Electronic Supplementary Information

Uranium(IV) Alkyl Cations: Synthesis, Structures, Comparison with Thorium(IV) Analogues, and the Influence of Arene-Coordination on Thermal Stability and Ethylene Polymerization Activity

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¹H NMR spectra of [(XA₂)U(CH₂SiMe₃)(C₆D₆)][B(C₆F₅)₄] (2-d₆)



Figure S1. ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_6D_6)][B(C_6F_5)_4]$ (**2-***d*₆) in bromobenzene*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₆D₆. * denotes bromobenzene-*d*₅ and × denotes *n*-pentane. Numbers below the baseline indicate the relative integration of each peak; the bromobenzene-*d*₅, benzene, C*Me*₃, and Si*Me*₃ signals are truncated.



Figure S2. Expanded region of the ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_6D_6)][B(C_6F_5)_4]$ (2-*d*₆) in bromobenzene-*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₆D₆. * denotes bromobenzene-*d*₅ and × denotes *n*-pentane. Numbers below the baseline indicate the relative integration of each peak; the bromobenzene-*d*₅, benzene, *CMe*₃, and *SiMe*₃ signals are truncated.

¹H NMR spectra of [(XA₂)U(CH₂SiMe₃)(C₇D₈)][B(C₆F₅)₄] (3-d₈)



Figure S3. ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4]$ (**3-***d*₈) in bromobenzene*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₇D₈. * denotes bromobenzene-*d*₅ and × denotes *n*-pentane. Numbers below the baseline indicate the relative integration of each peak; the bromobenzene-*d*₅, toluene, *CMe*₃, and *SiMe*₃ signals are truncated.



Figure S4. Expanded region of the ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4]$ (**3-***d*₈) in bromobenzene-*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₇D₈. Numbers below the baseline indicate the relative integration of each peak.



Figure S5. Expanded region of the ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4]$ (**3-***d*₈) in bromobenzene-*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₇D₈. * denotes bromobenzene-*d*₅ and × denotes *n*-pentane. Numbers below the baseline indicate the relative integration of each peak.

$\frac{\text{Comparison of the spectra of } [(XA_2)U(CH_2SiMe_3)(C_6D_6)][B(C_6F_5)_4] (2-d_6) \text{ and } }{[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4] (3-d_8) \text{ in } C_6D_5Br \text{ containing 100 equiv. of } C_6D_6 \text{ or } C_7D_8, \text{ respectively}}$



Figure S6. Comparison of the ¹H NMR spectra of: (a) Red, top: $[(XA_2)U(CH_2SiMe_3)(C_6D_6)][B(C_6F_5)_4]$ (**2-***d*₆) in bromobenzene-*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₆D₆, and (b) Blue, bottom: $[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4]$ (**3-***d*₈) in bromobenzene-*d*₅ (500.1 MHz, 298 K) with an added 100 equivalents of C₇D₈. The bromobenzene-*d*₅, benzene, toluene, C*Me*₃, and Si*Me*₃ signals are truncated.



¹H versus ²H NMR signals for the arene ligands in 2/2-d₆ and 3/3-d₈

Figure S7. Comparison of ¹H vs ²H NMR spectra: (a) Blue, bottom: Low-intensity ¹H resonance assigned to the coordinated C_6H_6 ligand of $[(XA_2)U(CH_2SiMe_3)(C_6H_6)][B(C_6F_5)_4]$ (2) (obtained by dissolving 2·2 C_6H_6 in bromobenzene- d_5 ; 500 MHz, 298 K),[§] and (b) Red, top: broad ²H resonance assigned to the coordinated C_6D_6 ligand of $[(XA_2)U(CH_2SiMe_3)(C_6D_6)][B(C_6F_5)_4]$ (2- d_6) in C_6H_5Br (obtained by dissolving 2- d_6 ·2 C_6D_6 in bromobenzene containing 5 equiv. of C_6D_6 ; 92.1 MHz, 298 K). § Note that when 2·2 C_6H_6 is dissolved in bromobenzene- d_5 , C_6D_5Br -coordinated 4- d_5 is the major species in solution, and benzene-coordinated 2 is the minor species.



Figure S8. Comparison of ¹H vs ²H NMR spectra: (a) Blue, bottom: Low-intensity ¹H resonances assigned to the coordinated C₇H₈ ligand of $[(XA_2)U(CH_2SiMe_3)(C_7H_8)][B(C_6F_5)_4]$ (**3**) (obtained by dissolving **2**·2 C₇H₈ in bromobenzene-*d*₅; 500 MHz, 298 K),[§] and (b) Red, top: broad ²H resonances assigned to the coordinated C₇D₈ ligand of $[(XA_2)U(CH_2SiMe_3)(C_7D_8)][B(C_6F_5)_4]$ (**3**-*d*₈) in C₆H₅Br (obtained by dissolving **3**-*d*₈·2 C₇D₈ in bromobenzene containing 5 equiv. of C₇D₈; 92.1 MHz, 298 K). § Note that when **2**·2 C₇H₈ is dissolved in bromobenzene-*d*₅, C₆D₅Br-coordinated **4**-*d*₅ is the major species in solution, and toluene-coordinated **2** is the minor species.

¹<u>H NMR spectra of [(XA₂)U(CH₂SiMe₃)(C₆D₅Br)][B(C₆F₅)₄] (4-d₅)</u>



Figure S9. ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_6D_5Br)][B(C_6F_5)_4]$ (**4-***d***5**) in bromobenzene-*d*₅ (500.1 MHz, 298 K). This sample of **4-***d***5** was generated by dissolving $[(XA_2)U(CH_2SiMe_3)(C_6H_6)][B(C_6F_5)_4] \cdot 2 C_6H_6$ (**2** $\cdot 2 C_6H_6$) in C_6D_5Br ; ~20% of **2** remains in solution. * denotes bromobenzene-*d*₅, × denotes *n*-pentane, † denotes the coordinated C_6H_6 ligand of **2**. Numbers below the baseline indicate the relative integration of each peak; the bromobenzene*d*₅, benzene, CMe_3 , and $SiMe_3$ signals are truncated.



Figure **S10.** Expanded region of the $^{1}\mathrm{H}$ NMR spectrum of [(XA₂)U(CH-₂SiMe₃)(C₆D₅Br)][B(C₆F₅)₄] (**4-d**₅) in bromobenzene-d₅ (500.1 MHz, 298 K). This sample of **4** was generated by dissolving $[(XA_2)U(CH_2SiMe_3)(C_6H_6)][B(C_6F_5)_4] \cdot 2 C_6H_6 (2 \cdot 2 C_6H_6)$ in C_6D_5Br ; ~20% of 2 remains in solution. * denotes bromobenzene- d_5 , and × denotes *n*-pentane. Numbers below the baseline indicate the relative integration of each peak; the bromobenzene- d_5 , benzene, CMe₃, and SiMe₃ signals are truncated.



Figure S11. ¹H NMR spectra of $[(XA_2)U(CH_2SiMe_3)(C_6D_5Br)][B(C_6F_5)_4]$ (**4-***d***s**) in bromobenzene-*d*₅ (500.1 MHz, 298 K) generated via different routes. The sample in the spectrum on the bottom (blue) was prepared by dissolving $[(XA_2)U(CH_2SiMe_3)(C_6H_6)][B(C_6F_5)_4] \cdot 2 C_6H_6$ (**2**·2 C₆H₆) in C₆D₅Br, whereas the sample in the spectrum at the top (red) was generated by dissolving $[(XA_2)U(CH_2SiMe_3)(C_7H_8)][B(C_6F_5)_4] \cdot 2 C_7H_8$ (**3**·2 C₇H₈) in C₆D₅Br. In both cases, some of compound **2** or **3** remains (i.e. not all benzene or toluene was displaced): * denotes signals corresponding to coordinated C₆H₆ or C₇H₈ ligands in residual **2** and **3**.



Figure S12. ¹H NMR spectra of $[(XA_2)U(CH_2SiMe_3)(C_6D_5Br)][B(C_6F_5)_4]$ (4-*d*₅) in bromobenzene-*d*₅ (500.1 MHz/600.1 MHz, 298 K) generated via 3 different routes. The sample in the spectrum in the middle (green) was prepared by dissolving $[(XA_2)U(CH_2SiMe_3)(C_6H_6)][B(C_6F_5)_4] \cdot 2 C_6H_6$ (2·2 C₆H₆) in C₆D₅Br. The sample in the spectrum at the top (red) was generated by dissolving $[(XA_2)U(CH_2SiMe_3)(C_7H_8)][B(C_6F_5)_4] \cdot 2 C_7H_8$ (3·2 C₇H₈) in C₆D₅Br. The sample in the spectrum at the bottom (blue) was generated directly via the reaction of $[(XA_2)U(CH_2SiMe_3)_2]$ (1) with $[CPh_3][B(C_6F_5)_4]$ in bromobenzene-*d*₅. Note: in the top (red) and middle (green) spectra, some of compound 2 or 3 remains (i.e. not all benzene or toluene was displaced).

¹H NMR spectra of [(XA₂)U(CH₂SiMe₃)(C₆H₅F)][B(C₆F₅)₄] (5)



Figure S13. ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_6H_5F)][B(C_6F_5)_4]$ (**5**) generated directly in a 9:1 mixture of fluorobenzene and cyclohexane- d_{12} (500 MHz, 298 K). * denotes C_6D_{12} , × denotes *n*-pentane, † denotes trityl by-products, and ‡ denotes remaining $[(XA_2)U(CH_2SiMe_3)_2]$ (**1**). Numbers below the baseline indicate the relative integration of each peak; the fluorobenzene, CMe_3 , and trityl by-product signals are truncated.



Figure S14. Variable Temperature ¹H NMR spectra of $[(XA_2)U(CH_2SiMe_3)(C_6H_5F)][B(C_6F_5)_4]$ (5) generated directly in a 9:1 mixture of fluorobenzene and cyclohexane- d_{12} (500.1 MHz). Temperatures range from 298 K to 237 K. * denotes fluorobenzene. The fluorobenzene, CMe_3 , and trityl by-product signals are truncated.



Figure S15. Selected Region of the ¹H NMR spectrum of $[(XA_2)U(CH_2SiMe_3)(C_6H_5F)][B(C_6F_5)_4]$ (5) generated directly in a 9:1 mixture of fluorobenzene and 10 % cyclohexane- d_{12} (500.1 MHz) at 237 K. Resonances arising at particularly high (>100 ppm) and particularly low (<-90 ppm) are not shown. * denotes C_6D_{12} , × denotes *n*-pentane, † denotes trityl by-products, and ‡ denotes remaining $[(XA_2)U(CH_2SiMe_3)_2]$ (1). Numbers below the baseline indicate the relative integration of each peak. The fluorobenzene, *CMe*₃, and trityl by-product signals are truncated.

<u>NMR spectra of the reaction between [(XA₂)U(CH₂SiMe₃)₂] and [CPh₃][B(C₆F₅)₄] in a 9:1 mixture of *o*-difluorobenzene and cyclohexane-*d*₁₂</u>



Figure S16. ¹H NMR spectra of the reaction of $[(XA_2)U(CH_2SiMe_3)_2]$ (1) with $[CPh_3][B(C_6F_5)_4]$ in a 9:1 mixture of *o*-difluorobenzene and cyclohexane- d_{12} (500 MHz, 298 K). This reaction did not proceed cleanly. The thermal stability of the putative $[(XA_2)U(CH_2SiMe_3)(\kappa^2-C_6H_4F_2)][B(C_6F_5)_4]$ cation was also monitored (spectra were recorded after 2h and 24h at 22 °C, and after 2h at 75 °C). * denotes C_6D_{12} , × denotes *n*-pentane, and † denotes remaining $[(XA_2)U(CH_2SiMe_3)_2]$ (1). The *o*-difluorobenzene, CMe_3 , *n*-pentane, C_6D_{12} , and SiMe₄ by-product signals are truncated.

¹H NMR spectra of [(XA₂)U(CH₂Ph)₂] (6)



Figure S17. Variable Temperature ¹H NMR spectra of $[(XA_2)U(CH_2Ph)_2]$ (6) in toluene- d_8 (500.1 MHz). Temperatures range from 298 K to 241 K; several peaks (e.g. toluene- d_8 , CMe_3 , etc.) are truncated. * Note: Several of the individual spectra in the figure are comprised of two separate spectra collected using different spectral windows in order to observe all peaks (the spectral window of the instrument is limited to <200 ppm)



Figure S18. Expanded Region of the Variable Temperature ¹H NMR spectra of $[(XA_2)U(CH_2Ph)_2]$ (6) in toluene- d_8 (500.1 MHz). Temperatures range from 298 K to 241 K. * denotes toluene- d_8 . Several peaks (e.g. toluene- d_8 , CMe_3 , etc.) are truncated.



Figure S19. ¹H NMR spectrum of $[(XA_2)U(CH_2Ph)_2]$ (6) in toluene- d_8 (500.1 MHz) at 262 K. The insets show regions of the spectrum at particularly high (>70 ppm) and particularly low (<-60 ppm) frequencies. Numbers below the baseline indicate the relative integration of each peak.

X-ray crystal structure of [(XA₂)U(CH₂Ph)₂]·THF (6·THF) and selected bond metrics



Figure S20. X-ray crystal structure of $[(XA_2)U(CH_2Ph)_2]$ ·THF (**6**·THF) with thermal ellipsoids at 50% probability. Hydrogen atoms and THF lattice solvent are omitted for clarity.

U–O	2.477(2)
U–N	2.270(2), 2.301(2)
U–CH ₂ in plane	2.462(3)
U–Cipso in plane	2.751(3)
U–Cortho in plane	3.220(3), 3.367(3)
U-CH _{2 apical}	2.451(4)
U-Cipso apical	3.036(3)
U-Cortho apical	3.550(4), 3.817(4)
Ligand Bend Angle ^a	4.0°
U-CH ₂ -C _{ipso in plane}	85.2(2)
U-CH ₂ -C _{ipso apical}	98.1(2)
O…(N/U/N-plane)	0.46
U…(N/O/N-plane)	0.31
$N(1)\cdots N(2)$	4.11

^{*a*} Ligand Bend Angle = the angle between the plane of the two aromatic rings of the xanthene ligand backbone.

Table S1. Selected bond lengths (Å) and angles (deg) for dibenzyl uranium complex 6.

<u>Gel Permeation Chromatography (GPC) data for polyethylene produced using the putative $[(XA_2)U(CH_2SiMe_3)(\kappa^2-C_6H_4F_2)][B(C_6F_5)_4]$ cation</u>



Figure S21. High-temperature (160 °C) Gel Permeation Chromatograms (GPCs) obtained with a differential refractive index (DRI) detector for 1,2,4-trichlorobenzene solutions of polyethylene (2 duplicates) produced using the putative $[(XA_2)U(CH_2SiMe_3)(\kappa^2-C_6H_4F_2)][B(C_6F_5)_4]$ cation (generated in situ via the reaction of **1** with [CPh₃][B(C_6F_5)_4] in *o*-difluorobenzene).



Figure S22. Molecular weight distribution plot, from DRI detector data, of polyethylene (2 duplicates) produced using the putative $[(XA_2)U(CH_2SiMe_3)(\kappa^2-C_6H_4F_2)][B(C_6F_5)_4]$ cation (generated in situ via the reaction of **1** with [CPh₃][B(C_6F_5)_4] in *o*-difluorobenzene).





Figure S23. Differential Scanning Calorimetry (DSC) trace for polyethylene produced using cation **5** in C₆H₅F (70 °C, 1 atm ethylene, 5 min polym. time; activity of 139,200 g mol⁻¹ h⁻¹ atm⁻¹). The polyethylene sample was melted, cooled, and then re-melted, and the $T_{\rm m}$ value is from re-melting. Heating and cooling rates were 10 °C/min.

<u>Overlay of DFT geometry optimized structures of 2', 2'-Th, 3', and 5' with the x-ray crystal structures of 2, 2-Th, 3, and 5</u>



Figure S24. Superimposed calculated (with C_s symmetry; red) and X-ray (blue) structures of, from top to bottom, $[(XA_2('))U(CH_2SiMe_3)(benzene)]^+$ (**2**('), $[(XA_2('))Th(CH_2SiMe_3)(benzene)]^+$ (**2**(')-**Th**), $[(XA_2('))U(CH_2SiMe_3)(toluene)]^+$ (**3**(')), and $[(XA_2('))U(CH_2SiMe_3)(fluorobenzene)]^+$ (**5**(')). Hydrogen atoms and 2,6-diisopropylphenyl groups are omitted for clarity. Three views are shown for each structure.

DFT geometry optimized structures of 5', 5a' and 5b'



Figure S25. Bottom: Geometry optimized structures of the three fluorobenzene-coordinated cations investigated in this work; $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (5'; left), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (5a'; middle), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (5b'; right). C_s symmetry was enforced for 5' and 5a', but not 5b'. Hydrogen atoms and 2,6-diisopropylphenyl groups have been removed for clarity, and all atoms, except for U and those in the arene ligand, are shown in wireframe. Atoms are coloured grey (carbon), red (oxygen), beige (silicon), blue (nitrogen), light green (fluorine), and dark green (uranium). Top; Chemdraw drawings of 5', 5a', and 5b', where Ar = 2,6-diisopropylphenyl.

Tables of DFT-calculated bond metrics, bond orders (Mayer,^[1] Gopinathan-Jug,^[2] and Nalewajksi-Mrozek-3^[3]), Hirshfeld charges,^[4] and Mulliken spin populations^[5] for 2', 2'-Th, 3', 5', 5a', 5b', and free arenes. Gibbs free energies are also provided for fluorobenzene, 5', 5a', and 5b'

	tBu Me ₃ Si	Me ₃ Si
	2; XRD	2'; DFT
$U-N_1$	2.223(2), 2.236(2)	2.24
U–O	2.440(2)	2.50
U–C _{alkyl}	2.365(3)	2.34
	3.097(3), 3.159(3),	3.13,
U–Carene	3.108(3),3.243(3),	3.22,
	3.187(3), 3.249(3)	3.31
U–cent	2.858	2.90
U-cent-C _N	86.82, 93.00	89.8
U-cent-CC _c	92.51	94.7
U-cent-CC _v	87.61	85.5
U–C _{alkyl} –Si	133.7(2)	136.7
O–U–C _{alkyl}	87.23(9)	83.1
N–U–N	124.29(9)	121.8
O-U-cent	176.04	176.6
N-N-C _N -C _N	179.4(1)	180.0

Table S2. Selected bond metrics (Å, °) from the X-ray crystal structure of $[(XA_2)U(CH_2SiMe_3)(benzene)]^+$ (2) and the DFT calculated structure of $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (2'). cent is the arene centroid, CC_c and CC_v are the centroids between the two arene carbon atoms closest to or farthest from, respectively, the alkyl group on uranium. C_N are the arene carbon atoms closest to the nitrogen atoms.

	tBu Me ₃ Si	Me ₃ Si
	2-Th ; XRD	2'-Th ; DFT
Th–N ₁	2.278(3), 2.288(3)	2.29
Th–O	2.496(3)	2.53
Th-Calkyl	2.433(4)	2.41
Th–Carene	3.179(8), 3.294(5), 3.310(7), 3.285(7), 3.299(7), 3.209(7)	3.24, 3.29, 3.36, 3.39
Th-cent	2.950	3.01
Th-cent-C ₁	86.78	92.9
Th-cent-C ₄	87.04	86.2
Th-cent-CC	91.87, 91.74	90.2
Th-Calkyl-Si	131.0(2)	130.8
O-Th-Calkyl	91.3(1)	88.1
N-Th-N	124.5(1)	121.5
O-Th-cent	168.35	178.6
$N-N-C_1-C_4$	76.5(2)	78.0

Table S3. Selected bond metrics (Å, °) from the X-ray crystal structure of $[(XA_2)Th(CH_2SiMe_3)(benzene)]^+$ (**2-Th**) and the DFT calculated structure of $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**). cent is the arene centroid and CC is a centroid between two adjacent arene carbons that are not located on the (for **2-Th**, approximate) mirror plane. C₁ and C₄ are the arene carbon atoms closest to and farthest away, respectively, from the alkyl group on thorium.

	tBu Me ₃ Si	Me ₃ Si
	3; XRD	3'; DFT
U–N	2.21(1), 2.22(1)	2.24
U–O	2.417(8)	2.48
U–Calkyl	2.35(2)	2.32
U–C(arene p)	3.05(2)	2.97
U–C(arene m)	3.13(2), 3.36(2)	3.29
$U \cdots C(arene o)$	3.47(2), 3.70(2)	3.89
U····C(arene i)	3.78(2)	4.20
U-cent	3.138	3.33
U-cent- C_p	73.81	62.9
U-cent- C_i	106.75	118.5
U-cent- $C_o C_m$	83.68, 95.68	89.6
$U \cdots C_{Me}$	4.88(3)	5.41
$U-C_{Me}-C_i$	35(1)	31.0
U–C _{alkyl} –Si	136.8(7)	137.5
O–U–C _{alkyl}	88.8(4)	86.4
N–U–N	128.0(4)	125.2
O-U-cent	167.86	168.7
$\overline{N-N-C_p-C_i}$	-85.1(6)	-90.9

Table S4. Selected bond metrics $(\text{\AA}, \circ)$ from the X-ray crystal structure of $[(XA_2)U(CH_2SiMe_3)(toluene)]^+$ (3) and the DFT calculated structure of $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (3'). cent is the arene centroid, C_{Me} is the methyl carbon on toluene, and C_oC_m is a centroid between the *ortho* and *meta* arene carbon atoms.

tBu、	Me ₃ Si		Me ₃ Si	
tBu				Ar Ar Ar
	(5) Me ₃ Si N F Ar		(5') Me ₃ Si Ar (5b')	
	5; XRD	5'; DFT	5a'; DFT	5 b'; DFT
U–N	2.215(3), 2.217(3)	2.24	2.23	2.24
U–O	2.431(3)	2.48	2.48	2.47
U–Calkyl	2.351(4)	2.32	2.32	2.33
U–C(arene p)	3.126(5)	3.06	4.66	—
U–C(arene m)	3.215(6), 3.296(5)	3.26	4.30	—
U–C(arene o)	3.434(5), 3.527(5)	3.67	3.45	—
U–C(arene i)	3.594(5)	3.84	2.95	—
U-cent	3.075	3.18	3.64	5.14, 5.15
U-cent- C_i	79.21	72.3	130.6	18.5, 20.4
U-cent- C_p	101.48	108.5	49.7	159.5, 161.4
U-cent- C_oC_m	87.54, 92.23	89.9	89.7	—
U…F	4.529(5)	4.81	2.77	2.69, 2.73
U–F–C	40.1(3)	37.9	83.3	139.5, 142.3
U-Calkyl-Si	134.9(2)	137.8	134.9	136.8
O–U–Calkyl	89.4(1)	86.0	88.4	86.2
N–U–N	127.6(1)	124.7	125.4	124.6
O-U-cent	167.33	171.3	161.2	152.5, 161.8
$N-N-C_i-C_p$	-84.3(2)	-86.5	-67.8	_

Table S5. Selected bond metrics (Å, °) from the X-ray crystal structure of $[(XA_2)U(CH_2SiMe_3)(fluorobenzene)]^+$ (**5**) and the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (**5**'), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (**5a'**), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**). cent is the arene centroid and C_oC_m is a centroid between the *ortho* and *meta* arene carbon atoms.

Me ₃ Si		Me ₃ S	i	Me ₃ Si			
Me ₃ Si N Ar Ar Ar Ar		(2'-Th) Me ₃ Si P P N F Ar			Me ₃ Si	Ar + F Ar Ar	
(5')		(5	a')	(5b')			
	2'	2'-Th	3'	5'	5a'	5b'	
An–O	0.2311	0.2348	0.2426	0.242	0.2366	0.2404	
An–N	0.6818	0.6411	0.6918	0.6941	0.685	0.6755, 0.6984	
An–C(alkyl)	0.7228	0.6577	0.7246	0.7241	0.7236	0.7492	
An–C(arene close to N)	0.1322	_	_	_	_	—	
An–C(arene close to alkyl)	0.1152	_	_	_	_	—	
An–C(arene opposite alkyl)	0.1384	_	_	_	_	—	
An– $C(arene i)$	_	0.0933	< 0.05	< 0.05	0.139	< 0.05	
An–C(arene <i>o</i>)	_	0.0907	< 0.05	0.0545	0.1014	< 0.05	
An–C(arene <i>m</i>)	_	0.0835	0.1025	0.1056	< 0.05	< 0.05	
An–C(arene <i>p</i>)	_	0.0886	0.1693	0.1426	< 0.05	< 0.05	
An–F [§]	_	_	_	< 0.05	< 0.05	0.0704, -0.0262	

Table S6. Selected An–X Mayer bond orders for the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (**2'**), $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (**5'**), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (**5a'**), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**). § The U–F Mayer bond orders for **5b'** are nonsensical, whereas the Gopinathan-Jug and Nalewajksi-Mrozek-3 U–F bond orders in **5b'** range from 0.18 to 0.29 (see tables below).

Me ₃ Si		Me ₃ Si			Me ₃ Si		
(2')		(2'-7	Γh)		(3	B')	
	•				Me ₃ Si	Ar F Ar	
(5')		(5 a	ı')	(5b')			
	2'	2'-Th	3'	5'	5a'	5b'	
An–O	0.4076	0.3728	0.4158	0.4224	0.4198	0.414	
An–N	1.0474	0.8826	1.0544	1.0579	1.048	1.0489	
An–C(alkyl)	1.0296	0.9178	1.0617	1.0625	1.0303	1.026	
An–C(arene close to N)	0.0898	_	_	_	_	—	
An–C(arene close to alkyl)	0.0838	_	_	_	_	—	
An–C(arene opposite alkyl)	0.112	_	_	_	_	—	
An– $C(arene i)$	_	0.0789	< 0.05	< 0.05	0.0979	< 0.05	
An–C(arene <i>o</i>)	-	0.0648	< 0.05	< 0.05	0.0553	< 0.05	
An–C(arene <i>m</i>)	_	0.051	0.0777	0.0819	< 0.05	< 0.05	
An–C(arene p)	_	0.057	0.1413	0.118	< 0.05	< 0.05	
An–F	—			< 0.05	0.1483	0.1948, 0.1803	

Me ₃ Si		Me ₃ Si			Me ₃ Si		
(2')		(2'-	Γh)		(3	3')	
	•	Me ₃ Si N G N F			Me ₃ Si	Ar F Ar	
(5')		(5a	ı')	(5b')			
	2'	2'-Th	3'	5'	5a'	5b'	
An–O	0.537	0.4055	0.5541	0.5612	0.5597	0.5562	
An–N	1.3631	0.9544	1.3858	1.3868	1.377	1.3909	
An–C(alkyl)	1.4006	1.0395	1.4574	1.455	1.4188	1.4242	
An–C(arene close to N)	0.1126	_	_	_	_	—	
An–C(arene close to alkyl)	0.1051	_	_	_	_	—	
An–C(arene opposite alkyl)	0.1405	_	—	-	—	—	
An–C(arene i)	-	0.0795	< 0.05	< 0.05	0.1197	< 0.05	
An–C(arene <i>o</i>)	_	0.0651	< 0.05	0.0576	0.0705	< 0.05	
An–C(arene <i>m</i>)	_	0.0513	0.0987	0.1036	< 0.05	< 0.05	
An– $C(\text{arene } p)$	_	0.0573	0.1803	0.15	< 0.05	< 0.05	
An–F	_			< 0.05	0.2208	0.2902, 0.2702	

	Me ₃ Si Ar (2')	Me ₃ Si Ar (2'-Th)	benzene
Mayer	1.27-1.33	1.31-1.32	1.38
Gopinathan-Jug	1.36-1.42	1.39-1.41	1.44
Nalewajksi-Mrozek-3	1.47-1.52	1.51-1.52	1.56

Table S9. C_{arene} — C_{arene} Mayer, Gopinathan-Jug, and Nalewajksi-Mrozek-3 bond orders for theDFTcalculatedstructuresof $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (2')and $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (2'-Th).



Table S10. C_{arene}–C_{arene} and C_{arene}–F Mayer bond orders for the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (**5'**), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (**5a'**), $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**), toluene, and fluorobenzene.

		Me ₃ Si			Me ₃ Si		
				< < <			
		(3')				(5')	
	I	Me ₃ Si	$ \land $			Me ₃ Si	
		>N< -Ar	//)		$\sqrt{-}$	\rightarrow N \rightarrow Ar \rightarrow	
		0U					
		 N, ``F	/				
		Ar				Ar	
		(5a')				(5b')	
	3'	toluene	5'	5a'	C_6H_5F	5b'	
$C_i - C_o$	1.3814	1.3958	1.3643	1.3606	1.3846	1.4007, 1.4033, 1.4052, 1.3995	
$C_o - C_m$	1.4231	1.4432	1.405	1.4068	1.4332	1.4225, 1.4131, 1.4129, 1.4219	
$C_m - C_p$	1.3688	1.4333	1.3783	1.4359	1.4358	1.4351, 1.4414, 1.4413, 1.4349	
C _i –F	_	_	0.9716	0.8762	0.954	0.8561, 0.8515	

Table S11. C_{arene}–C_{arene} and C_{arene}–F Gopinathan-Jug bond orders for the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (**5'**), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (**5a'**), $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**), toluene, and fluorobenzene.



Table S12. C_{arene} – C_{arene} and C_{arene} –F Nalewajksi-Mrozek-3 bond orders for the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3**'), $[(XA_2')U(CH_2SiMe_3)(\eta^3C, C, C-C_6H_5F)]^+$ (**5**'), $[(XA_2')U(CH_2SiMe_3)(\eta^4C, C, C, F-C_6H_5F)]^+$ (**5a'**), $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**), toluene, and fluorobenzene.

Me ₃ Si				Me ₃ Si			Me ₃ Si	
				Ar ⊕ U Ar				
$(2')$ $(2'-Th)$ Me_3Si $(2'-Th)$ Me_3Si $(2'-Th)$ Me_3Si $(3r)$ $(5')$ $(2'-Th)$ $(5')$ $(2'-Th)$ $(5')$					(3) $Me_{3}Si$ Ar F N F $(5b')$			
		2'	2'-Th	3'	5'	5a'	5b'	
	An	0.6499	0.6674	0.6802	0.6685	0.6403	0.6782	
	Ν	-0.1795	-0.1797	-0.1801	-0.1802	-0.1796	-0.1825, -0.1833	
	0	-0.0313	-0.0304	-0.0349	-0.0345	-0.0356	-0.0341	
rges	Cbenzene	-0.0139 to -0.0270	-0.0081 to -0.0246	_	_	_	_	
cha	C_i	_	_	0.0276	0.1039	0.0765	0.0830, 0.0843	
hfeld	C_o			-0.0314	-0.0405	-0.0401	$\begin{array}{c} -0.0485, -0.0501, \\ -0.0567, -0.0574 \end{array}$	
Hirs	\mathbf{C}_m	_	_	-0.031	-0.0234	-0.0152	-0.0245, -0.0259, -0.0282, -0.0287	
	C_p			-0.0486	-0.0382	-0.0189	-0.0341, -0.0345	
	Сме	_	_	-0.1011	_	_	_	
	F	_	_	_	-0.0407	-0.0178	-0.0287, -0.0292	
Mull. s.p.	U	2.2168	_	2.2161	2.2148	2.2082	2.2239	

Table S13. Selected Hirshfeld charges and Mulliken spin populations (Mull. s.p.) for the DFT calculated structures of $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (**2'**), $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), $[(XA_2')U(CH_2SiMe_3)(\eta^3C, C, C-C_6H_5F)]^+$ (**5'**), $[(XA_2')U(CH_2SiMe_3)(\eta^4C, C, C, F-C_6H_5F)]^+$ (**5a'**), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**).

Me ₃ Si		Me ₃ Si			Me ₃ Si			
(2')			(2'-Th)			(3')		
Me ₃ Si			Mea	Si 🔨		Me ₃ Si		
							Ar F Ar	
(5')		(5a')			(5b')			
		2'	2'-Th	3'	5'	5a'	5b'	
irshfeld harges	An	0.8036	0.8549	0.793	0.7947	0.7709	0.8043	
	Ν	-0.1753	-0.1753	-0.1754	-0.1757	-0.1754	-0.1760, -0.1772	
H	0	-0.0301	-0.0282	-0.0315	-0.0314	-0.0325	-0.0317	
Mull. s.p.	U	2.2836	_	2.2767	2.2749	2.2542	2.2805	

Table S14. Selected Hirshfeld charges and Mulliken spin populations (Mull. s.p.) for the DFT calculated structures of the geometry-frozen $(XA_2')An(CH_2SiMe_3)^+$ fragments in $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (2'), $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (2'-Th), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (3'), $[(XA_2')U(CH_2SiMe_3)(\eta^3 C, C, C-C_6H_5F)]^+$ (5'), $[(XA_2')U(CH_2SiMe_3)(\eta^4 C, C, C, F-C_6H_5F)]^+$ (5a'), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1 F-C_6H_5F)2]^+$ (5b').

Me ₃ Si			Me ₃ Si		Me ₃ Si		
(2')			(2'-Th)		(3')		
Me ₃ Si Me ₃ Si Me ₃ Si Ar F			Me ₃ Si N H H H H H H H H H H H H H H H H H H		Me ₃ Si N F N Ar F CELD		
(5')		(3a)					
	2	2'-1h		5'	5a'	56	
Cbenzene	-0.0469 to -0.0472	-0.0468 to -0.0472	_	_	_	_	
C_i	—	—	0.0071	0.0818	0.0825	0.0817, 0.0830	
C_o	_	—	-0.0526	-0.0625	-0.0585	-0.0561, -0.0569, -0.0570, -0.0576	
\mathbf{C}_m	_	_	-0.0489	-0.041	-0.0396	-0.0385, -0.0388, -0.0405, -0.0408	
\mathbf{C}_p	_	_	-0.0527	-0.053	-0.0523	-0.0529, -0.0529	
Сме	_	_	-0.1114	_	_	_	
F	_	_	_	-0.0849	-0.1062	-0.1002, -0.1050	

Table S15. Selected Hirshfeld charges for the DFT calculated structures of the geometry-frozen arene fragments in $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (**2**'), $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), $[(XA_2')U(CH_2SiMe_3)(\eta^3 C, C, C-C_6H_5F)]^+$ (**5'**), $[(XA_2')U(CH_2SiMe_3)(\eta^4 C, C, C, F-C_6H_5F)]^+$ (**5a'**), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1 F-C_6H_5F)2]^+$ (**5b'**). For **5'b**, this fragment contains both fluorobenzene ligands. C_{Me} is the methyl carbon of toluene.

	benzene	toluene	fluorobenzene
Cbenzene	-0.0471	_	—
C_i	-	0.0066	0.0817
Co	-	-0.0524	-0.0615
C_m	-	-0.0488	-0.0407
C_p	-	-0.0529	-0.0528
C _{Me}	-	-0.111	-
F	-	-	-0.0892

Table S16. Selected Hirshfeld charges for the DFT calculated structures of geometry-optimized arene fragments.



S17. Fragment Table Hirshfeld charges fragment interaction from calculations $\{(XA_2')Th(CH_2SiMe_3)^+$ [(XA₂')U(CH₂SiMe₃)(benzene)]⁺ +arene } on (2'). $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (3'), $[(XA_2')U(CH_2SiMe_3)(\eta^3C,C,C-C_6H_5F)]^+$ (5'), $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (5a'), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (5b'). For 5'b, the arene fragment contains both fluorobenzene ligands.



Table S18. Gibbs free energies (kJ mol⁻¹) of C₆H₅F, $[(XA_2')U(CH_2SiMe_3)(\eta^3C, C, C-C_6H_5F)]^+$ (**5**'), $[(XA_2')U(CH_2SiMe_3)(\eta^4C, C, C, F-C_6H_5F)]^+$ (**5a'**), and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**).

		Me ₃ Si N H H H H H H H H H H H H H H H H H H	Me ₃ Si Ar U F (5h')
DA	$\Delta E_{ m elec}$	-99.2	-75.5
	$\Delta E_{ m orb}$	-102.5	-57.9
	$\Delta E_{ m Pauli}$	147.0	89.1
	$\Delta E_{ m Disp}$	-53.1	-31.2
Щ	$\Delta E_{ m prep}$	21.7	21.1
	BSSE	-7.3	-4.3
	$\Delta E_{ m int}$	-78.8	-50.1
ETS-NOCV	ΔE_1	-29.0 (28%)	—
	ΔE_2	-9.6 (9%)	—
	ΔE_3	-17.5 (17%)	—
	ΔE_4	-6.2 (6%)	—
	ΔE_5	-5.9 (6%)	—
	rest	-35.0 (34%)	—

Table of EDA^[6] (for 5b' only) with ETS-NOCV^[7] (for 5a' and 5b') energies

Table S19. Data from fragment interaction calculations ([(XA₂')An(CH₂SiMe₃)]⁺ + arene) on [(XA₂')U(CH₂SiMe₃)($\eta^4 C, C, C, F$ -C₆H₅F)]⁺ (**5a'**) and [(XA₂')U(CH₂SiMe₃)($\kappa^1 F$ -C₆H₅F)₂]⁺ (**5b'**). All energies are in kJ mol⁻¹, and ΔE_{int} values are BSSE-corrected. For ETS-NOCV data, values in parentheses are a percentages of ΔE_{orb} , and ΔE_n are the energies of the deformation density contributions, $\Delta \rho_n$, as defined in Figures S37-S55. The fragment interaction calculation for **5b'** was conducted with both C₆H₅F ligands as a single neutral fragment. To describe the average bonding between uranium and a single C₆H₅F ligand, the EDA energy components for **5b'** were divided by two.





Figures S26. Overall deformation densities for bonding between the $(XA_2')An(CH_2SiMe_3)^+$ and arene fragments in $[(XA_2')U(CH_2SiMe_3)(benzene)]^+$ (**2'**), $[(XA_2')Th(CH_2SiMe_3)(benzene)]^+$ (**2'-Th**), $[(XA_2')U(CH_2SiMe_3)(toluene)]^+$ (**3'**), and $[(XA_2')U(CH_2SiMe_3)(fluorobenzene)]^+$ (**5'**). Increased (green) and decreased (yellow) electron density is presented relative to the fragments, and isosurfaces are set to 0.001. Three different views are shown for each structure.



Figures S27. Overall deformation densities for bonding between the $(XA_2')U(CH_2SiMe_3)^+$ and arene fragments in $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]^+$ (**5a'**) and $[(XA_2')U(CH_2SiMe_3)(\kappa^1F-C_6H_5F)_2]^+$ (**5b'**. Increased (green) and decreased (yellow) electron density is presented relative to the fragments, and isosurfaces are set to 0.001. Two or three different views are shown for each structure.

ETS-NOCV deformation densities, NOCV orbitals, and fragment orbital contributors for 2', 2'-Th, 3', 5', and 5a'



Figure S28. Arene fragment orbital contributors for fragment interaction calculations $((XA_2')An(CH_2SiMe_3)^+ \text{ plus arene})$ on $[(XA_2')U(CH_2SiMe_3)(\text{benzene})]^+$ (2'), $[(XA_2')Th(CH_2SiMe_3)(\text{benzene})]^+$ (2'-Th), $[(XA_2')U(CH_2SiMe_3)(\text{toluene})]^+$ (3'), and $[(XA_2')U(CH_2SiMe_3)(\text{fluorobenzene})]^+$ (5'). Inset shows the Chemdraw structure of the calculated complexes.



Figure S29. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_1$ of [(XA₂')U(CH₂SiMe₃)(benzene)] (**2**'). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S30. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_2$ of [(XA₂')U(CH₂SiMe₃)(benzene)] (**2**'). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S31. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_3$ of [(XA₂')U(CH₂SiMe₃)(benzene)] (**2**'). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.00005. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital). ETS-NOCV afforded two qualitatively identical deformation density components corresponding to $\Delta \rho_3$ for alpha-spin, which have been summed to provide the alpha-spin deformation density isosurface and contribution level for $\Delta \rho_3$.



Figure S32. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_4$ (top) and $\Delta \rho_5$ (bottom) of [(XA₂')U(CH₂SiMe₃)(benzene)] (2'). All data is alpha-spin. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.001. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S33. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_1$ of $[(XA_2')Th(CH_2SiMe_3)(benzene)]$ (**2'-Th**). Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of thorium atomic orbitals contributing to $(XA_2')Th(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all thorium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S34. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_2$ of $[(XA_2')Th(CH_2SiMe_3)(benzene)]$ (**2'-Th**). Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of thorium atomic orbitals contributing to $(XA_2')Th(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all thorium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S35. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_3$ of $[(XA_2')Th(CH_2SiMe_3)(benzene)]$ (**2'-Th**). Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.00005. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of thorium atomic orbitals contributing to $(XA_2')Th(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all thorium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S36. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_1$ of [(XA₂')U(CH₂SiMe₃)(toluene)] (**3'**). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital). At the bottom of the figure, the sum of the $\Psi_{\pi 1}$ and $\Psi_{\pi 3}$ orbitals are shown scaled with respect to their SFO contribution levels for $\Delta \rho_{1\alpha}$ (left) and $\Delta \rho_{1\alpha}$ (right) with isosurfaces set to 0.003.



Figure S37. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_2$ of [(XA₂')U(CH₂SiMe₃)(toluene)] (**3'**). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S38. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_3$ of [(XA₂')U(CH₂SiMe₃)(toluene)] (**3'**). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.00005. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S39. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_4$ (top) and $\Delta \rho_5$ (bottom) of [(XA₂')U(CH₂SiMe₃)(toluene)] (3'). All data is alpha-spin. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.001. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The %6d character (%5f. etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S40. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_1$ of [(XA₂')U(CH₂SiMe₃)($\eta^3 C, C, C-C_6H_5F$)] (**5'**). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to (XA₂')U(CH₂SiMe₃)⁺ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital). At the bottom of the figure, the sum of the $\Psi_{\pi 1}$ and $\Psi_{\pi 3}$ orbitals are shown scaled with respect to their SFO contribution levels for $\Delta \rho_{1\alpha}$ (left) and $\Delta \rho_{1\alpha}$ (right) with isosurfaces set to 0.003.



Figure S41. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_2$ of $[(XA_2')U(CH_2SiMe_3)(\eta^3 C, C, C-C_6H_5F)]$ (**5**'). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (% 5f, % 6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S42. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_3$ of $[(XA_2')U(CH_2SiMe_3)(\eta^3 C, C, C-C_6H_5F)]$ (**5**'). Alpha- and beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.00005. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S43. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_4$ (top) and $\Delta \rho_5$ (bottom) of [(XA₂')U(CH₂SiMe₃)($\eta^3 C, C, C$ - $C_{6}H_{5}F$] (5'). All data is alpha-spin. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.001. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f. %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S44. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_1$ of $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]$ (**5a'**). Alphaand beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S45. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_2$ of $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]$ (**5a'**). Alphaand beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.0003. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S46. ETS-NOCV main fragment orbital contributors (left), [§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_3$ of $[(XA_2')U(CH_2SiMe_3)(\eta^4C,C,C,F-C_6H_5F)]$ (**5a'**). Alphaand beta-spin data (fragment orbitals, NOCVs and deformation density) are shown at the top and bottom, respectively. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.00005. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. The character (%5f, %6d etc.) of uranium atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values \geq 3% are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).



Figure S47. ETS-NOCV main fragment orbital contributors (left),[§] NOCV orbitals (middle), and deformation densities (right) for $\Delta \rho_4$ (top) and $\Delta \rho_5$ (bottom) of [(XA₂')U(CH₂SiMe₃)($\eta^4 C, C, C, F$ - $C_{6}H_{5}F$] (5a'). All data is alpha-spin. Orbital isosurfaces are set to 0.03, and deformation density isosurfaces are set to 0.001. NOCVs and filled fragment orbitals are shaded dark blue and red, whereas fragment virtual orbitals are shaded in pale blue and orange. Deformation densities are presented with increased (green) and decreased (yellow) electron density relative to the fragments. character (%5f, uranium The %6d etc.) of atomic orbitals contributing to $(XA_2')U(CH_2SiMe_3)^+$ fragment orbitals is provided (only values $\geq 3\%$ are included) – these values are normalized to the total of all uranium contributions (those contributing 1% or more to the total for the fragment orbital).

<u>Notes</u>

§ Fragment orbitals were included in Figures S29-47 when the population met any of the following criteria relative to other SFO contributions in a given deformation density component: a) the fragment orbital has the highest magnitude donor or acceptor SFO contribution, b) the fragment orbital has the highest magnitude SFO contribution from a fragment UNLESS it is an order of magnitude lower than the highest SFO contribution for the other fragment, and/or c) the SFO population magnitude is ≥36% of the next highest SFO population of the same sign AND is greater in magnitude than 0.008.

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