060	11.356749583
H	17.025420623	11.562418056	12.123144638
H	14.160035108	13.944829200	10.319395784
H	12.694490385	12.966040927	10.328071808
H	13.792098167	10.747864534	13.018942785
H	14.653677442	9.448080163	12.172056917
H	13.336883594	17.463952219	4.448144380
H	13.596832989	17.560343285	8.514010249
H	13.899324217	16.613397573	7.046094789
H	13.277655513	18.266826041	6.922509412
H	10.834384759	18.171311177	9.470791042
H	11.877471551	15.552431322	9.786583350
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83
Complex U=O
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O	7.940422000	15.329783000	5.643261000
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Si	4.292983000	15.786733000	2.453141000
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C	3.862096000	16.483518000	0.725776000
C	3.709352000	13.969770000	2.423171000
N	4.891073000	15.859525000	6.785369000
Si	4.173544000	17.080328000	7.808128000
C	4.217821000	18.767181000	6.926317000
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Si	8.747792000	18.906723000	6.781052000
C	10.447721000	19.557372000	6.195379000
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C	5.074753000	17.315866000	9.472827000
Si	4.592183000	14.157980000	7.081992000
C	4.901691000	13.637421000	8.894203000
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Si	7.361302000	19.894161000	4.280734000
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Si       14.580289000     13.262829000      7.223609000
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Si       14.746586000     11.491467000      4.805592000
Si       15.579376000     10.690300000     11.184238000
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Si      17.158340000     10.033586000      9.298541000
Si      15.108542000     12.964918000      6.312393000
Si      14.175660000      6.450497000      7.468304000
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