Switchable π-coordination and C-H metallation in small-cavity macrocyclic uranium and thorium complexes

Supplementary Data: Experimental details and characterising data; crystallographic discussion and data summary; computational details, enlarged molecular orbital images of 3a and 4, from figures 4 and 5, and Cartesian atomic coordinates and SCF energies of 3a and 4.

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General Details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a glove box unless otherwise stated. Solvents (toluene, *n*-hexane, diethyl ether and tetrahydrofuran (THF)) were dried by passage through activated 4 Å molecular sieves or activated alumina towers and stored over activated 4 Å molecular sieves. Benzene was dried by refluxing over potassium, distilled and stored over activated 4 Å molecular sieves. Deuterated solvents were refluxed over potassium, free-pump-thaw degassed three times and vacuum transferred and prior to use. ^{1}H NMR spectra were recorded at 298 K unless otherwise stated on either a Bruker AVA400 at 399.90 MHz. ^{13}C NMR spectra were recorded at 298 K on a Bruker AVA500 at 125.77MHz. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) and are reported relative to tetramethylsilane (δ = 0 ppm). Chemical shifts are quoted in δ (ppm). Crystallographic data were collected at 150 K on an Oxford Diffraction Excalibur diffractometer using Cu-Kα radiation (λ = 1.5418 Å) or at 120 K on an Agilent Technologies SuperNova diffractometer with Cu-Kα radiation and X-ray mirror optics. $ThCl_4(DME)_2$,[1] $UI_4(Et_2O)_2$[2] KN",[3] and H_2L[4] were synthesised according to literature procedures. KH (30 wt. % dispersion in mineral oil) was washed with *n*-hexane then dried under reduced pressure and stored under N_2 prior to use. LiN" was recrystallized from *n*-hexane at -30 °C and then sublimed (85 °C, 1.33 x 10^{-5} mbar) prior to use. KC_8 was prepared by addition of potassium to eight molar equivalents of ground graphite at 160 °C. All other reagents were used as purchased.

Synthetic procedures

[$ThCl_2$(L)] (1)

To a Schlenk flask charged with a stirrer bar and a THF solution of H_2L (1.09 g, 2.41 mmol, 15 mL) was added a THF suspension of KH (3eq, 0.29 g, 7.23 mmol, 5 mL) at -30 °C. The suspension was allowed to warm to ambient temperature with stirring over 16 h, then cannula filtered into an ampoule charged with a THF slurry of $ThCl_4(DME)_2$ (1.34 g, 2.41 mmol, 15 mL) and a stirrer bar. The reaction mixture was heated with stirring at 80 °C for 72 h. The resulting yellow suspension was filtered and the insoluble KCl residue washed with THF (2 x 10 mL). Volatiles were removed from the combined extract and washings under reduced pressure and H_2L impurity was removed by sublimation from the beige solid (170 °C, 1.33 x 10^{-5} mbar) to yield [$ThCl_2$(L)] **1** as a yellow powder in a 66.3% yield (1.20 g, 1.60 mmol). Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of *n*-hexane into a THF solution of [Th(L)Cl$_2$] at ambient temperature over 3 d. **^{1}H NMR (C$_6$D$_6$):** δ 7.99 (br s, 2H, para-C$_6$H$_4$), 7.11 (s, 2H, ipso-C$_6$H$_4$), 7.05 (br, 8H, meta-C$_6$H$_4$ and pyrrolide C$\underline{H}$), 1.76 (s, 12H, C$\underline{H}_3$), 1.39 (s, 12H, C$\underline{H}_3$) ppm. **^{1}H NMR (d$_8$-THF):** δ 7.71 (s, 2H, ipso-C$_6$H$_4$), 7.40 (t, 2H, para-C$_6$H$_4$), 7.28 (d, 4H, meta-C$_6$H$_4$), 7.00 (s, 4H, pyrrolide C$\underline{H}$), 1.79 (s, 12 H, C$\underline{H}_3$), 1.47 (s, 12H, C$\underline{H}_3$) ppm. **^{13}C{^{1}H} NMR (C$_6$D$_6$):** δ 156.3 (quaternary aromatic), 153.4 (quaternary aromatic), 134.3 (pyrrolide $\underline{C}$H), 123.3 (m-C$_6$H$_4$) 122.1 (p-C$_6$H$_4$), 121.6 (i-C$_6$H$_4$), 42.0 (meso-quaternary), 30.4 ($\underline{C}$H$_3$), 27.7 ($\underline{C}$H$_3$) ppm. **Analysis (%) calc. for C$_{32}$H$_{36}$Cl$_2$N$_2$Th:** C 51.08; H 4.82; N 3.72, found C 50.97; H 4.72; N 3.84.

[UI$_2$(L)] (2)

Method (a) via K$_2$L

To a Schlenk flask charged with a stirrer bar and a THF solution of H$_2$L (0.38 g, 0.84 mmol, 15 mL) at -30 °C, was added a THF suspension of KH (3eq, 0.10 g, 2.52 mmol, 5 mL) with stirring. The suspension was allowed to warm to ambient temperature over 16 h, then cannula filtered into a teflon-valved ampoule charged with a THF solution of UI$_4$(Et$_2$O)$_2$ (0.75 g, 0.84 mmol, 15 mL) and a stirrer bar. The mixture was heated with stirring at 80 °C for 72 h. The resulting red suspension was filtered and the insoluble KI residue washed with THF (2 x 10 mL). Volatiles were removed from the combined filtrate and washings under reduced pressure and the resulting pale red solid extracted with warm (80 °C) toluene (3 x 15 mL). Removal of volatiles from the extract under reduced pressure and removal of H$_2$L impurity by sublimation (170 °C, 10^{-5} mbar) afforded [UI$_2$(L)] **2** as a red powder in 53.1% yield (0.42 g, 0.45 mmol). Single crystals suitable for X-ray diffraction studies were grown from a saturated toluene solution at -30 °C over 3 d. **^{1}H NMR (C$_6$D$_6$):** δ 109.47 (s, 4H, pyrrolide C$\underline{H}$), 26.55 (s, 12H, C$\underline{H}_3$), -3.31 (s, 12 H, C$\underline{H}_3$), -11.15 (d, 4H, meta-C$_6$H$_4$), -16.01 (t, 2H, para-C$_6$H$_4$) ppm. **Analysis (%) calc. for C$_{32}$H$_{36}$I$_2$N$_2$U:** C 40.89; H 3.86; N 2.98, found C 40.82; H 3.93; N 2.95

Method (b) via Li$_2$L

A toluene solution of Li{N(SiMe$_3$)$_2$} (177 mg, 1.27 mmol, 2.4 equiv., 10 mL) was added to an teflon-valved ampoule containing a toluene solution of H$_2$L (242 mg, 0.54 mmol, 10 mL) and the colourless solution stirred for 12 h at ambient temperature. Volatiles were removed under reduced pressure and the resultant colourless solid Li$_2$L washed with *n*-hexane (15 mL). To this was then added solid UI$_4$(Et$_2$O)$_2$ (456 mg, 0.51 mmol, 0.95 equiv.) and toluene (40 mL), and the mixture heated at 110 °C for 20 h. The resulting red suspension was cannula filtered to remove LiI and the solvent removed under reduced pressure. The residual H$_2$L impurity was removed by sublimation (170 °C, 10^{-6} Torr) to yield [UI$_2$(L)] **2** (221 mg, 44%) as a red powder.

[UI(THF)(L)] (3) and [UI(L)] (3a)

THF (30 mL) was added slowly to a cooled, stirred mixture of [UI$_2$(L)] **2** (200 mg, 0.21 mmol), KC$_8$ (30 mg, 0.22 mmol), and a stirrer bar in a Teflon-valved ampoule at -78 °C, and the mixture allowed to warm to ambient temperature over 12 h with stirring. The resulting green solution was filtered through celite, the residues washed with THF (5 mL), and volatiles removed under reduced pressure. The dark green solid was washed with C$_6$H$_6$ (5 mL) to remove residual H$_2$L impurity and dried *in vacuo* to yield [UI(THF)(L)] **3** (52 mg, 30%) as a dark brown powder. Single crystals of [UI(THF)(L)] **3** and [UI(L)] **3a** suitable for X-ray diffraction studies were grown from a saturated THF solution at -30 °C over 7 days and by layering a THF solution with *n*-hexane at ambient temperature, respectively. **^{1}H NMR (C$_6$D$_6$):** δ 18.65 (s, 4H, pyrrolide C$\underline{H}$), 5.92 (s, 12H, C$\underline{H}_3$), -2.48 (s, 12H, C$\underline{H}_3$), -15.98 (v br, s, 4H, meta-C$_6$H$_4$), -19.97 (v br, s, 2H, C$_6\underline{H}_4$), -34.40 (v br, s, 2H, C$_6\underline{H}_4$) ppm. **MS (EI):** m/z = 813 (100%, M$^+$(-THF)). **Analysis (%) calc. for C$_{32}$H$_{36}$IN$_2$U:** C 47.24; H 4.46; N 3.44, found C 47.35; H 4.56; N 3.31.

[U$_2$I$_4$(L)] (4)

Toluene (10 mL) was added to a Teflon-valved ampoule containing Li{N(SiMe$_3$)$_2$} (94 mg, 0.68 mmol, 2.7 equiv.), H$_2$L (111 mg, 0.25 mmol), and a stirrer bar and the colourless mixture stirred at ambient temperature for 6 h to afford Li$_2$L. Volatiles were removed under reduced pressure and the resultant white solid washed with *n*-

hexane (15 mL). The Li_2L was then redissolved in toluene (20 mL) and added dropwise to a dark blue-purple suspension of UI_3 (305 mg, 0.49 mmol, 1.95 equiv.) in toluene (20 mL) and stirred for 12 h at ambient temperature. The resultant brown solution was isolated by cannula filtration and the dark solids extracted with toluene (30 mL). Volatiles were removed from the combined filtrate and washings under reduced pressure and the resulting brown powder was washed with Et_2O (10 ml) and dried *in vacuo* to yield $[U_2I_4(L)]$ **4** (76 mg, 0.05 mmol, 22 %). Single crystals of **4** suitable for X-ray diffraction were grown either from allowing a hot, saturated C_6D_6 solution (80 °C) to cool to ambient temperature, or from layering a saturated toluene solution with *n*-hexane at ambient temperature. A polymorph of complex **4**, **4a.3(C_6H_6)** also crystallised from hot benzene. **^{1}H NMR (C_6D_6):** δ 59.31 (s, 4H, pyrrolide C$\underline{H}$), 19.84 (s, 12H, C$\underline{H}_3$), -9.07 (s, 12H, C$\underline{H}_3$), -33.13 (v br, s, 4H, meta-C_6H_4), -35.05 (v br, s, 2H, $C_6\underline{H}_4$) ppm. **MS (EI):** m/z = 1432 (100%, M^+), 1305 (95%, M^+(-I)), 813 (saturated, M^+(-UI_3)). **Analysis (%) calc. for $C_{32}H_{36}I_4N_2U_2$:** C 26.83; H 2.53; N 1.96, found C 26.71; H 2.58; N 2.01.

$[K(THF)_2Th(L^{-2H})(\mu\text{-}Cl)]_2$ (5)

Method (a) from reaction with K/ naphthalenide at 25 °C

A Schlenk flask was charged with **1** (0.1808 g, 0.241 mmol), K (18. 81 mg, 0.481 mmol), naphthalene (61.63 mg, 0.481 mmol), a stirrer bar, and THF (20 mL). The reaction mixture was allowed to stir at ambient temperature for 16 h. The resulting brown suspension was filtered through Celite to afford a clear brown solution. Any removal of volatiles from the resulting solution under reduced pressure resulted in the powdering out of the product **5**. Slow diffusion of *n*-hexane into the saturated THF solution afforded colourless crystals of **5** in 31 % yield (67.1 mg, 0.0374 mmol). **Analysis (%) calc. for $C_{80}H_{100}Cl_2K_2N_4O_4Th_2$:** C 53.53; H 5.62; N 3.12, found C 53.35; H 5.48; N 2.95. No re-dissolution of the crystals was observed after sonication and boiling of a THF suspension of **5** for 48 h. The insolubility of isolated **5** precluded analysis by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Control reaction of H_2L with K/ naphthalenide

A J-Young Teflon valve NMR tube was charged with H_2L (13.4 mg, 0.0297 mmol), excess K (4.65 mg, 0.119 mmol), naphthalene (15.2 mg, 0.119 mmol), a C_6D_6 capillary, and THF (0.5 mL). The reaction mixture was allowed to stand at ambient temperature for 48 h. Analysis of the solution by ^{1}H and ^{13}C NMR confirms the only compound present is K_2L.

Method (b) from reaction with K at 80 °C

A J-Young Teflon valve NMR tube was charged with **1** (12.0 mg, 0.0160 mmol), K (0.936 mg, 0.0240 mmol) and THF (0.5 mL), the reaction mixture was heated at 80 °C for 16 h. The solution changed colour from yellow to peach. The solution was filtered into a vial. Colourless crystals of **5** were grown by slow diffusion of *n*-hexane into a saturated THF solution of **5** at ambient temperature over a period of 24 h.

$K[Th(L^{-2H})N(SiMe_3)_2]$ (6)

A teflon-valved ampoule was charged with **1** (0.167 g, 0.222 mmol), $K(N(SiMe_3)_2)$ (3eq, 0. 133 g, 0.666 mmol), a stirrer bar, and toluene (20 mL), and the mixture was heated with stirring at 80 °C for 16 h. The resulting purple suspension was filtered and the insoluble KCl residue was washed with toluene (2 x 10 mL). The solvent was removed from the combined extract and washings under reduced pressure to yield a pink solid which was washed with *n*-hexane (3 x 10 mL). The product was dried under reduced pressure to yield $K[Th(L^{-2H})N(SiMe_3)_2]$ **6** as a pale pink powder in 29.2 % yield (0.0568 g, 0.0647 mmol). **^{1}H NMR (C_6D_6):** δ 7.26 (d, 4H, meta-C_6H_4), 7.17 (s, 2H, para-C_6H_4) 6.77 (s, 4H, pyrrolide C$\underline{H}$), 1.67 (s, 12H, C$\underline{H}_3$), 1.70 (s, 12H, C$\underline{H}_3$), 0.43 (s, 18H, Si(C$\underline{H}_3$)$_3$) ppm. **^{13}C{^{1}H} NMR (C_6D_6):** δ 211.7 (Th-$\underline{C}$), 166.8 (quaternary aromatic), 163.6 (quaternary aromatic), 126.4 (para-C_6H_4), 122.0 (meta-C_6H_4), 113.7 (pyrrolide $\underline{C}$H), 46.2 (quaternary), 33.5 ($\underline{C}H_3$), 31.9 ($\underline{C}H_3$), 5.7 (Si($\underline{C}H_3$)$_3$) ppm. **^{1}H NMR (C_5D_5N):** δ 7.37 (d, 4H, meta-C_6H_4), 7.24 (s, 2H, para-C_6H_4)

6.92 (s, 4H, pyrrolide C$\underline{H}$), 1.85 (s, 24H, C$\underline{H}_3$), 0.42 (s, 18H, Si(C$\underline{H}_3$)$_3$) ppm. **Analysis (%) calc. for $C_{38}H_{52}N_3Si_2Th$:** C 51.97; H 5.97; N 4.79, found C 52.04; H 5.87; N 4.69.

Crystallographic Details

Crystallographic X-ray data were collected using Mo-Kα radiation (λ = 0.71073) on a SuperNova (Cu) X-ray Source and an Oxford Diffraction Excalibur CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the WinGX32 suite of programs. X-ray crystallographic coordinates for the complexes have been deposited at the Cambridge Crystallographic Database, numbers **CCDC 951384-951390 and 964833**. Abbreviated versions of the crystallographic analyses below are in included in the manuscript.

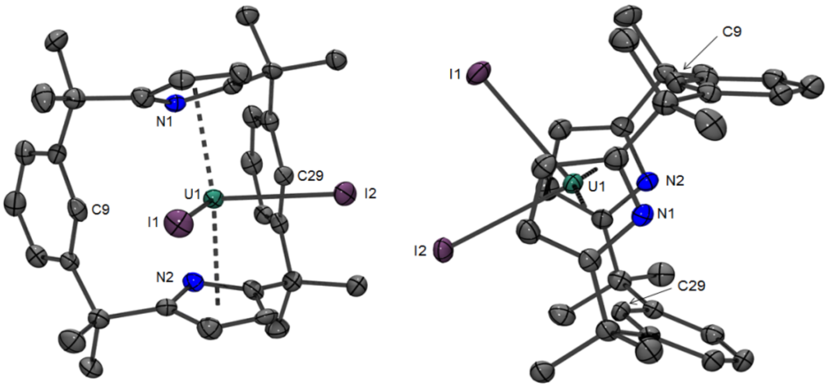


Figure SI.1: Displacement ellipsoid drawings of [UI_2(L)] **2** (probability set at 50 %). H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): U1-I1 3.0708(4), U1-I2 3.0573(4), U1-C9 3.045(5), U1-C29 3.022(5), U1-[κ^5-C_4N]$_{\text{cent(avg)}}$ 2.480, I1-U1-I2 = 81.51(1), [aryl1]$_{\text{cent}}$-U1-[aryl2]$_{\text{cent}}$ = 89.02, [κ^5-C_4N]$_{\text{cent}}$-U-[κ^5-C_4N]$_{\text{cent}}$ 163.26.

The molecular structures of **1** and **2** (Figure 1 and ESI respectively), are isomorphous and show that the An(IV) cation is positioned within the macrocyclic cavity with κ^5:κ^5 pyrrolide binding. This contrasts to the Sm complex [SmCl(L)] (paper, Scheme 1) which displays an η^6:κ^1:η^6:κ^1 mode but is similar to the singly aryl metalated [Sm(THF)(L^{-H})] which has a η^1:κ^5:κ^5 binding mode.[5] The average An-[C_4N]$_{\text{centroid}}$ distances and the metallocene angles [κ^5-C_4N]$_{\text{cent}}$-An-[κ^5-C_4N]$_{\text{cent}}$ are similar to those seen in the cyclopentadienyl An^{IV} complexes [$Cp^*_2AnX_2$]. [6,7] The average Th-[C_4N]$_{\text{cent}}$ distances of 2.557 Å and [κ^5-C_4N]$_{\text{cent}}$-Th-[κ^5-C_4N]$_{\text{cent}}$ angle of 163.60° in **1** are very similar to values in [$Cp^*_2ThCl_2$] (2.532 Å and 128.73°). Likewise, the geometrical data for **2** are comparable to those in [$Cp^*_2UI_2$]. The average Th-[C_4N]$_{\text{centroid}}$ distances of 2.557 Å and [κ^5-C_4N]$_{\text{cent}}$-Th-[κ^5-C_4N]$_{\text{cent}}$ angle of 163.60° in **1** are very similar to values in [Li(DME)$_3$] [(Et_8-calix[4]tetrapyrrole)Th{N($SiMe_3$)$_2$}][8] (2.578Å and 167.54°) and [$Cp^*_2ThCl_2$] (2.532 Å and 128.73°).[6] Likewise, the geometrical data for **2** are comparable to those in [Li(THF)$_2$](μ-Cl)$_2${U_2[(-CH_2-)$_5$]$_4$-calix[4]tetrapyrrole}Cl_2·THF[9] and [$Cp^*_2UI_2$].[7] No interactions between the An^{IV} centre and aryl ring carbons are observed for **1** or **2**. The distances to the *ipso*-carbon of the rings (Th1-C9, 3.024(2) Å, Th1-C29, 3.017(2) Å; U1-C9, 3.045(5) Å and U1-C29, 3.022(5) Å) are too long to suggest an agostic interaction.[10]

In contrast to the κ^5:κ^5 metallocene binding seen in **1**, **2**, **5** and **6**, **3** and **3a** adopt the η^6:κ^1:η^6:κ^1 binding mode.[5] This bis(arene) sandwiched structural motif is reminiscent of that seen in the bis(arene) complexes of the zero oxidation state lanthanides and early transition metals [M(η-Bz*)$_2$] (Bz* = 1,3,5-(Bu^t)$_3C_6H_3$), synthesised by metal vapour synthesis.[11-13] The [aryl]$_{\text{cent}}$-U1-[aryl]$_{\text{cent}}$ angles, 172° in **3** and 174° in **3a** are almost linear and similar to that found in [SmCl(L)] (176°). The U-N distances in **3** (2.530(6) and 2.501(7) Å) are identical within standard deviation to the σ-bound pyrrolide distances found in the related U^{III} complex [K(DME)][{[(-CH_2-)$_5$]$_4$-calix[4]tetrapyrrole}U(DME)][14] (2.525(14) and 2.526(15) Å) and longer than in the U^{IV} Pacman complex.[15]

The U1-O1 distance in **3** is 2.697(6) Å, similar to that found in the sterically saturated uranium complex [U($C_8H_6\{Si^iPr_3$-1,4$\}_2$)($CpMe_5$)(THF)] of 2.695(4) Å,[16,17] although in the latter example removal of THF requires heating under vacuum. The loss of coordinated THF from **3** to form **3a** results in a significant shortening of U-L bonds, for example U1-N1 contracts from 2.530(6) to 2.468(10) Å. The bonding parameters of **3a** (U1-N1 2.468(10), U1-N2 2.438(10), U1-[aryl]$_{\mathrm{cent(ave)}}$ 2.612 Å) and [SmCl(L)] (Sm-N 2.410(5), Sm-[aryl]$_{\mathrm{cent(ave)}}$ 2.638 Å) are in fact very similar as might be expected given the similar ionic radii of Sm^{III} and U^{III} cations. The U1-I1 distances in **3** (3.2092(9) Å) and **3a** (3.1112(15) Å) are within the range observed for U^{III} monoiodide complexes (3.103(2) to 3.220(1) Å),[18,19,20] and are significantly longer than those in the U^{IV} complex **2** (3.0708(4) and 3.0573(4) Å). The C-C(aryl) distances (range 1.360(11)-1.413(10) Å in **3)** are unchanged from **2** or benzene (average 1.40 Å).[21, 22] The U1-C_{avg} distances in both **3** (3.001 Å) and **3a** (2.970 and 2.950 Å) are much longer than those of the μ-arene complexes of uranium[23] and are comparable to the U^{III} aryloxide complex, [U(O-2,6-$Pr^i_2C_6H_3)_3]_2$,[24] U1-C_{avg} of 2.92(2) Å, which exists as a π-arene bridged dimer in the solid state, and to the two U^{III} adducts of hexamethylbenzene.[25, 26]

The κ^5:κ^5 pyrrolide binding of U2 in **4** is similar to that seen in **2**, although the U2-[κ^5-C_4N]$_{\mathrm{cent(ave)}}$ distance of 2.583 Å is longer (2.480 Å in **2**) and the metallocene angle is much smaller, [κ^5-C_4N]$_{\mathrm{cent}}$ -U2 -[κ^5-C_4N]$_{\mathrm{cent}}$ of 139° (163° in **2**) resulting in a more classic, bent-sandwich geometry. Likewise the η^6:κ^1:η^6:κ^1 bis-arene binding of U1 in **4** is very similar to that seen in **3** and **3a**. The interplanar arene angle is 16.41° in **4**, slightly larger than that in **3a** of 15.55°. The U1-N1 are necessarily lengthened in **4** (U1-N1 2.669(5) Å) from **3** (U-N 2.530(6) and 2.501(7) Å). The U1-[aryl]$_{\mathrm{cent(ave)}}$ distances are also lengthened (2.799 and 2.748 Å) from **3** (2.669 and 2.612 Å) and the [aryl1]$_{\mathrm{cent}}$-U1-[aryl2]$_{\mathrm{cent}}$ angle decreased to 164.99° from 172° in **3**. The U1···U2 separation of 3.8639(5) Å in **4** is longer than that in the U^{III}-U^{III} amide bridged complex, [U(C_8H_8)]$_2$[μ-η^4:η^4-HN$(CH_2)_3$N$(CH_2)_2$N$(CH_2)_3$NH] (3.3057(9) Å).[75]

The molecular structures of **5** and **6** show a κ^5:η^1:κ^5:η^1 ligand binding mode, but with two new Th-C bonds to C9 and C29, from the double metallation of the macrocycle. The potassium counter-ion balances the retained Th^{IV} formal oxidation state and occupies the cavity subtended by the two aryl rings in both cases. Complex **5** is a chloride bridged dimer in the solid state, whereas complex **6** exists as a K-bridged linear polymer (Figure 3). The Th1-N3(N") distance is 2.375(12) Å and is similar to other Th-N" distances.[8, 27-32] The chloride-bridge of **5** has a diamond-shaped core and displays Th1-Cl1 bond lengths of 2.840(2) and 3.060(2) Å, which are much greater than those in **1** (Th-Cl_{ave} 2.665 Å). There is no significant change to pyrrolide binding on double metallation, as seen by the Th-[κ^5-C_4N]$_{\mathrm{cent}}$ distances and metallocene angle, [κ^5-C_4N]$_{\mathrm{cent}}$-Th-[κ^5-C_4N]$_{\mathrm{cent}}$ in **1** (2.557 Å and 163.60°), in **5** (2.550 Å and 164.98°) and **6** (2.547 Å and 164.39°). However, the potassium incorporation into the previously unoccupied arene cavity and double metallation at C9 and C29, have opened up the arene cavity in **5** and **6** compared to **1**. The interplanar angle between the arene rings is 20.02° in **1** but 63.66° in **5** and 56.48° in **6**. The constrained geometry of the macrocycle is reflected in the long Th-C distances in **5** (Th1-C9 2.659(8) Å, Th1-C29 2.669(9) Å) and **6** (Th1-C9 2.691(16) Å, Th1-C29 2.693(12) Å), longer than those found in the similarly metallated complex [Li$(DME)_3$][ThCl_3(η^6-C_6H_4\{1,3-CMe_2[(2-C_4H_3N)CMe_2\}] (2.612(8) Å),[33] and are at the top end of the range observed for a Th-C single bond.[34-39]

The coordination of the Th^{IV} centre to the doubly metallated macrocycle in **5** and **6** can be compared to that in the singly metallated complex [Sm^{III}(THF)(L^{-H})] (Scheme 1). All three complexes show κ^5:κ^5 metallocene-like binding to both pyrrolide groups, and a near-linear M-C_{aryl} angle in the metallated portion of the macrocycle, but a much smaller [κ^5-C_4N]$_{\mathrm{cent}}$-M-[κ^5-C_4N]$_{\mathrm{cent}}$ angle of 136° is observed for Sm, compared to 164° in both **5** and **6**.

Table 1. Crystallographic data summary for complexes 1-3

	p12014c **[ThCl$_2$(L)]** **(1)**	**po2011** **[UI$_2$(L)]** **(2)**	**po3006_refinalized2** **[U(L)I(THF)] (3)**	**p12091** **[U(L)I] (3a)**
Chemical formula	$C_{32}H_{36}Cl_2N_2Th$	$C_{32}H_{36}I_2N_2U$	$C_{36}H_{44}IN_2OU \cdot C_6H_{12}O_{1.5}$	$C_{32}H_{36}IN_2U$
M_r	751.57	940.46	993.82	813.56
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
Temperature (K)	170	120	120	170
a, b, c (Å)	10.1650 (2), 15.5150 (4), 18.2424 (4)	10.6471 (1), 22.5946 (2), 12.5757 (1)	10.112 (5), 11.224 (5), 18.141 (5)	56.620 (2), 15.9509 (5), 24.5801 (10)
α, β, γ (°)	90, 91.134 (2), 90	90, 95.444 (1), 90	99.530 (5), 99.536 (5), 108.352 (5)	90, 115.031 (5), 90
V (Å^3)	2876.45 (11)	3011.65 (5)	1874.4 (14)	20114.2 (13)
Z	4	4	2	28
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	5.39	31.43	5.19	6.75
Crystal size (mm)	0.46 × 0.28 × 0.21	0.25 × 0.04 × 0.02	0.30 × 0.10 × 0.07	0.30 × 0.21 × 0.13
Diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Analytical numeric absorption correction using a multifaceted crystal model	Numerical absorption correction based on gaussian integration over a multifaceted crystal model	Multi-scan *SADABS*	Analytical numeric absorption correction using a multifaceted crystal model
T_{min}, T_{max}	0.651, 0.801	0.087, 0.624	0.516, 0.790	0.953, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34644, 6582, 5907	90561, 6091, 5507	87370, 6851, 6421	116453, 23044, 11955
R_{int}	0.034	0.099	0.067	0.079
(sin θ/λ)$_{max}$ (Å^{-1})	0.649	0.623	0.602	0.649
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.039, 1.05	0.034, 0.100, 1.06	0.047, 0.113, 1.12	0.064, 0.178, 1.06
No. of reflections	6582	6091	6851	23044
No. of parameters	342	342	468	1136
No. of restraints	0	0	137	6
H-atom treatment	Riding	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.57, -0.60	2.30, -2.26	2.95, -2.64	4.80, -2.10

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET) (compiled Jan 23 2012,18:06:46), *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49), *SHELXS97* (Sheldrick, 2008), *SHELXS*, sir-92, *SHELXL97* (Sheldrick, 2008), *ORTEP*, Mercury.

Table 2. Crystallographic data summary for complexes 4-6.

	p12140 **[$U_2I_4(L)$] (4)**	**p12141** **[$U_2I_4(L)$].3(C_6H_6) (4a)**	**p12117-sr** **[K[Th$(L)^{-2H}$Cl](THF)$_2$]$_2$** **(5)**	**po3003_refinalized** **K[Th(L^{-2H})N($SiMe_3$)$_2$]** **(6)**
Crystal data				
Chemical formula	$C_{32}H_{36}I_4N_2U$	$C_{32}H_{36}I_4N_2U_2.C_{18}H_{18}$	$C_{86}H_{114}Cl_2K_2N_4O_4Th_2$	$C_{38}H_{52}KN_3Si_2Th$
***M*$_r$**	1432.29	1666.61	1880.99	878.15
Crystal system, space group	Orthorhombic, *Pnma*	Monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$
Temperature (K)	170	170	170	120
***a*, *b*, *c* (Å)**	31.0498 (7), 11.5475 (2), 10.1812 (2)	10.3932 (3), 26.6221 (7), 18.2814 (7)	10.5523 (2), 18.0034 (5), 23.5696 (7)	12.232 (5), 12.893 (5), 23.252 (5)
α, β, γ (°)	90, 90, 90	90, 97.105(3), 90	90, 98.237 (2), 90	90.000 (5), 90.000 (5), 90.000 (5)
***V* (Å^3)**	3650.44(13)	5019.4 (3)	4431.5 (2)	3667 (2)
Z	4	4	2	4
Radiation type	Mo *Ka*	Mo *Kα*	Mo *Kα*	Cu *Kα*
μ (mm^{-1})	12.277	8.94	3.55	14.98
Crystal size (mm)	0.36 × 0.27 × 0.12	0.39 × 0.07 × 0.02	0.61 × 0.05 × 0.05	0.13 × 0.11 × 0.04
Data collection				
Diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan □*CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Numerical absorption correction based on gaussian integration over a multifaceted crystal model
***T*$_{min}$, *T*$_{max}$**	0.210, 1.000	0.386, 1.000	0.556, 1.000	0.940, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38038, 4380, 3924	46069, 7949, 5997	10153, 10153, 7806	28994, 7189, 6871
***R*$_{int}$**	0.067	0.089	0.0000	0.033
(sin θ/λ)$_{max}$ (Å^{-1})	0.649	0.575	0.649	0.622
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.075, 1.15	0.043, 0.088, 0.95	0.065, 0.149, 1.15	0.062, 0.165, 1.12

No. of reflections	4380	7949	10153	7189
No. of parameters	197	507	460	420
No. of restraints	0	48	101	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	Riding	Riding
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	2.87, -1.61	1.10, -1.05	5.09, -1.86	1.97, -1.40

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET) (compiled Jan 23 2012,18:06:46), *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49), *SHELXS97* (Sheldrick, 2008), *SHELXS*, sir-92, *SHELXL97* (Sheldrick, 2008), *ORTEP*, Mercury.

Computational Details

Density functional theory calculations were carried out on **3a** and **4** using the PBE0 hybrid functional,[40] as implemented in the Gaussian 09 Rev. C.01[41] quantum chemistry code. For the geometry optimisations, 60- and 46-electron Stuttgart-Bonn relativistic pseudopotentials were used for U and I respectively, together with a (14s 13p 10d 8f 6g)/[10s 9p 5d 4f 3g] segmented valence basis set for the former[42] and (16s 12p 4d 1f)/[3s 3p 2d 1f] for I.[43, 44] Dunning's cc-pVTZ basis sets were employed for N and C, and cc-pVDZ for H. Spin-unrestricted (S = 3 and 6 respectively for **3a** and **4**) calculations were performed. Wavefunction stability was confirmed, and spin-contamination verified as minimal (deviation from the ideal value of $<S^2>$ was c. 0.0001). The ultrafine integration grid was employed, as were the default geometry and SCF convergence criteria. No symmetry constraints were imposed for **3a**, while **4** was constrained to the C_{2v} point group.

Single point calculations were performed at the optimised geometries using the SARCP all-electron basis set of Pantazis and Neese for U,[45] their relativistically recontracted variant of the Karlsruhe def-2 I basis set[46] and the Dunning basis sets for all other atoms. The DKH2 Hamiltonian was employed in these calculations.

Atoms-in-molecules analysis was performed using the AIMAll programme[47] version 13.01.27, using formatted G09 checkpoint files from the all-electron calculations as input.

Table 3. Comparison of selected distances for 3a and 4 (Å)

Parameter	**[UI(L)] 3a**		**Parameter**	**$[U_2I_4(L)]$ 4**	
	Experimental	**Calculated**		**Experimental**	**Calculated**
N1—U1	2.468(10)	2.455$_{ave}$	N1—U1	2.669(5)	2.644
N2—U1	2.438(10)		N1—U2	2.738(5)	2.718
I1—U1	3.1112(15)	3.150	I1—U1	3.1095(6)	3.119
C_{ave}-U1	2.96	2.926	I2—U2	3.0434(7)	3.025
			I3—U2	3.0258(8)	
			C_{ave}-U1	3.105	3.126
			C_{ave}-U2	2.869	2.870
			U1—U2	3.8639(5)	3.768

Table 4. Valence MO compositions (alpha spin only) for 3a

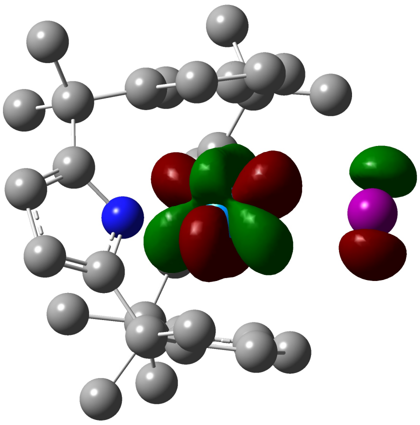
MO	Energy (eV)	Principal character	Key contributors (%)
142	-5.039	U f	84 U f, 7 I p
141	-5.078	U f	91 U f
140	-5.192	U f	94 U f
139	-5.368	pyrrole π	4 U f
138	-5.381	pyrrole π	
137	-6.402	pyrrole π	25 I p_π
136	-6.411	pyrrole π	6 I p_σ
135	-6.537	I p_π	58 I p_π, 9 U f
134	-6.675	I p_π	89 I p_π, 3 U f, 2 U d
133	-7.243	I p_σ	71 I p_σ, 10 U d, 2 U s
132	-8.103	arene π	3 U f
131	-8.292	arene π	2 U f, 2 U d
130	-8.431	arene-U δ	6 U d
129	-8.523	N-U σ	7 U d
128	-8.777	arene-U δ	8 U d
127	-8.928	N-U σ	4 U d, 4 U s, 2 U f

Table 5. Valence MO compositions (alpha spin only) for 4

MO	Energy (eV)	Principal character	Key contributors (%)
170	-5.389	U f	84 U f, 12 I p_π
169	-5.425	U f	76 U f, 16 I p_π
168	-5.454	U f	91 U f
167	-5.550	U f	89 U f, 6 I p_π
166	-5.681	U f	84 U f, 6 U d
165	-5.695	U f	86 U f, 12 I p_π
164	-6.441	I p_π	94 I p_π, 2 U f
163	-6.690	I p_π	72 I p_π, 14 U f
162	-6.701	I p_π	64 I p_π, 8 U f
161	-6.762	I p_π	84 I p_π, 7 U f
160	-6.941	I p_π	64 I p_π, 18 U f
159	-7.000	I p_π	80 I p_π, 9 U f
158	-7.047	I p_π	84 I p_π, 5 U d, 3 U f
157	-7.073	pyrrolide π	
156	-7.249	I p_σ	74 I p_σ, 8 U d, 4 U f, 2 U p
155	-7.349	I p_π	84 I p_π, 6 U d, 2 U f
154	-7.409	I p_σ	76 I p_σ, 3 U f, 2 U d, 3 U p, 4 U s
153	-7.666	I p_σ	80 I p_σ, 13 U d, 2 U p
152	-7.837	I p_σ	80 I p_σ, 2 U f, 4 U d, 8 U s
151	-7.918	pyrrolide-U δ	18 I p_π, 15 U d
150	-8.362	pyrrolide π, arene π	
149	-8.564	arene π	
148	-8.598	pyrrolide π, U-N σ	24 N p, 6 U d, 2 U f
147	-8.871	pyrrolide π, arene π	
146	-9.056	arene-U δ	8 U d
145	-9.251	arene-U δ	9 U d

Enlarged molecular orbital images of 3a and 4, from figures 4 and 5

Compound 3a



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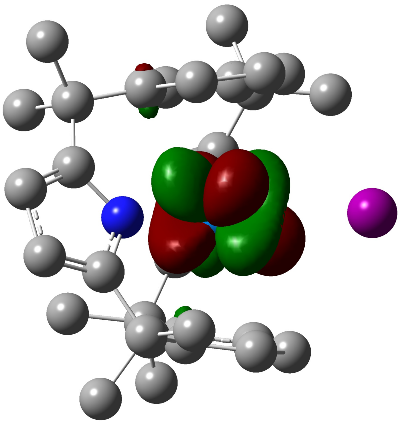

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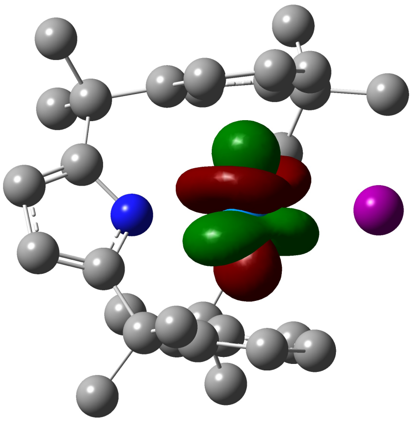

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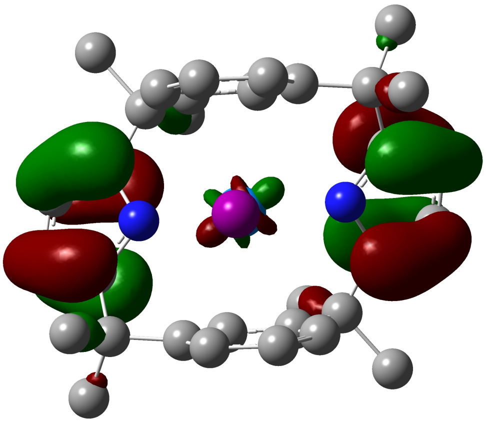

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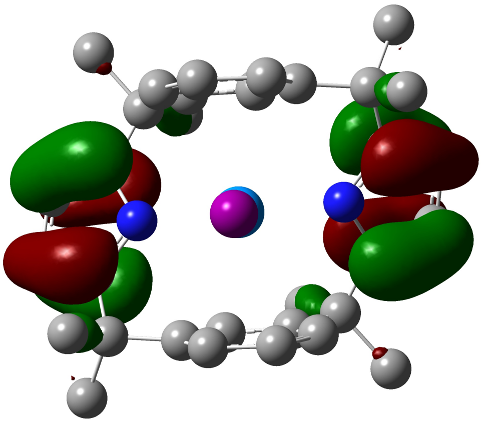

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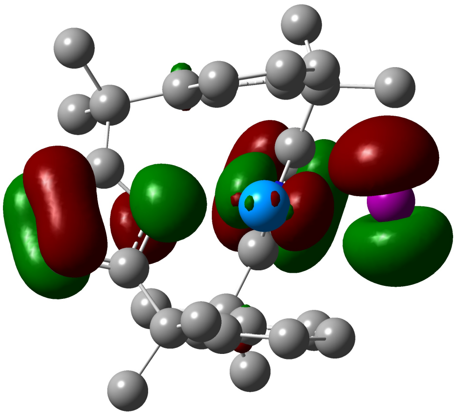

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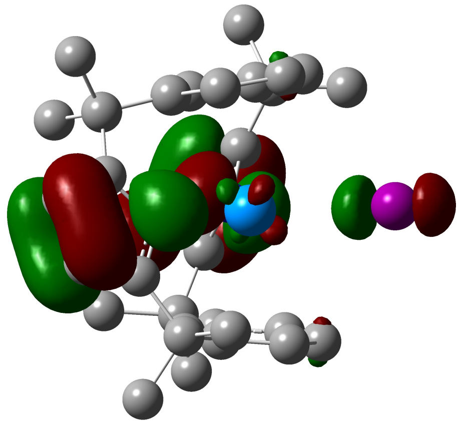

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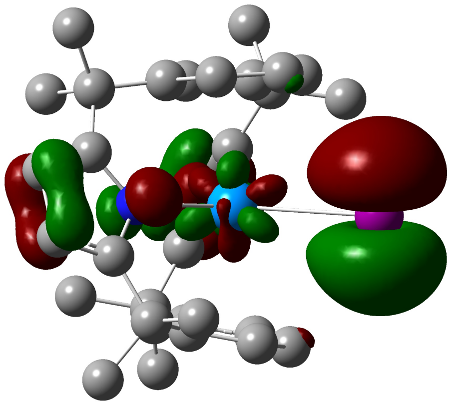

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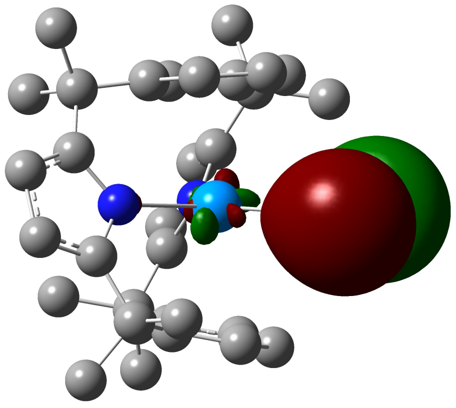

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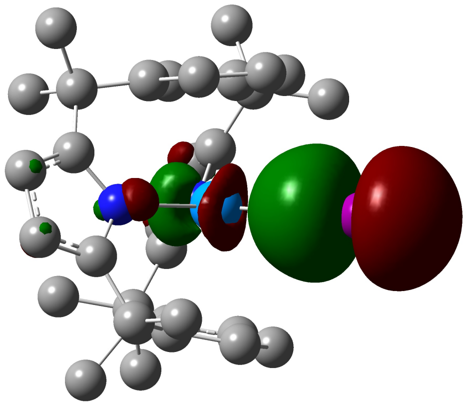

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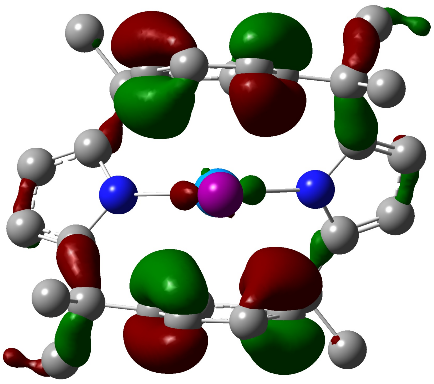

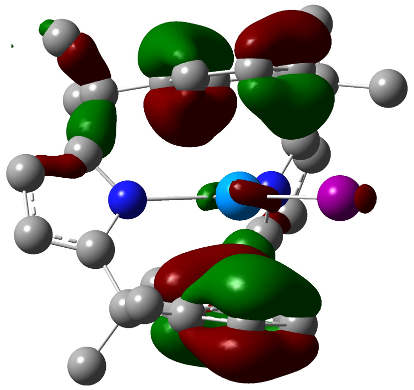

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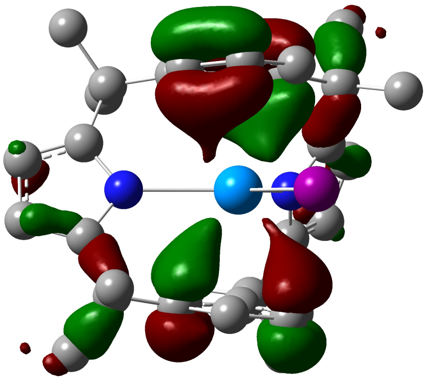

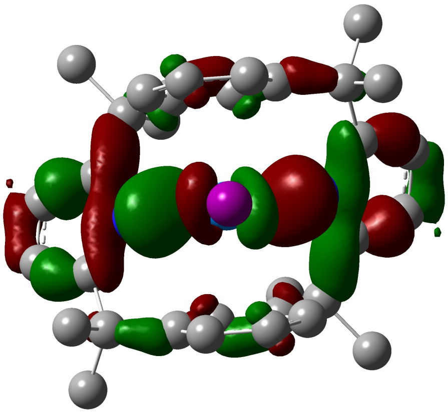

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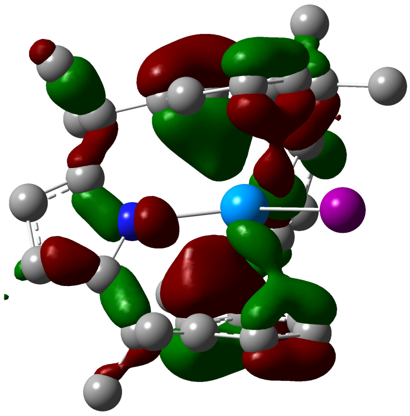

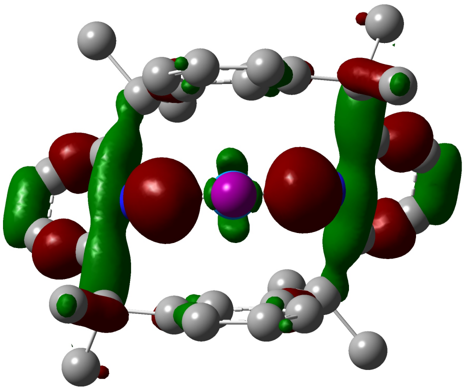

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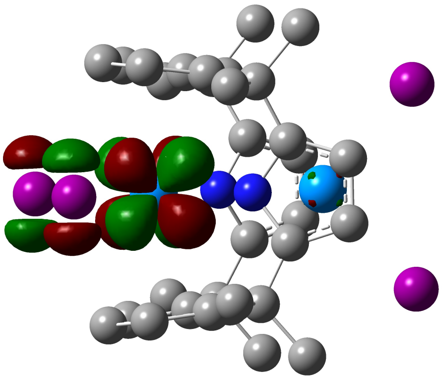
Compound 4



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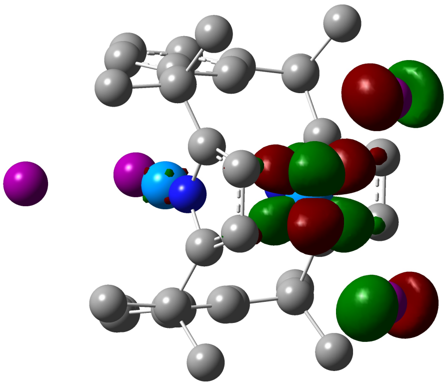

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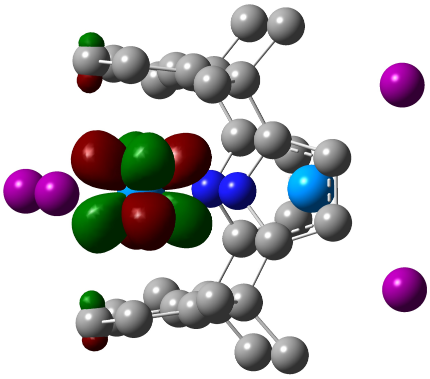

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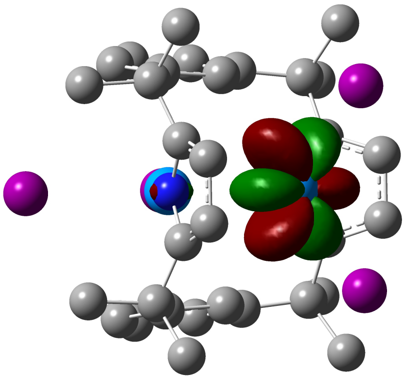

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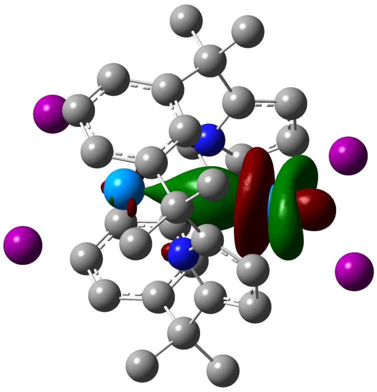

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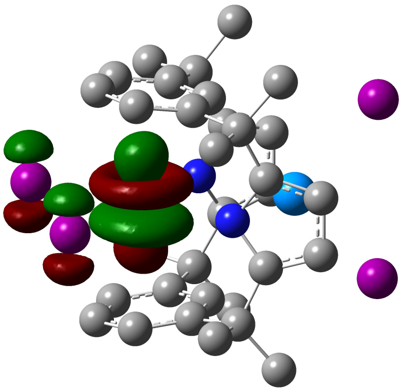

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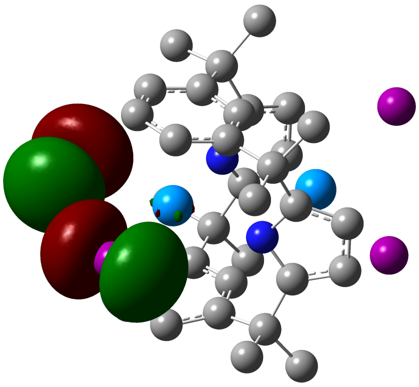

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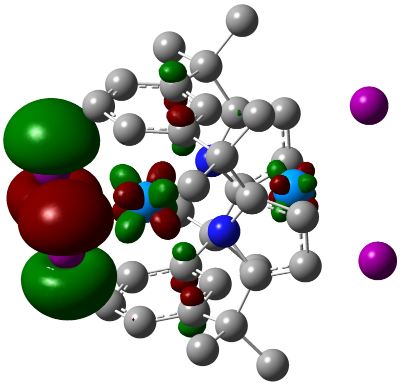

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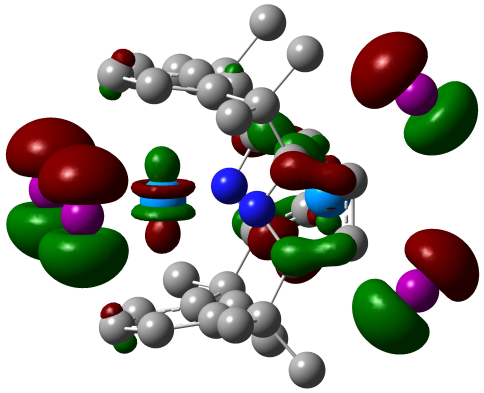

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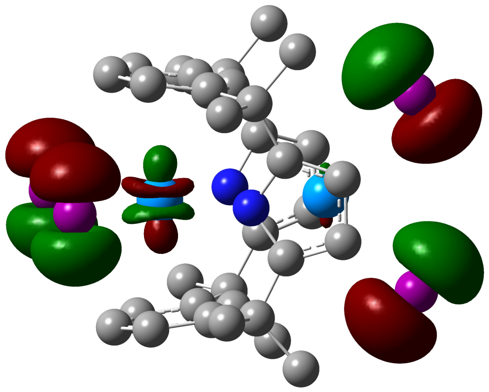

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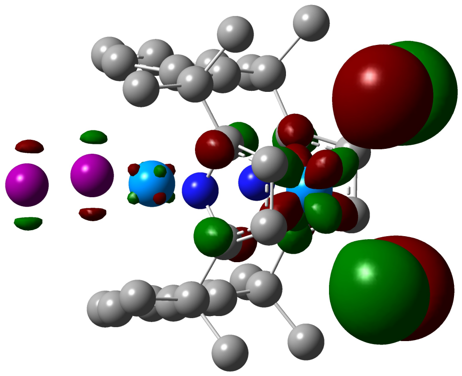

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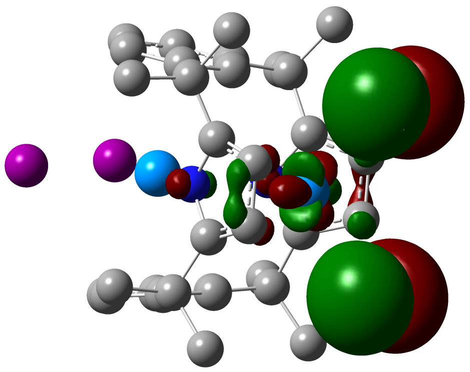

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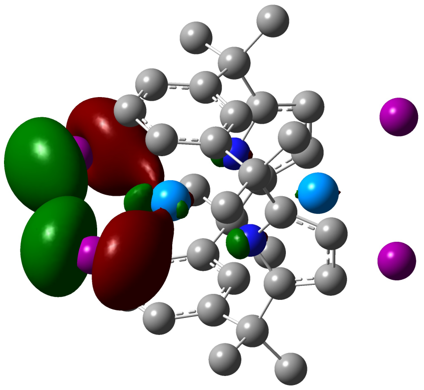

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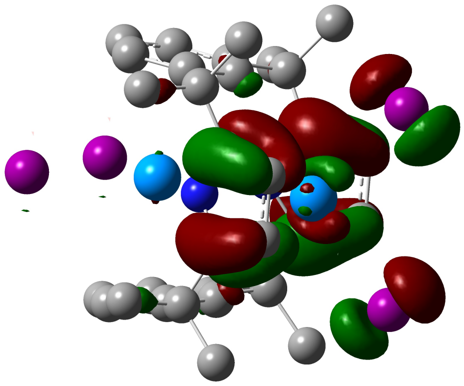

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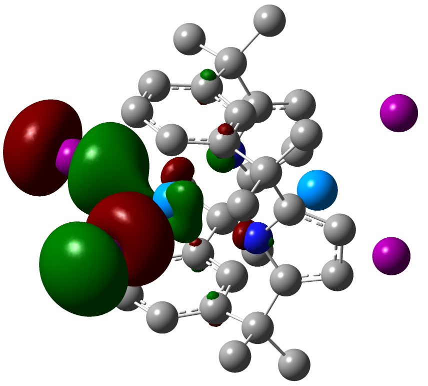

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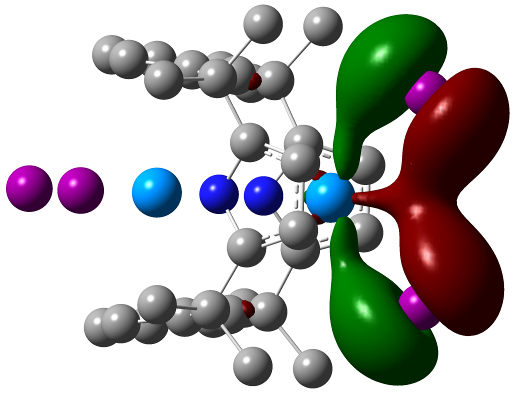

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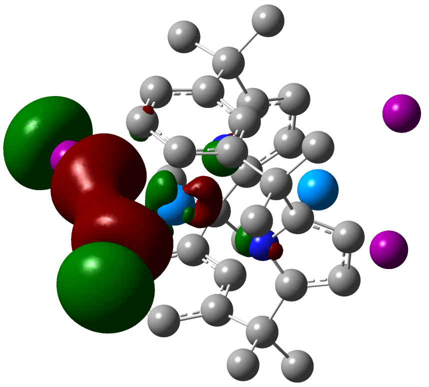

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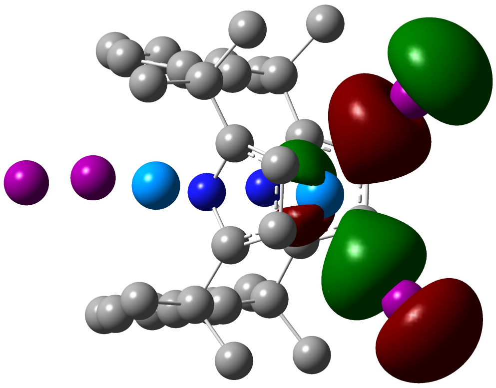

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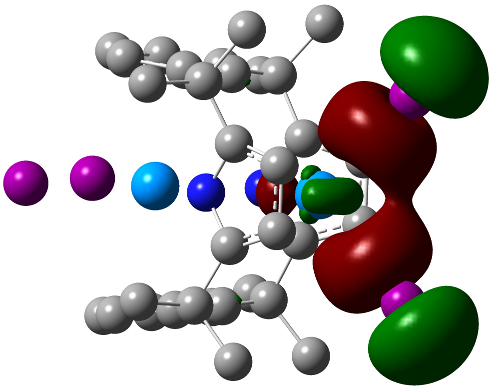

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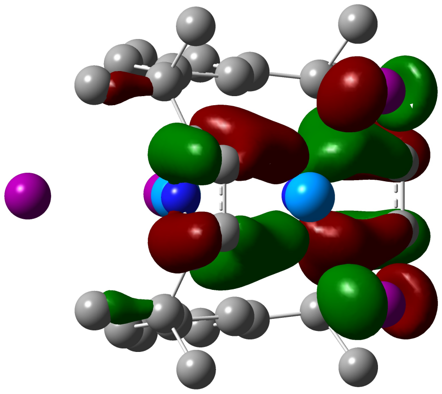

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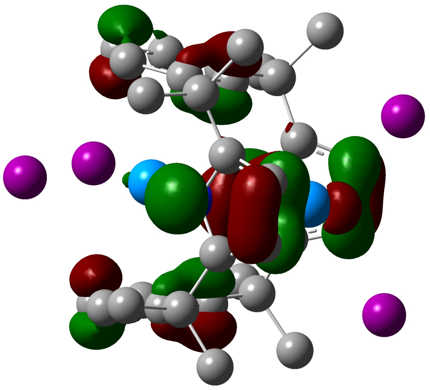
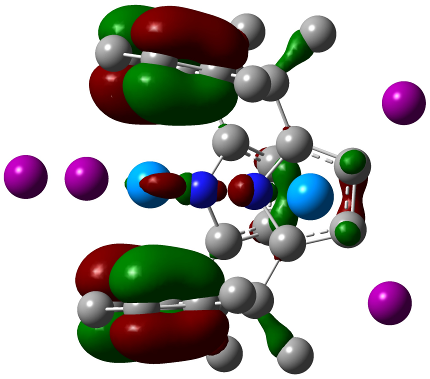
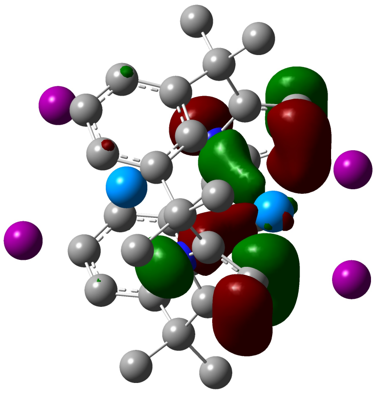


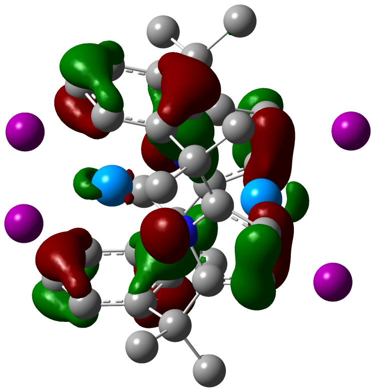
150



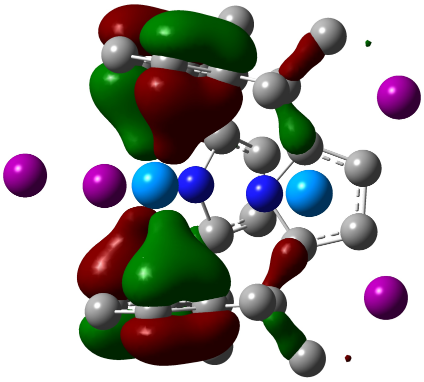
149



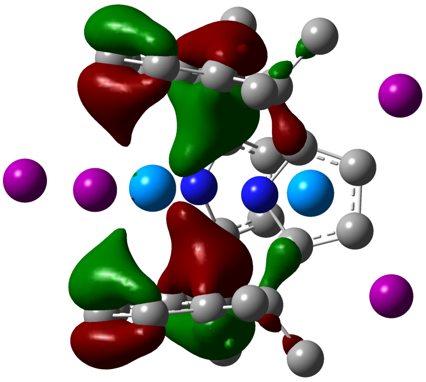
148



147



146



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Converged Cartesian coordinates for 3a.

SCF energy = -1837.8530272 H

C	-3.167258	-0.994868	-0.486234
C	-3.944447	-1.801477	-1.282713
H	-4.997085	-2.013021	-1.157649
C	-3.106446	-2.290818	-2.308580
H	-3.390611	-2.965161	-3.104158
C	-1.857189	-1.763558	-2.084582
C	-0.575175	-2.088108	-2.816165
C	-0.008480	-3.416143	-2.303839
H	-0.739320	-4.206469	-2.489249
H	0.179870	-3.390263	-1.226493
H	0.923285	-3.686505	-2.814549
C	-0.825844	-2.233321	-4.323062
H	-1.512317	-3.063225	-4.509043
H	0.111441	-2.446062	-4.847848
H	-1.270050	-1.332103	-4.751771
C	0.373532	-0.931203	-2.578129
C	1.580949	-1.064401	-1.906995
H	1.908468	-2.039856	-1.572044
C	2.379639	0.048959	-1.573884
C	1.964398	1.303871	-1.996349
H	2.535868	2.187798	-1.748056
C	0.766741	1.454222	-2.704088
H	0.445248	2.445850	-2.996798
C	-0.031555	0.359180	-2.965379
H	-0.990593	0.489973	-3.453267
C	3.603082	-0.174270	-0.705754
C	4.656050	-0.930371	-1.527424
H	4.951158	-0.342094	-2.402584
H	4.282268	-1.899835	-1.866594
H	5.549318	-1.107585	-0.922820
C	4.219767	1.145221	-0.230181
H	4.595900	1.747121	-1.065541
H	5.061068	0.922964	0.430232
H	3.502770	1.747132	0.337530
C	3.167189	-0.994871	0.486178
C	3.944544	-1.801182	1.282806
H	4.997266	-2.012402	1.157894
C	3.106592	-2.290755	2.308602
H	3.390881	-2.964971	3.104241
C	1.857188	-1.763945	2.084409
C	0.575098	-2.088762	2.815728
C	0.825580	-2.234434	4.322604
H	1.512081	-3.064357	4.508407
H	-0.111756	-2.447398	4.847205
H	1.269672	-1.333321	4.751655
C	0.008487	-3.416641	2.302909
H	0.739319	-4.207017	2.488143
H	-0.179757	-3.390415	1.225553
H	-0.923328	-3.687189	2.813429
C	-0.373575	-0.931777	2.577913
C	-1.580975	-1.064770	1.906732
H	-1.908481	-2.040122	1.571460
C	-2.379624	0.048705	1.573882
C	-1.964369	1.303482	1.996693
H	-2.535786	2.187496	1.748583
C	-0.766724	1.453617	2.704513
H	-0.445217	2.445164	2.997483
C	0.031540	0.358498	2.965533
H	0.990561	0.489130	3.453498
C	-3.603099	-0.174300	0.705744
C	-4.656170	-0.930331	1.527319
H	-4.951229	-0.342106	2.402532
H	-4.282533	-1.899879	1.866409
H	-5.549449	-1.107361	0.922673
C	-4.219598	1.145302	0.230235
H	-4.595640	1.747221	1.065624
H	-5.060938	0.923207	-0.430182
H	-3.502504	1.747127	-0.337442
N	-1.872072	-0.951661	-0.965210
N	1.871925	-0.952065	0.965037
I	-0.000068	3.459410	0.000304
U	0.000062	0.309146	-0.000022

Converged Cartesian coordinates for 4.

SCF energy = -2349.2829207 H

C	-2.306025	1.106577	0.796250
C	-2.794359	0.708974	2.031555
C	-2.794359	-0.708974	2.031555
C	-2.306025	-1.106577	0.796250
C	-2.452802	2.434038	0.090387
C	-2.566533	3.599829	1.075425
C	-3.734818	2.364421	-0.745814
C	-1.222947	2.601832	-0.772769
C	-1.213844	2.778818	-2.154871
C	0.000000	2.868320	-2.833550
C	0.000000	2.517533	-0.119656
C	-2.452802	-2.434038	0.090387
C	-3.734818	-2.364421	-0.745814
C	-2.566533	-3.599829	1.075425
C	-1.222947	-2.601832	-0.772769
C	-1.213844	-2.778818	-2.154871
C	0.000000	-2.868320	-2.833550
C	0.000000	-2.517533	-0.119656
N	-1.907145	0.000000	0.064839
I	-2.201167	0.000000	-3.976680
U	0.000000	0.000000	-1.767047
C	2.306025	1.106577	0.796250
C	2.794359	0.708974	2.031555
C	2.794359	-0.708974	2.031555
C	2.306025	-1.106577	0.796250
C	2.452802	2.434038	0.090387
C	2.566533	3.599829	1.075425
C	3.734818	2.364421	-0.745814
C	1.222947	2.601832	-0.772769
C	1.213844	2.778818	-2.154871
C	2.452802	-2.434038	0.090387
C	3.734818	-2.364421	-0.745814
C	2.566533	-3.599829	1.075425
C	1.222947	-2.601832	-0.772769
C	1.213844	-2.778818	-2.154871
N	1.907145	0.000000	0.064839
I	2.201167	0.000000	-3.976680
I	0.000000	-2.239345	4.035589
I	0.000000	2.239345	4.035589
U	0.000000	0.000000	2.001341
H	2.625175	4.544068	0.526507
H	1.723054	3.646080	1.769112
H	3.480594	3.501121	1.667952
H	3.907099	3.313742	-1.263593
H	4.589149	2.181831	-0.089087
H	3.689250	1.562286	-1.488019
H	2.625175	-4.544068	0.526507
H	3.480594	-3.501121	1.667952
H	1.723054	-3.646080	1.769112
H	3.689250	-1.562286	-1.488019
H	4.589149	-2.181831	-0.089087
H	3.907099	-3.313742	-1.263593
H	-2.625175	-4.544068	0.526507
H	-1.723054	-3.646080	1.769112
H	-3.480594	-3.501121	1.667952
H	-3.907099	-3.313742	-1.263593
H	-4.589149	-2.181831	-0.089087
H	-3.689250	-1.562286	-1.488019
H	-3.689250	1.562286	-1.488019
H	-4.589149	2.181831	-0.089087
H	-3.907099	3.313742	-1.263593
H	-2.625175	4.544068	0.526507
H	-3.480594	3.501121	1.667952
H	-1.723054	3.646080	1.769112
H	0.000000	2.472062	0.973789
H	-2.137592	2.824970	-2.713974
H	0.000000	2.971823	-3.912398
H	2.137592	2.824970	-2.713974
H	0.000000	-2.472062	0.973789
H	-2.137592	-2.824970	-2.713974
H	0.000000	-2.971823	-3.912398
H	2.137592	-2.824970	-2.713974
H	3.151000	-1.351200	2.822249
H	3.151000	1.351200	2.822249
H	-3.151000	-1.351200	2.822249
H	-3.151000	1.351200	2.822249

References

1. T. Cantat, B. L. Scott and J. L. Kiplinger, *Chemical Communications*, 2010, 46, 919.
2. C. D. Carmichael, N. A. Jones and P. L. Arnold, *Inorganic Chemistry*, 2008, 47, 8577.
3. S. M. Mansell, B. F. Perandones and P. L. Arnold, *Journal of Organometallic Chemistry*, 2010, 695, 2814.
4. J. L. Sessler, W.-S. Cho, V. Lynch and V. Král, *Chemistry � A European Journal*, 2002, 8, 1134.
5. S. Ilango, B. Vidjayacoumar and S. Gambarotta, *Dalton Transactions*, 2010, 39, 6853.
6. M. R. Spirlet, J. Rebizant, C. Apostolidis and B. Kanellakopulos, *Acta Cryst. C*, 1992, 48, 2135.
7. C. R. Graves, E. J. Schelter, T. Cantat, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2008, 27, 5371.
8. I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angewandte Chemie International Edition*, 2003, 42, 814.
9. I. Korobkov, S. Gambarotta, G. P. A. Yap, L. Thompson and P. J. Hay, *Organometallics*, 2001, 20, 5440.
10. M. Brookhart, M. L. H. Green and G. Parkin, *Proceedings of the National Academy of Sciences*, 2007, 104, 6908.
11. F. G. N. Cloke, *Chemical Society Reviews*, 1993, 22, 17.
12. F. G. N. Cloke and P. B. Hitchcock, *Journal of the American Chemical Society*, 1997, 119, 7899.
13. M. N. Bochkarev, *Chemical Reviews*, 2002, 102, 2089.
14. I. Korobkov, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2001, 20, 2552.
15. P. L. Arnold, N. A. Potter, C. D. Carmichael, A. M. Z. Slawin, P. Roussel and J. B. Love, *Chemical Communications*, 2010, 46, 1833.
16. O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green and N. Hazari, *Science*, 2006, 311, 829.
17. O. Summerscales and F. G. Cloke, in *Organometallic and Coordination Chemistry of the Actinides*, ed. T. Albrecht-Schmitt, Springer Berlin Heidelberg, 2008, pp. 87.
18. D. L. Clark, S. K. Grumbine, B. L. Scott and J. G. Watkin, *Organometallics*, 1996, 15, 949.
19. J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, 114, 10811.
20. S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein and K. Meyer, *J. Am. Chem. Soc.*, 2008, 130, 12536.
21. J. Plíva, J. W. C. Johns and L. Goodman, *Journal of Molecular Spectroscopy*, 1990, 140, 214.
22. S. G. Kukolich, *Journal Of The American Chemical Society*, 1995, 117, 5512.
23. P. L. Arnold, S. M. Mansell, L. Maron and D. McKay, *Nat. Chem.*, 2012, 4, 668.
24. W. G. Van der Sluys, C. J. Burns, J. C. Huffman and A. P. Sattelberger, *Journal Of The American Chemical Society*, 1988, 110, 5924.
25. M. Cesari, U. Pedretti, Z. Zazzetta, g. Lugli and W. Marconi, *Inorganica Chimica Acta*, 1971, 5, 439.
26. P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood and H. Zhang, *Inorg. Chim. Acta*, 1987, 139, 13.
27. W. J. Evans, S. A. Kozimor, J. W. Ziller and N. Kaltsoyannis, *Journal Of The American Chemical Society*, 2004, 126, 14533.
28. K. R. D. Johnson and P. G. Hayes, *Chemical Society Reviews*, 2013, 42, 1947.
29. D. M. Barnhart, D. L. Clark, S. K. Grumbine and J. G. Watkin, *Inorganic Chemistry*, 1995, 34, 1695.
30. B. D. Stubbert and T. J. Marks, *Journal of the American Chemical Society*, 2007, 129, 6149.
31. R. J. Butcher, D. L. Clark, S. K. Grumbine and J. G. Watkin, *Organometallics*, 1995, 14, 2799.
32. T. M. Gilbert, R. R. Ryan and A. P. Sattelberger, *Organometallics*, 1988, 7, 2514.

33. I. Korobkov, B. Vidjayacoumar, S. I. Gorelsky, P. Billone and S. Gambarotta, *Organometallics*, 2010, 29, 692.
34. K. C. Jantunen, C. J. Burns, I. Castro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, F. L. Taw and J. L. Kiplinger, *Organometallics*, 2004, 23, 4682.
35. I. Korobkov, A. Arunachalampillai and S. Gambarotta, *Organometallics*, 2004, 23, 6248.
36. W. Ren, X. Deng, G. Zi and D.-C. Fang, *Dalton Transactions*, 2011, 40, 9662.
37. W. Ren, G. Zi, D.-C. Fang and M. D. Walter, *Chemistry � A European Journal*, 2011, 17, 12669.
38. C. A. Cruz, D. J. H. Emslie, C. M. Robertson, L. E. Harrington, H. A. Jenkins and J. F. Britten, *Organometallics*, 2009, 28, 1891.
39. M. J. Monreal, S. I. Khan, J. L. Kiplinger and P. L. Diaconescu, *Chemical Communications*, 2011, 47, 9119.
40. C. Adamo and V. Barone, *J. Chem. Phys*, 1999, 110, 6158.
41. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, M. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. E. Gomperts, O. Stratmann, A. J. Yazyev, R. Austin, C. Cammi, J. W. Pomelli, R. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
42. X. Y. Cao and M. Dolg, *J. Mol. Struct. (TheoChem)*, 2004, 673, 203.
43. A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, 80, 1431.
44. J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, 114, 3408.
45. D. A. Pantazis and F. Neese, *J. Chem. Theory Comput.*, 2011, 7, 677.
46. D. A. Pantazis, Personal Communication.
47. T. A. Keith, TK Gristmill Software, 2013.