Carbene Complexes of Neptunium

Conrad A. P. Goodwin,1,2 Ashley J. Woole,1 Jesse Murillo,2 Erli Lu,1 Josef T. Boronski,1 Brian L. Scott,3 Andrew J. Gaunt,2* and Stephen T. Liddle1*

1 Department of Chemistry and Centre for Radiochemistry Research, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK.
2 Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.
3 Materials Physics & Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545 (USA).

*To whom correspondence should be addressed: gaunt@lanl.gov; steve.liddle@manchester.ac.uk

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General considerations

Caution! Compounds of $^{237}$Np radionuclide decay principally through $\alpha$-emission ($Q_\alpha = 4.958$ MeV, $t_{1/2} = 2.144(7) \times 10^6$ years)\(^1\) with a relatively high specific-activity ($a = 26.04$ MBq g\(^{-1}\)) in comparison to $^{238}$U and $^{232}$Th requiring analyses of hazards and implementation of additional safety controls. $^{237}$Np establishes a secular equilibrium (asymptotical concentration at 34.6 ppb) with the potent $\beta$-emitter $^{233}$Pa ($t_{1/2} = 26.975(13)$ days, $a = 777$ TBq g\(^{-1}\)) and associated $\gamma$-ray emission (most significant $\gamma$-branching ratio for $^{233}$Pa is 39% for the 312 keV line). Hence, all studies that involved manipulation of $^{237}$Np material were conducted in a specialist transuranium radiological designated area equipped with high efficiency particulate in air (HEPA) filtered hoods and in negative pressure gloveboxes. Safety controls included continuous air monitoring for airborne $\alpha$-emitting particles and use of hand-held radiation monitoring equipment. Entrance to the laboratory space was controlled with a hand and foot radiation monitoring instrument and a full body personal contamination monitoring station. The handling of free-flowing solids was restricted to be within negative pressure gloveboxes equipped with HEPA filters. In addition to standard laboratory PPE, aqueous solutions were handled using multiple layers of gloves (of a material compatible with the chemicals being handled) combined with DuPont™ Tyvek® 400 sleeves to provide overlapping coverage of the arms. Due to these radiological hazards, elemental analyses were not possible.

Unless otherwise described, all syntheses and manipulations were conducted under UHP argon (AirGas) or UHP helium (AirGas) with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques (employing a negative-pressure, transuranium-capable, MBraun LabMaster, helium atmosphere glovebox where required). 4 Å molecular sieves were activated by heating for 36 hrs at 200 °C, $10^{-4}$ mbar. Anhydrous DME (Sigma Aldrich) was transferred onto activated 4 Å molecular sieves, stored for 1 week prior to use, and degassed before use. Anhydrous Et\(_2\)O containing BHT (100 ppm, Sigma Aldrich) was degassed, distilled from Na\(_2\)Ph\(_2\)CO, stored over
activated 4 Å molecular sieves for 1 week and degassed again before use. \(d_8\)-THF, \(d_6\)-benzene, anhydrous \(n\)-hexane and anhydrous toluene (Sigma Aldrich) were stored over activated 4 Å molecular sieves and degassed before use. All solvents were tested with a dilute THF solution of \(\text{Na}_2\text{Ph}_2\text{CO}\) (150 mg \(\text{Ph}_2\text{CO}\) in 20 mL of THF with an excess of Na metal) such that ethereal solvents (including \(d_8\)-THF) required 1 drop / mL to retain purple coloration and hydrocarbon solvents (including \(d_6\)-benzene) required 1 drop / 2 mL.

The compounds \([\text{Li}_2\{\text{C}(\text{PPh}_2\text{NSiMe}_3)_2\}\}_2\) \(([\text{Li}_2\text{BIPM}^{\text{TMS}}]_2)\), \(^2,^3\) \([\text{Rb}((\text{BIPM}^{\text{TMS}})_2)]\), \(^4\) \([\text{Np}^{IV}\text{Cl}_4(\text{DME})_2]\), \(^5\) \([\text{Np}^{III}\text{I}_3(\text{THF})_4]\), \(^6\) 1,3,4,5-tetramethylimidazol-2-thione \((\text{IMe}_4=S)\), \(^7\) 1,3,4,5-tetramethylimidazol-2-ylidene \((\text{IMe}_4)\), \(^8\) benzyl potassium, \(^9\) and \([(\text{BIPM}^{\text{TMS}})_2\text{UI}_2(\text{THF})]\) \(^10\) were prepared as previously described. \([\text{U}^{IV}\text{Cl}_4(\text{DME})_2]\) was prepared by dissolving \(\text{UCl}_4\) in DME prior to use. \([\text{CeI}_3(\text{THF})_4]\) was prepared \textit{in situ} by stirring \(\text{CeI}_3\) in THF prior to use.

The glovebox atmosphere was maintained with a standalone Vacuum Atmosphere Genesis™ oxygen and moisture removal system, and atmosphere suitability was verified using a dilute toluene solution of \([\text{Ti}(\text{Cp})_2(\mu-\text{Cl})]_2\) (200 mg of commercial \([\text{Ti}(\text{Cp})_2(\text{Cl})_2]\) reduced over an excess of Zn powder in 20 mL of toluene, and filtered) prior to any manipulations, such that the residue dried to a dark green color each time (a color change to yellow or orange indicates decomposition of the Ti test compound and that atmospheric \(\text{O}_2/\text{H}_2\text{O}\) levels are too high to be conducive to this chemistry, requiring removal to lower levels before performing reactions/exposing reagents to the glovebox atmosphere). All glassware, and glass-fiber filter discs, was stored in a vacuum oven \((>150 \, ^\circ\text{C})\) for 24 hrs prior to being brought into the glovebox, and FEP (fluorinated ethylene propylene) NMR tube liners were brought into the glovebox \textit{via} overnight or multi-hr vacuum cycles in the antechamber port.

Crystals for single-crystal X-ray diffraction studies were mounted either in Fomblin oil on a micromount \((2)\) or in Paratone-N or NVH oil inside 0.5 mm quartz capillaries (Charles Supper) \((1,\)
The quartz capillaries were inserted through silicone stoppers and placed inside test tubes to allow handling inside the transuranium glovebox while mounting crystals without contaminating the exterior surface of the capillary. The capillaries were then cut with nail clippers to appropriate size for mounting on a goniometer. The ends of the cut capillaries were sealed with hot capillary wax before being removed from the glovebox for coating with clear nail varnish (Hard as Nails™) to provide shatter-resilience. During the clipping and wax sealing steps, care must be taken to avoid the capillary touching any contaminated surfaces (this is achieved by the introduction of fresh petri dishes, forceps, clippers, and wax, as needed in conjunction with careful handling techniques to avoid contamination transfer). Following removal from the glovebox, the exterior surfaces of the capillaries were monitored with α-particle detection instruments prior to transport to the X-ray diffraction laboratory.

Solution phase electronic absorption spectra were collected at ambient temperature using a Varian Cary 6000i UV/vis/NIR spectrometer. The solution was contained in a low volume (1 mL) screw-capped quartz cuvette (1 cm path length) that was loaded in a transuranium glovebox using Parafilm™ to protect the exterior surface of the cuvette and cap from radioactive contamination (Parafilm™ is removed in a fume hood and exterior surfaces of the cuvettes were monitored with α-particle detection instruments prior to data acquisition). Data was collected from 40,000 to 6,250 cm⁻¹ (250 to 1,600 nm).

For NMR spectroscopy, a solution was loaded into a fresh FEP NMR tube liner that was protected from surface contamination with Parafilm™ while inside a transuranium glovebox. The liner was sealed with two PTFE plugs, brought out of the glovebox and verified to be free of surface contamination after the Parafilm™ was removed (using α-particle detection instruments and a Ludlum 3030E instrument to detect both α- and β-particles on smear surveys of the exterior surfaces) and the liner loaded into a J. Young tap appended 5 mm NMR tube. The headspace was then
evacuated and refilled with He to provide an inert atmosphere headspace above the sample and exterior NMR tube/cap surfaces surveyed to check for contamination before transport to the NMR laboratory. NMR data collection was performed on a 400 MHz Bruker Advance II at room temperature unless otherwise indicated. The spectra were referenced to internal solvent residuals ($^1$H and $^{13}$C) or externally to 10% TMS in CDCl$_3$ ($^{31}$P and $^{77}$Se) via Equation S1, which is the IUPAC recommended convention.

$$\Delta (Hz) = \frac{SR^{1H}}{SF^{1H}} \times SF^{NUC}$$

**Equation S1.** Where $SR^{1H}$ is the spectrum reference frequency (in Hz) of a reference $^1$H NMR spectrum collected with TMS set to 0 ppm collected under the same experimental conditions; $SF^{1H}$ is the spectrometer frequency (in MHz) for the $^1$H nucleus; $SF^{NUC}$ is the spectrometer frequency (in MHz) of the nucleus in question. The answer is given in Hz.

Where $\varepsilon$ values are reported for molecular complexes below there is a modest error due to the small quantities of weighed material, as is nearly always the case when these values are reported from synthetic chemistry (as opposed more rigorous and quality-assured analytical determination methods that are generally unfeasible to apply to non-aqueous synthetic chemistry). Nonetheless, the $\varepsilon$ values we determine herein are still useful metrics that we determine based on weight of crystal dissolved and solvent weight, but should not be used as analytically to assay these compounds.

ATR-IR spectra of 4Ce and 6Ce were recorded on a Bruker Alpha spectrometer with a Platinum-ATR module in the glovebox.

CHN microanalyses on 4Ce and 6Ce were carried out by London Metropolitan University.
**Synthesis of \([(\text{BIPM}^{\text{TMS}}\text{H})\text{Np}^{\text{III}}(\text{Cl})(\mu-\text{Cl})_2\text{Np}^{\text{III}}\{\mu-\text{Cl}\text{Li(DME)}(\text{OEt}_2)\}](\text{BIPM}^{\text{TMS}}\text{H})) (1)\)**

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, solid \([\text{Np}^{\text{IV}}\text{Cl}_4(\text{DME})_2]\) (37.0 mg, 66 \(\mu\)mol) was mixed with 0.5 equiv of solid \([\text{Li}_2(\text{BIPM}^{\text{TMS}})]_2\) (37.7 mg, 33 \(\mu\)mol) and cooled to \(-35^\circ\text{C}\) in the glovebox freezer. \(\text{Et}_2\text{O}\) (1.5 mL) and toluene (1.5 mL) were mixed together and also cooled to \(-35^\circ\text{C}\). Immediately upon removal from the freezer, the solvent mixture was added to the solid mixture and stirred for 1 minute. No color change was apparent and the mixture was placed back in the freezer at \(-35^\circ\text{C}\) for 15 minutes. The yellow suspension with visible chunks of undissolved materials was removed from the freezer and stirred for 2 minutes, then placed back in the freezer at \(-35^\circ\text{C}\) for 15 minutes. The yellow/brown suspension was removed from the freezer and stirred for 3 minutes (still with visible undissolved white-ish solid – presumed \([\text{Li}_2(\text{BIPM}^{\text{TMS}})]_2\) or possible LiCl salt elimination). The mixture was placed back in the freezer at \(-35^\circ\text{C}\) for 150 minutes. The resultant yellow/orange suspension was removed from the freezer and stirred for 20 minutes resulting in an orange suspension which was then allowed to stir further at room temperature overnight. Volatiles were removed \textit{in vacuo} from the orange solution over a solid yellow/off-white powder. The solids were extracted with toluene (3 mL) to separate from LiCl, filtered through Celite packed on top of a glass fiber filter circle in a glass pipette to afford a deep orange filtrate, that was then concentrated \textit{in vacuo} to \(~1\text{ mL}\) in volume. The solution was stored in the glovebox freezer at \(-35^\circ\text{C}\) overnight. A tiny wisp of powder was visible in the bottom of the vial, so the still deep orange solution was layered with \(\text{Et}_2\text{O}\) (2 mL) and stored in the glovebox freezer at \(-35^\circ\text{C}\) for 3 days. No further precipitate and no crystals were evident. Volatiles were removed \textit{in vacuo} and the resultant solid dissolved in \(\text{Et}_2\text{O}\) (1 mL) to afford a deep orange solution. After storage in the glovebox freezer at \(-35^\circ\text{C}\) for 3 days, several orange block-shaped crystals had deposited, which were determined by single-crystal X-ray diffraction to be \textbf{1}. 

S6
Synthesis of [(BIPMTMS)UIV(µ-Cl)₆Li(DME)]₂ (2)

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, Et₂O (1 ml) was added to [UIVCl₄(DME)]₂ (30 mg, 54 µmol) and stored at -35 °C for 1 hr. In a separate 20 mL glass scintillation vial with a PTFE-coated stirrer bar, toluene (1 ml) was added to [Li₂(BIPMTMS)]₂ (61.1 mg, 107 µmol) and stored at -35 °C for 1 hr. The toluene solution of [Li₂(BIPMTMS)]₂ was then added to the Et₂O solution of [UIVCl₄(DME)]₂ to afford a pale yellow suspension. This suspension was stood at room temperature without stirring for 72 hrs, after which time the brown crystals of 2 were deposited in the vial. The identity of 2 was confirmed by single-crystal X-ray diffraction studies. Yield: 22 mg, 36%. Since the sole purpose of this synthesis was to scope the analogous Np preparation no data other than the single-crystal X-ray diffraction molecular structure were collected.

Synthesis of [(BIPMTMSH)CeIII(I)₂(THF)] (3Ce)

Complex 3Ce was synthesized as previously reported,12 with some modifications. In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, CeI₃ (23 mg, 44 µmol) was stirred with THF (1.5 mL) at room temperature for 5 minutes which gave a turbid colorless solution with white solids. Solid [Rb(BIPMTMSH)] (28.3 mg, 44 µmol, 1 equiv.) was added in a 2 portions which caused the mixture to immediately turn pale yellow with concomitant dissolution of the white solids, followed by rapid precipitation of fine white solids (presumably RbI). The mixture was stirred for 10 minutes and then reduced to dryness in vacuo. The yellow solids were suspended in toluene (1 mL) and warmed gently (45 °C on a hot plate). Once cooled to room temperature, the mixture was centrifuged (5 minutes, 5,000 rpm) and filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette. The yellow solution was concentrated to the point of incipient crystallization, warmed gently (45 °C on a hot plate) and then stored at room temperature overnight (16 hrs). Several flaky colorless crystals grew and these were inspected by single-crystal X-ray diffraction and found to be 3Ce. Characterization data on this material matched the previously reported data.12 The poor quality of the crystals meant that this motif was not extended to studies with Np.
**Synthesis of [(BIPMTMSH)CeII(I)2(PMe4)] (4Ce)**

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, CeI₃ (23 mg, 44 µmol) was stirred with THF (1.5 mL) at room temperature for 5 minutes which gave a turbid colorless solution with white solids. Solid [Rb(BIPMTMSH)] (28.3 mg, 44 µmol, 1 equiv.) was added in 2 portions which caused the mixture to immediately turn pale yellow with concomitant dissolution of the white solids, followed by rapid precipitation of fine white solids (presumably RbI). The mixture was stirred for 10 minutes and then reduced to dryness *in vacuo*. The yellow solids were suspended in toluene (1.5 mL) and warmed gently (45 °C on a hot plate). Once cooled to room temperature, the mixture was centrifuged (5 minutes, 5,000 rpm) and filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette. Solid PMe₄ (5.2 mg, 42 µmol, 0.95 equiv.) was added to the yellow solution, which upon gentle agitation became more intensely yellow as the PMe₄ dissolved. Manual agitation for 2 minutes resulted in the precipitation of a substantial quantity of pale yellow solids. The mixture was heated strongly (130 °C on a hot plate) and gently refluxed inside the vial for ~2 minutes which resulted in most of the solids redissolving. The yellow solution was then filtered into a fresh 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette while still warm and then stored at room temperature overnight (16 hrs). Large yellow blocks formed and these were inspected by single-crystal X-ray diffraction and found to be 4Ce. Anal. Calcd for C₃₈H₅₁Ce₂N₄P₂Si₂: C, 42.42; H, 4.78; N, 5.21%. Found: C, 42.79; H, 4.94; N, 5.08%. ¹H NMR (d₈-THF, 400.13 MHz, 298 K): δ 1.21 (br s, ν½ = 370 Hz), 3.23 (br s, ν½ = 47 Hz), 5.58 (br s, ν½ = 180 Hz), 6.69 (br s, ν½ = 29 Hz), 6.99 (br s, ν½ = 40 Hz). These resonances could not be assigned due to their broad natures and the presence of contaminant BIPMTMSH₂ (at −0.15 ppm) and toluene giving overlapping peaks. The low solubility of 4Ce precluded the measurement of its magnetic moment by the Evans’ method and ¹³C and ²⁹Si NMR measurements. ³¹P{¹H} NMR (d₈-THF, 161.94 MHz, 298 K): δ −17.94 (br) ppm. ATR-IR ν/cm⁻¹: 3057 (w), 2944 (2), 14.36 (s), 1372 (m), 1261 (m), 1143 (s), 1100 (m), 1066 (s), 999 (w), 936 (m), 833 (s), 782 (w), 762 (m), 742 (m), 723 (m), 695 (m), 659 (m), 612 (m), 591 (m), 549 (m), 509 (w), 466 (w), 440 (w).
Synthesis of \([(\text{BIPM}^\text{TMS})\text{Ce}^{\text{III}}(\text{I})(\text{DME})]\) (5Ce)

In a modification of the previously reported procedure, a 20 mL glass scintillation vial with a PTFE-coated stirrer bar and \(\text{CeI}_3\) (23 mg, 44 \(\mu\)mol) was stirred with THF (1.5 mL) at room temperature for 5 minutes which gave a turbid colorless solution with white solids. Solid \([\text{Rb(BIPM}^\text{TMS} \text{H})]\) (28.3 mg, 44 \(\mu\)mol, 1 equiv.) was added in a 2 portions which caused the mixture to immediately turn pale yellow with concomitant dissolution of the white solids, followed by rapid precipitation of fine white solids (presumably RbI). The mixture was stirred for 5 minutes and then dried \textit{in vacuo} to a pale yellow powder. DME (1.5 mL) was added, and then solid KBn (5.7 mg, 44 \(\mu\)mol, 1 equiv.) was added to the pale yellow suspension in several portions which caused the mixture to immediately turn from pale yellow to a slightly more intense yellow – the vivid orange color of the KBn discharged rapidly as each portion dissolved. The cloudy mixture was stirred for a further 5 minutes and then reduced to a yellow powder \textit{in vacuo}. Toluene (1.5 mL) and DME (3 drops) were added to the yellow solids, which was then warmed gently (45 °C on a hot plate). Once cooled to room temperature, the mixture was centrifuged (5 minutes, 5,000 rpm) and filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette. The yellow solution was concentrated to \(\sim 0.5 \text{ mL}\) which caused a large quantity of pale yellow solids to form on the vial walls. The mixture was heated strongly (130 °C on a hot plate) and gently refluxed inside the vial for \(\sim 2 \text{ minutes}\) which resulted in all of the solids redissolving. The yellow solution was stored at room temperature overnight (16 hrs). Large yellow blocks formed and these were inspected by single-crystal X-ray diffraction and found to be 5Ce. Characterization data on this material matched the previously reported data.

Synthesis of \([(\text{BIPM}^\text{TMS})\text{Ce}^{\text{III}}(\text{I})(\text{Me}_4^\text{I})_2]\) (6Ce)

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, \(\text{CeI}_3\) (23 mg, 44 \(\mu\)mol) was stirred with THF (1.5 mL) at room temperature for 5 minutes which gave a turbid colorless solution with white solids. Solid \([\text{Rb(BIPM}^\text{TMS} \text{H})]\) (28.3 mg, 44 \(\mu\)mol, 1 equiv.) was added in a 2 portions which caused the mixture to immediately turn pale yellow with concomitant dissolution of the white solids,
followed by rapid precipitation of fine white solids (presumably RbI). The mixture was stirred for 10 minutes and then solid KBn (5.7 mg, 44 µmol, 1 equiv.) was added in several portions which caused the mixture to immediately turn from pale yellow to a slightly more intense yellow – the vivid orange color of the KBn discharged instantaneously as each portion dissolved. The cloudy mixture was stirred for a further 15 minutes and then reduced to a yellow powder in vacuo. The yellow solids were suspended in toluene (1.5 mL) and warmed gently (45 °C on a hot plate). Once cooled to room temperature, the mixture was centrifuged (5 minutes, 5,000 rpm) and filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette. Solid 1Me4 (10 mg, 78 µmol, 1.78 equiv.) was added to the yellow solution, which upon gentle agitation became more intensely yellow as the 1Me4 dissolved. Manual agitation for 2 minutes resulted in the precipitation of a substantial quantity of yellow solids. The mixture was heated strongly (130 °C on a hot plate) and gently refluxed inside the vial for ~2 minutes which resulted in all of the solids redissolving. The yellow solution was stored at room temperature overnight (16 hrs). Large yellow blocks formed and these were inspected by single-crystal X-ray diffraction and found to be 6Ce. Despite multiple attempts, satisfactory elemental analyses data could not be obtained, attributed to incomplete combustion due to the instrument temperature limit. 1H NMR (d8-THF, 400.13 MHz, 298 K): δ –3.78 (br s, ν½ = 310 Hz, 4 H, BIPM TMS Ar p–CH×4), 1.86 (br s, ν½ = 19 Hz, 18 H, BIPM TMS Si(CH3)3 × 2), 6.11 (br s, ν½ = 71 Hz, 8 H, BIPM TMS Ar o/m–CH × 8), 6.66 (br s, ν½ = 26 Hz, 8 H, BIPM TMS Ar o/m–CH × 4). The low solubility of 6Ce precluded the measurement of its magnetic moment by the Evans’ method and 13C and 29Si NMR measurements. 31P{1H} NMR (d8-THF, 161.94 MHz, 298 K): δ –37.04 (br) ppm. ATR-IR ν/cm–1: 3049 (w), 2947 (w), 1434 (m), 1368 (m), 1236 (s), 1102 (m), 1090 (m), 1062 (s), 826 (s), 763 (m), 750 (m), 731 (m), 698 (m), 649 (m), 601 (m), 548 (m), 509 (m), 467 (m), 435 (m).

**Synthesis of [(BIPM TMSH)NpIII(I)2(1Me4)] (4Np)**

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, solid [Rb(BIPM TMSH)] (21 mg, 33 µmol, 1 equiv.) was added in 2 portions to a turbid orange suspension of [NpIII3(THF)4] (30 mg, 33
µmol) in THF (1.5 mL) at room temperature, which caused the mixture to immediately turn cloudy yellow with concomitant precipitation of fine white solids (presumably Rbi). The mixture was stirred for 30 minutes and then reduced to dryness in vacuo. The orange solids were washed with hexane (1 × 4 mL) and dried again to an orange powder. Toluene (3 mL) was added and the mixture was stirred for several minutes then filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette to give an orange solution. Solid 1Me4 (4.1 mg, 33 µmol, 1 equiv.) was added which caused the orange solution to rapidly turn red and somewhat cloudy as the solid 1Me4 dissolved with manual agitation. The mixture was concentrated to 2 mL which caused some colorless solids to precipitate, and the solution was filtered again as above into a 4 mL glass vial. Storage of this red solution at −35 °C for 48 hrs caused more colorless solids to form, and the solution was filtered again as above into a 4 mL glass vial. The solution was then concentrated to 0.5 mL and layered with hexane (0.5 mL). Storage of the layered solution for 15 minutes at room temperature resulted in large ruby-red planks of 4Np to form. The crystals were washed with hexane at room temperature (2 × 2 mL) to give 4Np as flowing red planks. Yield: 6.2 mg, 16%. 1H NMR (d6-benzene, 400.13 MHz, 298 K): δ −54.61 (br s, ν½ = 17 Hz, 1 H, BIPMTMSH ipso-C(H)), −4.79 (s, 18 H, BIPMTMSH Si(CH3)3 × 2), 1.82 (s, 6 H, 1Me4 C(CH3) × 2), 10.61 (s, 6 H, 1Me4 N(CH3) × 2). 13C{1H} NMR (d6-benzene, 100.62 MHz, 298 K): δ −27.69 (s, BIPMTMSH Si(CH3)3 × 2), 4.35 (t, J = 1.7 Hz, BIPMTMSH ipso-C), 11.80 (s, 1Me4 N(CH3) × 2) ppm. The triplet at 4.35 ppm is only tentatively assigned due to the unusual chemical shift. Peaks attributable to the 1Me4 C(CH3) and C(CH3) resonances could not be located, nor could peaks be assigned that were definitively due to complexed BIPMTMSH, rather than trace H2BIPMTMS. 31P{1H} NMR (d6-benzene, 161.94 MHz, 298 K): δ −488.05 ppm. UV-vis-NIR (toluene): λmax (cm⁻¹; ε) 363 (27,533, 1,490), 429 (23,310, 1,270), 568 (17,618, 210), 619 (16,150, 70), 674 (14,846, 40), 802 (12,466, 50), 868 (11,526, 50), 922 (10,844, 20), 946 (10,571, 20), 965 (10,361, 20), 1,001 (9,986, 30), 1,008 (9,921, 30), 1,031 (9,699, 20), 1,046 (9,564, 20), 1,144 (8,740, 10), 1,152 (8,678, 10), 1,210 (8,262, 10), 1,335 (7,490, 20), 1,352 (7,398, 30), 1,412 (7,084, 20) nm.
Synthesis of [(BIPM<sub>TMS</sub>)Np<sup>III</sup>](1)(DME) (5Np)

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, solid [Rb(BIPM<sup>TMS</sup>H)] (28.3 mg, 44 µmol, 1 equiv.) was added in 2 portions to a turbid orange suspension of [Np<sup>III</sup>]<sub>3</sub>(THF)<sub>4</sub> (40 mg, 44 µmol) in THF (1.5 mL) at room temperature, which caused the mixture to immediately turn orange, and then cloudy and yellow with concomitant precipitation of fine white solids (presumably Rbl). The mixture was stirred for 5 minutes and then dried in vacuo to an orange powder. DME (1.5 mL) was added, and then solid KBn (5.7 mg, 44 µmol, 1 equiv.) was added to the orange suspension in several portions which caused the mixture to immediately turn from orange to red/purple – the vivid orange color of the KBn discharged instantaneously as each portion dissolved. The cloudy mixture was stirred for a further 5 minutes and then reduced to a red powder in vacuo. Toluene (1.5 mL) and DME (3 drops) were added to the orange solids and the mixture was stirred for 1 minute at room temperature. The mixture was filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette, then concentrated to ~0.3 mL in vacuo without agitation which caused a red/orange seed crystal to form at the solution surface. The solution was then left at room temperature for 20 minutes which caused a single large crop of orange parallelepiped-shaped plates of 5Np to grow. Yield: 17.4 mg, 37%.

<sup>1</sup>H NMR (<sup>d</sup><sub>6</sub>-benzene, 400.13 MHz, 298 K): δ −6.56 (br s, ν<sub>½</sub> = 34 Hz, 18 H, BIPM<sub>TMS</sub>Si(CH<sub>3</sub>)<sub>3</sub> × 2), 1.74 (br s, ν<sub>½</sub> = 98 Hz, 6 H, DME O(CH<sub>3</sub>)<sub>2</sub> × 2) ppm. Broad features around 6.61 (ν<sub>½</sub> = 311 Hz), 9.43 (ν<sub>½</sub> = 488 Hz), and 14.56 (ν<sub>½</sub> = 575 Hz) ppm could be BIPM<sub>TMS</sub>Ph peaks or the DME C<sub>2</sub>H<sub>4</sub> peak, but we could not definitively assign these given the significant broadening which affects the reliability of integration. <sup>13</sup>C<sup>1</sup>H NMR (d<sub>6</sub>-benzene, 100.62 MHz, 298 K): δ −26.59 (s, BIPM<sub>TMS</sub>Si(CH<sub>3</sub>)<sub>3</sub> × 2) ppm. No other peaks unattributed to BIPM<sub>TMS</sub>H<sub>2</sub> or a BIPM<sub>TMS</sub>H species could be definitively assigned. <sup>31</sup>P<sup>1</sup>H NMR (d<sub>6</sub>-benzene, 161.94 MHz, 298 K): δ −789.02 ppm. UV-vis-NIR (toluene): λ<sub>max</sub> (cm<sup>−1</sup>; ε) 295 (33,921, 5,220), 409 (24,450, 1,570), 567 (17,649, 260), 609 (16,426, 180), 757 (13,210, 50), 798 (12,528, 70), 819 (12,216, 709), 834 (11,990, 50), 852 (11,740, 60), 865 (11,563, 70), 893 (11,193, 60), 982 (10,181, 50), 1,001 (9,990, 50), 1,332 (7,506, 30) nm.
Synthesis of [(BIPMTMS)Np(III)(I)(Me4)]2 (6Np)

In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, THF (1.5 mL) was added to solid [Rb(BIPMTMSH)] (28.3 mg, 44 µmol, 1 equiv.) and [Np(III)(THF)4] (40 mg, 44 µmol), which caused the mixture to immediately turn cloudy orange/yellow with precipitation of fine white solids (presumably Rbl). The mixture was stirred for 15 minutes and then solid KBn (5.7 mg, 44 µmol, 1 equiv.) was added in several portions which caused the mixture to immediately turn from orange to red and then purple/brown. The cloudy mixture was stirred for a further 15 minutes and then reduced to an oily solid in vacuo. Toluene (1 mL) was added and the mixture was stirred for 5 minutes then filtered into a 20 mL glass scintillation vial through two glass microfiber filter discs packed in a glass pipette, to give a clear red/purple solution. A PTFE-coated stirrer bar was added, and then solid IMe4 (10 mg, 78 µmol, 1.78 equiv.) was added in several portions to the stirred solution which caused a color change from red to purple as the IMe4 dissolved. Note: attempts to isolate 6Np have been unsuccessful when 2 equiv. of IMe4 have been used. Similar reactions have resulted in the isolation of imidazolinium iodide salts in our hands. The solution became slightly cloudy, but rapid stirring did not result in further precipitation unlike the synthesis of 6Ce. The mixture was heated to a gentle reflux (130 °C on a hot plate) for 1 minute and then filtered into a 4 mL glass vial through two glass microfiber filter discs packed in a glass pipette and stored overnight (16 hrs) at room temperature which caused a small crop of red/black blocks to form (see below for yields). The small quantity of red/purple solids that remained on the filter discs was extracted with THF (1 mL) into a fresh 4 mL glass vial and dried in vacuo to a red powder. This was then dissolved in toluene (1 mL) after 2 minutes of gentle refluxing (130 °C hot plate) and the hot solution was stored at room temperature overnight (16 hrs) – crystals of 6Np then grew from this aliquot once it was cooled (~35 °C) in the glovebox freezer and then again when stored again at room temperature for 20 minutes. The supernatants from both of these crops of crystals was decanted and layered with hexane (1 mL) and stored overnight (16 hrs) which caused a third crop of crystals of 6Np to form. All three crops were washed with hexane (2 × 1 mL) separately and dried in vacuo to a red/purple powder. Combined
yield: combined 15.7 mg, 32%. $^1$H NMR ($d_6$-benzene, 400.13 MHz, 298 K): $\delta$ −9.17 (br s, $v_1/2 = 50$ Hz, 18 H, BIPM$^{\text{TMS}}$ Si(CH$_3$)$_3$ $\times$ 2) ppm. We tentatively assign this peak due to its intensity and position which is similar to that of 5Np. No other peak that could be definitively assigned to this complex rather than BIPM$^{\text{TMSH}_2}$, or a BIPM$^{\text{TMSH}}$ complex (like 4Np), could be identified. $^{13}$C{$^1$H} NMR ($d_6$-benzene, 100.62 MHz, 298 K): Only peaks assignable to a BIPM$^{\text{TMSH}}$ complex (like 4Np) could be identified, presumably due to the very large number of scans needed, combined with the limitations of our sample sealing procedure. $^{31}$P{$^1$H} NMR ($d_6$-benzene, 161.94 MHz, 298 K): $\delta$ −739.51 ppm. UV-vis-NIR (toluene): $\lambda_{\text{max}}$ (cm$^{-1}$; $\varepsilon$) 306 (32,680, 4,530), 429 (23,310, 1,520), 496 (20,153, 1,290), 550 (18,188, 890), 584 (17,123, 610), 616 (16,234, 350), 644 (15,538, 210), 677 (14,775, 110), 777 (12,877, 40), 815 (12,273, 80), 833 (12,008, 70), 871 (11,478, 90), 889 (11,244, 90), 941 (10,632, 50), 991 (10,089, 50), 1,006 (9,936, 80), 1,013 (9,874, 80), 1,069 (9,353, 20), 1,152 (8,679, 10), 1,196 (8,361, 10), 1,251 (7,994, 10) nm.

**Attempted Synthesis of [(BIPM$^{\text{TMS}}$)UIII(I)(DME)] (5U)**

[(BIPM$^{\text{TMSH}}$)UI$_2$(THF)] was dissolved in DME (5 mL), stirred for several hrs, then all volatiles are removed in vacuo to give [(BIPM$^{\text{TMSH}}$)UI$_2$(DME)]. In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, [(BIPM$^{\text{TMSH}}$)UI$_2$(DME)] (55 mg, 49 µmol) was stirred in DME (5 mL) at room temperature for 5 minutes to give a dark blue solution. KBn (6.5 mg, 50 µmol, 1 equiv.) was added portionwise upon which a color change to brown was observed. The resulting mixture was stirred for 15 minutes after which time all the volatiles were removed in vacuo to afford a brown solid, which was extracted into toluene and filtered through a syringe filter to afford a pale brown solution. Attempts to prepare crystalline material was unsuccessful despite several attempts using different solvents and solvent ratios (Toluene, DME).
**Attempted Synthesis of [(BIPM^{TMS})U^{III}(I)(I^{Me4})_2] (6U)**

**Attempt 1.** In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, [(BIPM^{TMS}H)UI_2(THF)] (36 mg, 33 µmol) was stirred with toluene (3 mL) at room temperature for 5 minutes to give a dark blue solution. Solid I^{Me4} (4.2 mg, 33 µmol, 1 equiv.) was added and the resulting mixture stirred for 5 minutes to afford a dark blue/purple solution. KBn (4.3 mg, 33 µmol, 1 equiv.) was added and the resulting mixture stirred for 5 minutes after which all the KBn appeared to be consumed and the solution changed to a dark brown color with a colorless precipitate. The mixture was filtered through a syringe filter to afford a pale brown solution. Attempts to prepare crystalline material was unsuccessful despite several attempts using different solvents and solvent ratios (Toluene, Et_2O, THF).

**Attempt 2.** In a 20 mL glass scintillation vial with a PTFE-coated stirrer bar, [(BIPM^{TMS}H)UI_2(THF)] (36 mg, 33 µmol) was stirred with toluene (5 mL) at room temperature for 5 minutes to give a dark blue solution. Solid I^{Me4} (8.4 mg, 66 µmol, 2 equiv.) was added and the resulting mixture stirred for 30 minutes to afford a dark blue/purple solution. The solution was then stored at −30 °C for 30 minutes. KBn (4.3 mg, 33 µmol, 1 equiv.) was added and the resulting mixture stirred for 20 minutes after which time all the KBn appeared to be consumed, affording a dark blue/brown solution with precipitation of a pale solid. Volatiles were removed from the solution to afford a sticky brown solid, which was extracted into toluene and filtered through a syringe filter to afford a pale brown solution. Attempts to prepare crystalline material was unsuccessful despite several attempts using different solvents and solvent ratios (Toluene, Et_2O, THF).
**Reaction of 5Np with PhCHO to give PhC(H)=C(PPh\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{2} (7)**

In a 5 mL glass scintillation vial with a glass stirrer bar, 5Np (10.0 mg, 9.36 µmol) was dissolved 1.0 mL of d\textsubscript{6}-benzene, forming a red solution. To this, a solution of PhCHO (1.0 mg (9.32 µmol) in 1.0 mL of d\textsubscript{6}-benzene) was added dropwise while stirring at room temperature. The reaction was left to stir for 72 hrs. The solution was then filtered through a glass microfiber filter disk packed in a glass pipette to give a clear brown/red filtrate. The filtrate was concentrated to approximately 0.5 mL *in vacuo* and used as-eluted for NMR experiments. \textsuperscript{1}H NMR (d\textsubscript{6}-benzene, 400.13 MHz, 298 K): \(\delta\) 0.37 (s, 9 H, NSi(CH\textsubscript{3})\textsubscript{3}), 0.39 (s, 9 H, NSi(CH\textsubscript{3})\textsubscript{3}), 6.78 (br, 2 H, m-Ph-CH\textsubscript{2}), 6.89 (br, 6 H, p-Ph-CH\textsubscript{2} and o-Ph-CH\textsubscript{2}), 7.02 (br, 8 H, m-Ph-CH\textsubscript{2}), 7.39 (br, 1 H, p-Ph-CH\textsubscript{2}), 7.78 (m, 8 H, o-Ph-CH\textsubscript{2}), 8.04 (dd, \(^3J_{PH} = 28.4\) and 28.3 Hz, 1 H, PhH\textsubscript{C}═CP\textsubscript{2}). \textsuperscript{31}P NMR (d\textsubscript{6}-benzene, 161.94 MHz, 298 K): \(\delta\) -6.75 (d, \(^2J_{pp} = 35.2\) Hz), -7.79 (d, \(^2J_{pp} = 35.3\) Hz). Analysis of the unpurified reaction mixture by NMR (\(^1\)H and \(^{31}\)P) matches that of the previously reported alkene\textsuperscript{13} revealing the formation of PhC(H)=C(PPh\textsubscript{2}NSiMe\textsubscript{3})\textsubscript{2} (7), along with minor paramagnetic species that are presumed to be Np byproducts. Further characterization of the reaction products was impractical given the scarce nature of neptunium precursors.
S2. Selected photographs taken during the syntheses

Figure S1. From left to right: 1) Crystals of 5Ce under toluene; 2) Crystals of 6Ce under toluene.

Figure S2. From left to right: 1) Solution of putative 3Np in toluene, prior to addition of solid 1Me4; 2) The same material as on the left, but after addition of 1Me4. The pale precipitate can be clearly seen. More of this same material formed after subsequent concentration and storage at –35 °C. Only once all of this material was removed could crystals of 4Np be isolated.
Figure S3. Crystals of 4Np under hexane during the washing procedure.

Figure S4. From left to right: 1) Suspension of putative 3Np in THF, prior to addition of KBn; 2) The same material as on the left, but after addition of KBn.

Figure S5. From left to right: 1) Suspension of putative 3Np (from Figure S4) in toluene, prior to addition of solid IMe4 to form 6Np; 2) The same material as on the left, but after addition of IMe4 to form 6Np. The small quantity of precipitated material can be seen on the vial walls.
Figure S6. From left to right: 1) Crystals of 5Np under NVH oil, viewed through a microscope; 2) Crystals of 6Np prior to washing and drying.

Figure S7. Solutions of 4Np (orange, left in both images) and 6Np (orange/red, right in both images) in toluene for UV-vis-NIR spectroscopy.
S3. Crystallography

General considerations

The crystal data for all complexes are compiled in Table S1 to Table S3. All crystals were examined with either a Bruker Apex II diffractometer equipped with an Apex II CCD detector and using mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å); a Bruker D8 Quest diffractometer equipped with a Photon II CPAD detector and using mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) operating in shutterless mode; a Bruker microsource diffractometer equipped with a Photon III CPAD detector and using mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å); or a Rigaku FR-X diffractometer equipped with a HyPix 6000HE photon counting pixel array detector with mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). APEX II, APEX III or CryAlisPro software were used for control and solving the unit cells prior to data collection.\textsuperscript{14,15} Intensities were integrated from data recorded on 0.5° frames by $\omega$ rotation with 0.5s (2), 4s (5Ce), 10s (4Ce, 4Np, 5Np), 20s (1, 6Ce) or 30s (3Ce) exposures; or by both $\omega$ and $\phi$ rotation (0.5°) with 10s (6Np) frame exposures. CrysAlisPro\textsuperscript{14} was used for final unit cell determination and parameters were refined from the observed positions of all strong reflections in each data set. Analytical absorption corrections were applied to 1 and 3-6, and face indexed absorption corrections were applied to 2.\textsuperscript{15} The Olex2\textsuperscript{16} GUI was used for structure solution and refinement utilizing the ShelX software packages.\textsuperscript{17,18} The structures were solved using ShelXT\textsuperscript{17}; the datasets were refined by ShelXL\textsuperscript{18} using full-matrix least-squares on all unique $F^2$ values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{iso}(H)$ was set at 1.2 (1.5 for methyl groups if applicable) times $U_{eq}$ of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Ortep and PovRay were employed for molecular graphics.\textsuperscript{19,20} The CCDC deposits contain the supplementary crystal data for this article. 2125323 (1), 2125324 (2), 2125325 (3Ce), 2125326 (4Ce), 2125327 (4Np), 2125328 (5Ce), 2125329 (5Np), 2125330 (6Ce), and 2125331 (6Np). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
|                  | 1           | 2           | 3Ce         |
|------------------|-------------|-------------|-------------|
| CCDC ref code    | 2125323     | 2125324     | 2125325     |
| Formula          | C_{78}H_{118}Li_{6}N_{4}P_{2}O_{5}P_{4}Si_{2} | C_{88}H_{122}Li_{2}N_{4}O_{5}P_{4}Si_{4} | C_{38.5}H_{51}Ce_{2}N_{2}OP_{2}Si_{2} |
| Fw               | 2086.19     | 2254.77     | 1069.85     |
| Crystal syst     | Monoclinic  | Triclinic   | Triclinic   |
| Space group      | P_{2}1/c    | P-1         | P-1         |
| a, Å             | 11.9971(2)  | 12.4707(2)  | 9.7913(7)   |
| b, Å             | 17.7775(3)  | 14.1981(2)  | 11.9571(8)  |
| c, Å             | 43.6609(7)  | 14.6654(2)  | 19.1734(12) |
| α, °             | 89.2160(10) | 77.161(5)   | 77.102(5)   |
| β, °             | 97.229(2)   | 73.7920(10) | 83.627(5)   |
| γ, °             | 87.5900(10) | 83.627(5)   |             |
| V, Å³            | 9237.9(3)   | 2491.24(6)  | 2128.9(3)   |
| Z                | 4           | 1           | 2           |
| ρ_{calcd}, g cm^{-3} | 1.500      | 1.503       | 1.669       |
| μ, mm^{-1}       | 2.550       | 3.568       | 2.682       |
| F(000)           | 4176        | 1126        | 1052        |
| Cryst size, mm   | 0.24 × 0.12 × 0.08 | 0.339 x 0.295 x 0.23 | 0.10 x 0.10 x 0.10 |
| Temperature, K    | 100(2)      | 150(2)      | 100(2)      |
| K                |             |             |             |
| no. reflections (unique) | 95472 (18839) | 35124 (10117) | 19776 (8599) |
| R_{int}          | 0.054       | 0.0339      | 0.0811      |
| R_{I}(wR^2) (F^2 > 2σ(F^2)^[a]) | 0.0361 (0.0771) | 0.0242, 0.0615 | 0.0642, 0.1307 |
| S^[a]            | 1.01        | 1.081       | 1.016       |
| min./max. diff. map, Å^{-3} | -0.90, 1.23 | -1.153, 1.375 | -1.828, 2.219 |

^[a] R = \sum||F_o| - |F_c||/\sum|F_o|; R_W = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}; S = [\sum w(F_o^2 - F_c^2)^2/(no. data - no. params)]^{0.5} for all data.
Table S2. Crystallographic data for 3Np, 4Ce, and 4Np.

|                | 4Ce                      | 4Np                      | 5Ce                      |
|----------------|--------------------------|--------------------------|--------------------------|
| CCDC ref code  | 2125326                  | 2125327                  | 2125328                  |
| Formula        | C_{38}H_{51}Ce_{2}N_{4}P_{2}Si_{2} | C_{38}H_{51}I_{2}Np_{2}P_{2}Si_{2} | C_{38.5}H_{52}CeI_{2}O_{2}Np_{2}P_{2}Si_{2} |
| Fw             | 1075.86                  | 1172.74                  | 959.96                   |
| Crystal syst   | Monoclinic               | Monoclinic               | Monoclinic               |
| Space group    | C2/c                     | C2/c                     | P2_1/n                   |
| a, Å           | 19.7305(5)               | 19.7438(5)               | 9.6163(5)                |
| b, Å           | 11.8965(3)               | 11.8689(3)               | 22.1127(12)              |
| c, Å           | 36.6720(9)               | 36.4644(8)               | 20.7529(11)              |
| α, °           | 90                       | 90                       | 90                       |
| β, °           | 98.893(2)                | 98.841(2)                | 99.555(5)                |
| γ, °           | 90                       | 90                       | 90                       |
| V, Å³          | 8504.3(4)                | 8443.4(4)                | 4351.7(4)                |
| Z              | 8                        | 8                        | 4                        |
| ρcalc., g cm⁻³ | 1.681                    | 1.845                    | 1.465                    |
| µ, mm⁻¹        | 2.685                    | 4.088                    | 1.916                    |
| F(000)         | 4232                     | 4512                     | 1928                     |
| Cryst size, mm | 0.20 x 0.05 x 0.05       | 0.15 x 0.10 x 0.01       | 0.20 x 0.20 x 0.05       |
| Temperature, K | 100(2)                   | 100(2)                   | 120(2)                   |
| no. reflections (unique) | 38348 (10051) | 35797 (8638) | 86241 (13220) |
| R_{int}        | 0.1183                   | 0.0644                   | 0.0416                   |
| R₁(wR₂) (F² > 2σ(F²))[a] | 0.0636, 0.1457 | 0.0476, 0.1145 | 0.0268, 0.0623 |
| S[a]           | 1.124                    | 1.033                    | 1.048                    |
| min./max. diff map, Å⁻³ | -1.603, 1.996 | -2.290, 1.940 | -0.964, 2.380 |

[a] R = \sum||F₀| - |F_C||/\sum|F₀|; R_w = [\sum w(F_0^2 - F_C^2)^2/\sum w(F_0^2)^2]^{0.5}; S = [\sum w(F_0^2 - F_C^2)^2/(\text{no. data} - \text{no. params})]^{0.5} for all data.
Table S3. Crystallographic data for 5Ce, 5Np, and 6.

|                      | 5Np                     | 6Ce                     | 6Np                     |
|----------------------|-------------------------|-------------------------|-------------------------|
| CCDC ref code        | 2125329                 | 2125330                 | 2125331                 |
| Formula              | C_{38.5}H_{52}IN_{2}NpO_{2}P_{2}Si_{2} | C_{48.5}H_{66}CeIN_{6}P_{2}Si_{2} | C_{48.5}H_{66}IN_{6}NpP_{2}Si_{2} |
| Fw                   | 1056.84                 | 1118.21                 | 1215.09                 |
| Crystal syst         | monoclinic              | monoclinic              | monoclinic              |
| Space group          | P2_1/n                  | P2_1/n                  | P2_1/n                  |
| a, Å                 | 9.5530(2)               | 15.7692(2)              | 15.7683(4)              |
| b, Å                 | 21.8585(6)              | 20.5022(2)              | 20.4116(4)              |
| c, Å                 | 20.4993(5)              | 16.3718(2)              | 16.3581(4)              |
| α, °                 | 90                      | 90                      | 90                      |
| β, °                 | 99.295(2)               | 100.4870(10)            | 100.497(2)              |
| γ, °                 | 90                      | 90                      | 90                      |
| V, Å³                | 4224.34(18)             | 5204.64(11)             | 5176.8(2)               |
| Z                    | 4                       | 4                       | 4                       |
| ρ_{calcd}, g cm⁻³    | 1.662                   | 1.427                   | 1.559                   |
| μ, mm⁻¹              | 3.357                   | 1.613                   | 2.750                   |
| F(000)               | 2068                    | 2272                    | 2412                    |
| Cryst size, mm       | 0.20 x 0.20 x 0.05      | 0.20 x 0.20 x 0.05      | 0.20 x 0.20 x 0.05      |
| Temperature, K       | 100(2)                  | 100(2)                  | 120(2)                  |
| no. reflections (unique) | 62482 (7686)         | 68943 (15874)           | 84005 (10520)           |
| R_{int}              | 0.1790                  | 0.0978                  | 0.1256                  |
| R_{1}(wR_2) (F^2 > 2σ(F^2))[^a] | 0.0643, 0.1679       | 0.0426, 0.1025          | 0.0486, 0.0971          |
| S[^a]                | 1.051                   | 1.040                   | 1.126                   |
| min./max. diff map, Å⁻³ | -4.414, 4.772       | -1.808, 2.465           | -1.029, 2.087           |

[^a] R = Σ||F_0|| – |F_C||/Σ|F_0|; R_w = [Σw(F_0^2 – F_C^2)^2]/Σw(F_0^2)^2]^{0.5}; S = [Σw(F_0^2 – F_C^2)^2]/(no. data – no. params)]^{0.5} for all data.

\[ esd3 = \sqrt{(esd1)^2 + (esd2)^2} \]

Equation S2. The combined standard uncertainty from two individual metrics that have their own associated uncertainties can be calculated as the root of the sum of the square of each error. This is not strictly appropriate for combining more than two individual errors.\textsuperscript{21}
S4. Molecular structures

*Complex 1*

![Molecular Structure Diagram](image)

**Figure S8.** Solid state molecular structure of complex 1 at 100K. Displacement ellipsoids are set at 30% probability and non-methanide hydrogen atoms, disordered components and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Np1-Cl1 2.7325(12), Np1-Cl2 2.8675(11), Np1-Cl3 2.9473(11), Np1-Cl4 2.8423(11), Np1-N1 2.451(4), Np1-N2 2.473(4), Np1-C1 2.831(4), Np2-Cl2 2.8344(12), Np2-Cl3 2.7972(11), Np2-Cl4 2.9223(11), Np2-Cl5 2.8092(13), Np2-N3 2.452(3), Np2-N4 2.467(3), Np2-C32 2.838(4), P1-C1 1.745(5), P2-C1 1.730(4), P3-C32 1.736(4), P4-C32 1.738(4), P1-C1-Np1 85.53(17), P2-C1-Np1 86.40(16), P1-C1-P2 130.2(3), P3-C32-Np2 85.35(16), P3-C32-P4 129.4(3), P4-C32-Np2 86.59(15), N1-Np1-N2 106.45(12), N3-Np2-N4 104.02(12), Np2-Cl2-Np1 92.88(3), Np2-Cl3-Np1 91.95(3), Np1-Cl4-Np2 91.56(3), Li1-Cl5-Np2 140.9(2).
**Figure S9.** Solid state molecular structure of complex 2 at 150K. Displacement ellipsoids are set at 30% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: U1-Cl1 2.7309(7), U1-Cl2 2.8840(6), U1-Cl3 2.7080(6), U1-N1 2.443(2), U1-N2 2.396(2), U1-C1 2.314(3), P1-N1 1.631(2), P1-C1 1.680(3), P2-N2 1.627(2), P2-C1 1.664(3), Cl1-U1-Cl2A 81.36(2), Cl1-U1-Cl2 75.933(19), Cl2-U1-Cl2A 71.85(2), Cl3A-U1-Cl1 158.79(2), Cl3A-U1-Cl2 101.99(2), Cl3A-U1-Cl2 78.015(19), N1-U1-Cl1 112.38(5), N1-U1-Cl2A 142.34(5), N1-U1-Cl2 77.74(5), N1-U1-Cl3A 87.31(5), N2-U1-Cl1 89.45(6), N2-U1-Cl2A 87.00(5), N2-U1-Cl2 155.69(6), N2-U1-Cl3A 84.60(5), N2-U1-N1 126.28(7), C1-U1-Cl1 89.15(7), C1-U1-Cl2A 151.63(7), C1-U1-Cl2 131.60(7), C1-U1-Cl3A 106.81(7), C1-U1-N1 65.88(8), C1-U1-N2 66.12(8).
**Complex 3Ce**

**Figure S10.** Solid state molecular structure of complex 3Ce at 100K. Displacement ellipsoids are set at 50% probability and non-methanide hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1-I1 3.1504(7), Ce1-I2 3.1714(8), Ce1-O1 2.605(6), Ce1-N1 2.437(7), Ce1-N2 2.383(6), Ce1-C1 2.806(9), P1-N1 1.616(7), P1-C1 1.737(8), P2-N2 1.608(7), P2-C1 1.737(8), C1-Ce1-I1 117.48(17), C1-Ce1-I2 80.40(17), O1-Ce1-C1 159.1(2), P1-C1-P2 135.3(5).
Complex 4Ce

Figure S11. Solid state molecular structure of complex 4Ce at 100K. Displacement ellipsoids are set at 50% probability and non-methanide hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1-I1 3.1111(6), Ce1-I2 3.2092(6), Ce1-N1 2.493(6), Ce1-N2 2.448(6), Ce1-C1 2.768(6), Ce1-C32 2.731(8), P1-N1 1.608(6), P1-C1 1.731(7), P2-N2 1.612(6), P2-C1 1.761(7), I1-Ce1-I2 135.964(19), N1-Ce1-I1 91.19(13), N1-Ce1-I2 131.69(13), N1-Ce1-C1 61.26(18), N1-Ce1-C32 110.1(2), N2-Ce1-I1 94.16(13), N2-Ce1-I2 84.80(13), N2-Ce1-N1 104.94(18), N2-Ce1-C1 62.87(19), N2-Ce1-C32 144.9(2), C1-Ce1-I1 134.05(13), C1-Ce1-I2 84.01(13), C32-Ce1-I1 87.70(16), C32-Ce1-I2 70.22(16), C32-Ce1-C1 134.5(2), P1-C1-P2 128.4(4)
Complex 5Ce

*Figure S12.* Solid state molecular structure of complex 5Ce at 120K. Displacement ellipsoids are set at 50% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1-I1 3.1753(2), Ce1-N1 2.4585(17), Ce1-N2 2.4557(16), Ce1-O3 2.5697(15), Ce1-O4 2.6763(15), Ce1-C1 2.4772(19), P1-N1 1.6375(17), P1-C1 1.655(2), P2-N2 1.6244(17), P2-C1 1.657(2), N1-Ce1-I1 94.91(4), N1-Ce1-O3 101.98(6), N1-Ce1-O4 101.90(5), N1-Ce1-C1 64.56(6), N2-Ce1-I1 104.67(4), N2-Ce1-N1 128.35(5), N2-Ce1-O3 80.64(6), N2-Ce1-O4 122.82(5), N2-Ce1-C1 63.87(6), O3-Ce1-I1 153.47(4), O3-Ce1-O4 61.82(5), O4-Ce1-I1 94.92(3), C1-Ce1-I1 110.00(5), C1-Ce1-O3 95.77(6), C1-Ce1-O4 152.05(6), P1-C1-P2 171.57(14).
Complex 6Ce

Figure S13. Solid state molecular structure of complex 6Ce at 100K. Displacement ellipsoids are set at 50% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1-I1 3.2054(2), Ce1-N1 2.510(2), Ce1-N2 2.494(2), Ce1-C1 2.519(2), Ce1-C32 2.737(3), Ce1-C39 2.806(2), P1-N1 1.624(2), P1-C1 1.667(3), P2-N2 1.622(2), P2-C1 1.679(2), P1-C1 1.62(2), N1-Ce1-C1 63.75(7), N1-Ce1-C32 132.22(7), N1-Ce1-C39 81.24(7), N2-Ce1-I1 98.36(5), N1-Ce1-C1 63.75(7), N1-Ce1-C32 132.22(7), N1-Ce1-C39 81.24(7), N2-Ce1-C1 63.76(7), N2-Ce1-C32 81.69(7), N2-Ce1-C39 154.07(8), C1-Ce1-I1 128.10(6), C1-Ce1-C32 99.50(8), C1-Ce1-C39 124.47(7), C32-Ce1-I1 123.70(5), C32-Ce1-C39 72.82(7), C39-Ce1-I1 97.02(5), P1-C1-P2 137.37(16).
**Complex 4Np**

*Figure S14.* Solid state molecular structure of complex 4Np at 100K. Displacement ellipsoids are set at 50% probability and non-methanide hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Np1-I1 3.0727(6), Np1-I2 3.1798(6), Np1-N1 2.423(6), Np1-N2 2.458(6), Np1-C1 2.753(7), Np1-C32 2.676(8), P1-N1 1.612(6), P1-C1 1.749(7), P2-N2 1.618(6), P2-C1 1.723(7), I1-Np1-I2 135.874(19), N1-Np1-I1 93.13(14), N1-Np1-I2 84.69(14), N1-Np1-N2 105.8(2), N1-Np1-C1 63.3(2), N1-Np1-C32 144.1(2), N2-Np1-I1 91.10(13), N2-Np1-I2 131.94(13), N2-Np1-C1 62.0(2), N2-Np1-C32 110.0(2), C1-Np1-I1 133.83(14), C1-Np1-I2 83.80(14), C32-Np1-I1 88.22(16), C32-Np1-I2 70.04(17), C32-Np1-C1 134.6(2), P1-C1-P2 128.6(4).
Complex 5Np

**Figure S15.** Solid state molecular structure of complex 5Np at 100K. Displacement ellipsoids are set at 50% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Np1-I1 3.1065(5), Np1-O1 2.524(5), Np1-O2 2.636(5), Np1-N1 2.431(6), Np1-N2 2.414(6), Np1-C1 2.425(7), P1-N1 1.602(6), P1-C1 1.627(7), P2-N2 1.631(6), P2-C1 1.652(7), O1-Np1-I1 153.90(12), O1-Np1-O2 61.84(16), O2-Np1-I1 95.27(10), N1-Np1-I1 103.57(13), N1-Np1-O1 81.28(18), N1-Np1-O2 122.42(17), N2-Np1-I1 95.23(12), N2-Np1-O1 101.53(18), N2-Np1-O2 102.19(17), N2-Np1-N1 128.81(18), N2-Np1-C1 65.2(2), C1-Np1-I1 109.31(17), C1-Np1-O1 95.9(2), C1-Np1-O2 152.9(2), C1-Np1-N1 63.6(2), P1-C1-P2 170.4(5).
Figure S16. Solid state molecular structure of complex 6Np at 120K. Displacement ellipsoids are set at 50% probability and hydrogen atoms and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Np1-I1 3.1571(4), Np1-N1 2.485(4), Np1-N2 2.492(5), Np1-C1 2.490(6), Np1-C32 2.677(5), Np1-C39 2.751(6), P1-N1 1.620(5), P1-C1 1.675(6), P2-N2 1.614(5), P2-C1 1.671(5), N1-Np1-I1 91.83(10), N1-Np1-N2 120.88(15), N1-Np1-C1 64.04(17), N1-Np1-C32 81.36(16), N1-Np1-C39 154.19(15), N2-Np1-I1 98.08(10), N2-Np1-C32 132.67(17), N2-Np1-C39 81.04(16), C1-Np1-I1 127.54(12), C1-Np1-N2 64.08(16), C1-Np1-C32 98.69(17), C1-Np1-C39 123.63(17), C32-Np1-I1 124.26(13), C32-Np1-C39 73.21(17), C39-Np1-I1 98.69(11), P1-C1-P2 136.5(3).
S5. UV-vis-NIR spectra

**Figure S17.** Solution UV-vis-NIR spectrum of 4Np (0.49 mM) in toluene shown between 7,000–35,000 cm⁻¹ (1,429–286 nm) at ambient temperature.

**Figure S18.** Solution UV-vis-NIR spectrum of 5Np (0.51 mM) in toluene shown between 7,000–35,000 cm⁻¹ (1,429–286 nm) at ambient temperature.
Figure S19. Solution UV-vis-NIR spectrum of 6Np (0.58 mM) in toluene shown between 7,000–35,000 cm$^{-1}$ (1,429–286 nm) at ambient temperature.

Figure S20. Comparison of solution UV-vis-NIR spectra of 4Np (black line, 0.49 mM), 5Np (blue line, 0.51 mM), and 6Np (red line, 0.58 mM), all in toluene shown between 7,000–35,000 cm$^{-1}$ (1,429–286 nm) at ambient temperature.
Figure S21. The same spectra as Figure S20 (4Np black line, 5Np blue line, and 6Np red line), but shown in the region between 7,400–18,000 cm⁻¹ (1,351–556 nm) – the region typically associated with f→f transitions (5f→5f here).

Figure S22. Comprison of solution UV-vis-NIR spectra of 5Np (black line, 0.51 mM) and 6Np (red line, 0.58 mM) – the two (BIPM<sub>TMS</sub>)<sup>2-</sup> complexes, all in toluene shown between 7,000–35,000 cm⁻¹ (1,429–286 nm) at ambient temperature.
Figure S23. The same spectra as Figure S22 (5Np black line and 6Np red line), but shown in the region between 7,400–16,500 cm$^{-1}$ (1,351–606 nm) – the region typically associated with $f\rightarrow f$ transitions ($5f\rightarrow 5f$ here).

S6. NMR spectra

Figure S24. $^1$H NMR spectrum of 4Ce in $d_8$-THF.
Figure S25. $^{31}$P{$^1$H} NMR spectrum of $4$Ce in $d_8$-THF. The BIPM$^{TMS}$H$_2$ peak is from a small amount of decomposition during sample preparation.

Figure S26. $^1$H NMR spectrum of $6$Ce in $d_8$-THF.
Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 6Ce in $d_8$-THF.

Figure S28. $^1\text{H}$ NMR spectrum of 4Np in $d_6$-benzene.
**Figure S29.** $^1$H NMR spectrum of 4Np in $d_6$-benzene, showing the full spectral window collected.

**Figure S30.** $^{13}$C\{$^1$H} NMR spectrum of 4Np in $d_6$-benzene.
Figure S31. $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 4Np in $d_6$-benzene, showing the full spectral window collected.

Figure S32. $^{31}\text{P}^{1}\text{H}$ NMR spectrum of 4Np in $d_6$-benzene. The BIPM$^{\text{TMS}}\text{H}_2$ peak is likely from a small amount of decomposition given the limitations of our sample containment procedure.
Figure S33. $^{31}$P NMR spectrum of 4Np in $d_6$-benzene. The BIPM$^\text{TMS}H_2$ peak is likely from a small amount of decomposition given the limitations of our sample containment procedure.

Figure S34. $^1$H NMR spectrum of 5Np in $d_6$-benzene. The BIPM$^\text{TMS}H_2$ peak (✳️) is likely from a small amount of decomposition given the limitations of our sample containment procedure.
Figure S35. $^1$H NMR spectrum of 5Np in $d_6$-benzene, showing the full spectral window collected.

Figure S36. $^{13}$C{${}^1$H} NMR spectrum of 5Np in $d_6$-benzene. No peaks readily attributable to the ipso-C on the {BIPM$^{TMS}$}$_2^-$ ligand could be located, or any other peaks not due to solvents or BIPM$^{TMS}$H$_2$.
Figure S37. $^{13}$C{${}^1$H} NMR spectrum of 5Np in $d_6$-benzene, showing the full spectral window collected.

Figure S38. $^{31}$P{${}^1$H} NMR spectrum of 5Np in $d_6$-benzene. The H$_2$BIPMTMS peak is likely from a small amount of decomposition given the limitations of our sample containment procedure.
Figure S39. $^{31}$P NMR spectrum of 5Np in $d_6$-benzene. The BIPM$^{TMS}H_2$ peak is likely from a small amount of decomposition given the limitations of our sample containment procedure.

Figure S40. $^1$H NMR spectrum of 6Np in $d_8$-THF. The BIPM$^{TMS}H_2$ and BIPM$^{TMS}H$ peaks (see below) are likely from a small amount of decomposition given the limitations of our sample containment procedure combined with the need to heat the sample of 6Np strongly to dissolve it in $d_8$-THF – the complex is essentially insoluble in $d_6$-benzene.
Figure S41. $^1$H NMR spectrum of 6Np in $d_8$-THF, showing the full spectral window collected.

Figure S42. $^{13}$C{$^1$H} NMR spectrum of 6Np in $d_8$-THF. No peaks definitively assignable to 6Np could be identified.
Figure S43. $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of 6Np in $d_8$-THF, showing the full spectral window collected.

Figure S44. $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of 6Np in $d_8$-THF.
Figure S45. $^{31}$P NMR spectrum of 6Np in $d_8$-THF.

Figure S46. $^1$H NMR spectrum of in situ generated 7 in $d_6$-benzene.
**Figure S47.** $^1$H NMR spectrum of *in situ* generated 7 in $d_6$-benzene, showing the full spectral window collected.

**Figure S48.** $^{31}$P NMR spectrum of *in situ* generated 7 in $d_6$-benzene.
S7. ATR-IR Spectra

**Figure S49.** ATR-IR spectrum of 4Ce.

**Figure S50.** ATR-IR spectrum of 6Ce.
### S8. Magnetic moments determined by NMR spectroscopy (Evans method)

Table S4. Data for the determination of the magnetic moments of complexes 5Np and 6Np.

| Sample / peak | \(\mu_{\text{eff}} / \text{B.M mol}^{-1}\) | \(^a\) sample mass / g | solvent mass / g | \(M_r / \text{g mol}^{-1}\) | \(^b\) \(\Delta\) peak / Hz |
|---------------|------------------------------------------|-------------------------|-----------------|-----------------|-----------------|
| 5Np           | 1.36                                     | 0.0097                  | 0.3704          | 718.203         | 98.16           |
| 6Np           | 1.46                                     | 0.0060                  | 0.4019          | 908.20          | 2.84            |

\(^a\) The small masses engender large errors in this methodology, the results should be cautiously interpreted along with other data. \(^b\) Spectrometer frequency 400.130 MHz. Simple diamagnetic correction of \(M_r / -2,000,000\) applied. \(\rho_{d_6}\)-benzene = 0.950 g mL\(^{-1}\); \(\rho_{d_8}\)-THF = 0.985 g mL\(^{-1}\).

We were unable to obtain magnetic susceptibility measurements for complex 4Np due to the very limited sample quantity combined with difficulty fully solubilizing the sample in \(d_6\)-benene at room temperature (for example, it crystallizes overnight from \(d_6\)-benzene solutions in NMR tubes). As our sample sealing procedure makes it impractical to safely bring the sample back into the glovebox without decomposition, we were unable to add additional solvent (e.g. some \(d_8\)-THF) to ensure complete dissolution of the sample, and we did not have enough material to gather new NMR spectra in a different solvent.

### S9. Computational studies

Geometry optimizations for 4Np-6Np were performed using coordinates derived from their crystal structures as the starting points. No constraints were imposed on the structures during the geometry optimizations. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2017 with standard convergence criteria, Tables S5-S19.\(^{22,23}\) The DFT geometry optimizations employed Slater type orbital (STO) triple-\(\zeta^\ast\)-plus polarization all-electron basis sets (from the Dirac and ZORA/TZP database of the ADF suite). Scalar relativistic approaches (spin-orbit neglected) were used within the ZORA Hamiltonian\(^{24-26}\) for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation potential due to Vosko et al was used in.
all of the calculations. Generalized gradient approximation corrections were performed using the functionals of Becke and Perdew. Natural Bond Order (NBO) analyses were carried out with NBO 6.0.19. The Quantum Theory of Atoms in Molecules analysis was carried out within the ADF program, and those data were checked by comparing to values computed with Xaim-1.033 using WFN files generated by ADF. The ADF-GUI (ADFview) was used to prepare the three-dimensional plots of the electron density. In all cases, Aubau formulations were found with the appropriate spin formulations (5f\(^{4}\) Np(III), quintet; 5f\(^{6}\) U(III), quarted, 4f\(^{5}\) Ce(III), doublet, 4f\(^{6}\) Pm(III), quintet).

Table S5. Computed bond, indices, charges, and spin densities of 4M-6M (M = Np, U, Ce, Pm).

| Cmpd | Bond | M-C bond lengths and indices | MDC\(_q\) charges | MDC\(_m\) spin density |
|------|------|-----------------------------|-------------------|---------------------|
|      |      | Expt. | Calc. | BI\(^a\) | M | C | M | C |
| 4Np  | Np-CH\(_{\text{BIPM}}\) | 2.753(7) | 2.7437 | 0.59 | 1.51 | -1.64 | 4.21 | -0.01 |
|      | Np<-C\(_{\text{NHC}}\) | 2.676(8) | 2.6805 | 0.83 | -0.43 | -0.02 |
| 5Np  | Np=C\(_{\text{BIPM}}\) | 2.425(7) | 2.3899 | 1.40 | 1.54 | -1.96 | 4.36 | -0.07 |
| 6Np  | Np=C\(_{\text{BIPM}}\) | 2.490(6) | 2.4700 | 1.20 | 1.51 | -1.64 | 4.22 | -0.05 |
|      | Np<-C\(_{\text{NHC}}\) | 2.751(6) | 2.7321 | 0.65 | -0.44 | -0.03 |
|      | Np<-C\(_{\text{NHC}}\) | 2.677(5) | 2.6719 | 0.69 | -0.46 | -0.03 |
| 4U   | U-CH\(_{\text{BIPM}}\) | - | 2.7492 | 0.58 | 1.58 | -1.65 | 3.09 | -0.01 |
|      | U<-C\(_{\text{NHC}}\) | - | 2.6738 | 0.82 | -0.45 | -0.02 |
| 5U   | U=C\(_{\text{BIPM}}\) | - | 2.4232 | 1.28 | 1.57 | -2.00 | 3.28 | -0.04 |
| 6U   | U=C\(_{\text{BIPM}}\) | - | 2.4618 | 1.17 | 1.62 | -1.67 | 3.08 | -0.04 |
|      | U<-C\(_{\text{NHC}}\) | - | 2.7153 | 0.77 | -0.50 | -0.03 |
|      | U<-C\(_{\text{NHC}}\) | - | 2.6538 | 0.81 | -0.48 | -0.03 |
| 4Ce  | Ce-CH\(_{\text{BIPM}}\) | 2.768(6) | 2.7717 | 0.46 | 1.20 | -1.54 | 1.04 | -0.01 |
|      | Ce<-C\(_{\text{NHC}}\) | 2.731(8) | 2.7492 | 0.60 | -0.31 | -0.01 |
| 5Ce  | Ce=C\(_{\text{BIPM}}\) | 2.4772(19) | 2.4402 | 1.05 | 1.32 | -1.82 | 1.07 | -0.01 |
| 6Ce  | Ce=C\(_{\text{BIPM}}\) | 2.519(2) | 2.4880 | 0.96 | 1.29 | -1.53 | 1.01 | -0.01 |
|      | Ce<-C\(_{\text{NHC}}\) | 2.737(3) | 2.7576 | 0.52 | -0.38 | -0.01 |
|      | Ce<-C\(_{\text{NHC}}\) | 2.806(2) | 2.8207 | 0.58 | -0.36 | -0.01 |
| 4Pm  | Pm-CH\(_{\text{BIPM}}\) | - | 2.7674 | 0.31 | 1.06 | -1.47 | 4.38 | -0.04 |
|      | Pm<-C\(_{\text{NHC}}\) | - | 2.7061 | 0.39 | -0.26 | -0.05 |
| 5Pm  | Pm=C\(_{\text{BIPM}}\) | - | 2.4077 | 0.94 | 1.26 | -1.76 | 4.40 | -0.02 |
| 6Pm  | Pm=C\(_{\text{BIPM}}\) | - | 2.4809 | 0.76 | 1.11 | -1.48 | 4.39 | -0.02 |
|      | Pm<-C\(_{\text{NHC}}\) | - | 2.8097 | 0.28 | -0.31 | -0.02 |
|      | Pm<-C\(_{\text{NHC}}\) | - | 2.7385 | 0.33 | -0.29 | -0.02 |

\(^a\) Nalewajski-Mrozek bond indices.
Table S6. Computed NBO data for 4M-6M (M = Np, U, Ce, Pm).

| Cmpd | Bond   | M-C σ-bond (%) | M-C π-bond (%) |
|------|--------|----------------|----------------|
|      |        | M  | C | M s/p/d/f | C s/p | M | C | M s/p/d/f | C s/p |
| 4Np  | Np-CHBIPM | 9  | 91 | 9/0/45/46 | 9/91  |   |   |   |   |
|      | Np-CNHC   | 0  | 100 |   |   | 45/55  |   |   |   |   |
| 5Np  | Np=CNHC   | 17 | 83 | 4/1/32/63 | 13/87 | 14 | 86 | 0/0/38/62 | 0/100 |
| 6Np  | Np=CNHC   | 15 | 85 | 9/1/39/51 | 22/78 | 10 | 90 | 0/0/43/56 | 1/99  |
|      | Np-CNHC   | 0  | 100 |   |   | 46/54  |   |   |   |   |
|      | Np-CNHC   | 0  | 100 |   |   | 46/54  |   |   |   |   |
| 4U   | U-CHBIPM  | 9  | 91 | 8/0/47/45 | 8/92  |   |   |   |   |
|      | U-CNHC    | 0  | 100 |   |   | 44/56  |   |   |   |   |
| 5U   | U=CNHC    | 14 | 86 | 4/1/42/53 | 14/86 | 13 | 87 | 0/0/40/60 | 0/100 |
| 6U   | U=CNHC    | 14 | 86 | 10/1/46/43 | 24/76 | 10 | 90 | 0/0/50/49 | 1/99  |
|      | U-CNHC    | 0  | 100 |   |   | 46/54  |   |   |   |   |
|      | U-CNHC    | 0  | 100 |   |   | 46/54  |   |   |   |   |
| 4Ce  | Ce-CHBIPM | 0  | 100 |   |   |   |   |   |   |
|      | Ce-CNHC   | 0  | 100 |   |   | 45/55  |   |   |   |   |
| 5Ce  | Ce=CNHC   | 10 | 90 | 1/1/61/37 | 8/92  | 8  | 92 | 0/0/65/35 | 0/100 |
| 6Ce  | Ce=CNHC   | 9  | 91 | 7/1/65/27 | 20/80 | 7  | 93 | 2/1/60/37 | 2/98  |
|      | Ce-CNHC   | 0  | 100 |   |   | 46/54  |   |   |   |   |
|      | Ce-CNHC   | 0  | 100 |   |   | 46/54  |   |   |   |   |
| 4Pm  | Pm-CHBIPM | 10 | 90 | 5/0/32/63 | 6/97  |   |   |   |   |
|      | Pm-CNHC   | 0  | 100 |   |   | 45/55  |   |   |   |   |
| 5Pm  | Pm=CNHC   | 18 | 82 | 1/0/24/75 | 7/93  | 19 | 81 | 0/0/20/80 | 0/100 |
| 6Pm  | Pm=CNHC   | 15 | 85 | 5/1/31/63 | 17/83 | 14 | 86 | 1/0/24/75 | 2/98  |
|      | Pm-CNHC   | 0  | 100 |   |   | 44/56  |   |   |   |   |
|      | Pm-CNHC   | 0  | 100 |   |   | 43/57  |   |   |   |   |

* The NBO cut-off is 5%, so M% = 0 means only that the M contribution to that bond is <5%.

Table S7. Computed QTAIM data for 4M-6M (M = Np, U, Ce, Pm).

| Cmpd | Bond   | ρ<sup>a</sup> | ∇<sup>b</sup>ρ<sup>c</sup> | H<sup>d</sup> | ϕ<sup>e</sup> |
|------|--------|---------------|----------------|---------|---------|
| 4Np  | Np-CHBIPM | 0.04          | 0.09            | -0.07   | 0.05    |
|      | Np-CNHC   | 0.05          | 0.11            | -0.01   | 0.01    |
| 5Np  | Np-CNHC   | 0.08          | 0.13            | -0.04   | 0.21    |
| 6Np  | Np-CNHC   | 0.08          | 0.12            | -0.03   | 0.18    |
|      | Np-CNHC   | 0.04          | 0.11            | -0.01   | 0.03    |
| 4U   | U-CNHC    | 0.05          | 0.01            | -0.01   | 0.01    |
| 5U   | U-CNHC    | 0.08          | 0.12            | -0.03   | 0.20    |
| 6U   | U-CNHC    | 0.08          | 0.11            | -0.03   | 0.17    |
|      | U-CNHC    | 0.05          | 0.10            | -0.01   | 0.03    |
|      | U-CNHC    | 0.05          | 0.11            | -0.01   | 0.03    |
| 4Ce  | Ce-CNHC   | 0.04          | 0.08            | -0.01   | 0.05    |
| 5Ce  | Ce-CNHC   | 0.07          | 0.12            | -0.03   | 0.22    |
| 6Ce  | Ce-CNHC   | 0.07          | 0.10            | -0.02   | 0.19    |
|      | Ce-CNHC   | 0.04          | 0.08            | -0.01   | 0.03    |
| 4Pm  | Pm-CNHC   | 0.04          | 0.08            | -0.01   | 0.05    |
| 5Pm  | Pm-CNHC   | 0.07          | 0.12            | -0.03   | 0.16    |
| 6Pm  | Pm-CNHC   | 0.06          | 0.11            | -0.02   | 0.13    |

* Topological electron density. ∇<sup>b</sup> Laplacian. ∇<sup>c</sup> Electronic energy density. ϕ<sup>d</sup> Bond ellipticity.
Figure S51. Selected frontier Kohn Sham molecular orbitals of 4Np. a) HOMO (284a, –2.792 eV), b) HOMO–1 (283a, –2.802 eV), c) HOMO–2 (282a, –2.848 eV), d) HOMO–3 (281a, –2.864 eV), e) HOMO–5 (279a, –5.060 eV), f) HOMO–23 (261a, –6.663 eV). Hydrogen atoms are omitted for clarity.

Figure S52. Selected frontier Kohn Sham molecular orbitals of 5Np. a) HOMO (248a, –2.363 eV), b) HOMO–1 (247a, –2.503 eV), c) HOMO–2 (246a, –2.533 eV), d) HOMO–3 (245a, –2.565 eV), e) HOMO–4 (244a, –4.515 eV), f) HOMO–5 (243a, –4.951 eV). Hydrogen atoms are omitted for clarity.
Figure S53. Selected frontier Kohn Sham molecular orbitals of 6Np. a) HOMO (291a, −2.195 eV), b) HOMO–1 (290a, −2.243 eV), c) HOMO–2 (289a, −2.319 eV), d) HOMO–3 (288a, −2.392 eV), e) HOMO–4 (287a, −4.297 eV), f) HOMO–5 (286a, −4.521 eV), g) HOMO–19 (272a, −6.141 eV). Hydrogen atoms are omitted for clarity.

Figure S54. Selected frontier Kohn Sham molecular orbitals of 4U. a) HOMO (283a, −2.251 eV), b) HOMO–1 (282a, −2.268 eV), c) HOMO–2 (281a, −2.299 eV), d) HOMO–4 (279, −5.121 eV), e) HOMO–22 (261a, −6.424 eV). Hydrogen atoms are omitted for clarity.
Figure S55. Selected frontier Kohn Sham molecular orbitals of 5U. a) HOMO (247a, −1.941 eV), b) HOMO−1 (246a, −1.969 eV), c) HOMO−2 (245a, −1.999 eV), d) HOMO−3 (244a, −4.538 eV), e) HOMO−4 (243a, −4.983 eV). Hydrogen atoms are omitted for clarity.

Figure S56. Selected frontier Kohn Sham molecular orbitals of 6U. a) HOMO (290a, −1.844 eV), b) HOMO−1 (289a, −1.870 eV), c) HOMO−2 (288a, −1.989 eV), d) HOMO−3 (287a, −24.364 eV), e) HOMO−4 (286a, −4.627 eV), f) HOMO−18 (272a, −6.160 eV). Hydrogen atoms are omitted for clarity.
Figure S57. Selected frontier Kohn Sham molecular orbitals of 4Ce. a) HOMO (265a, –2.461 eV), b) HOMO–2 (263a, –5.032 eV), c) HOMO–19 (246a, –6.549 eV). Hydrogen atoms are omitted for clarity.

Figure S58. Selected frontier Kohn Sham molecular orbitals of 5Ce. a) HOMO (229a, –2.086 eV), b) HOMO–1 (228a, –4.406 eV), c) HOMO–2 (227a, –4.770 eV). Hydrogen atoms are omitted for clarity.

Figure S59. Selected frontier Kohn Sham molecular orbitals of 6Ce. a) HOMO (272a, –1.952 eV), b) HOMO–1 (271a, –4.240 eV), c) HOMO–2 (270a, –4.391 eV), d) HOMO–21 (251a, –6.457 eV). Hydrogen atoms are omitted for clarity.
Figure S60. Selected frontier Kohn Sham molecular orbitals of 4Pm. a) HOMO (268a, −4.231 eV), b) HOMO–1 (267a, −4.254 eV), c) HOMO–2 (266a, −4.294 eV), d) HOMO–3 (265a, −4.329 eV), e) HOMO–5 (263a, −5.042 eV), f) HOMO–22 (246a, −6.583 eV). Hydrogen atoms are omitted for clarity.

Figure S61. Selected frontier Kohn Sham molecular orbitals of 5Pm. a) HOMO (232a, −3.673 eV), b) HOMO–1 (231a, −3.776 eV), c) HOMO–2 (230a, −3.790 eV), d) HOMO–3 (229a, −3.822 eV), e) HOMO–4 (228a, −4.469 eV), f) HOMO–5 (227a, −4.872 eV). Hydrogen atoms are omitted for clarity.
**Figure S62.** Selected frontier Kohn Sham molecular orbitals of 6Pm. a) HOMO (275a, −3.477 eV), b) HOMO–1 (274a, −3.505 eV), c) HOMO–2 (273a, −3.551 eV), d) HOMO–3 (272a, −3.600 eV), e) HOMO–4 (271a, −4.259 eV), f) HOMO–5 (270a, −4.444 eV), g) HOMO–18 (257a, −5.995 eV). Hydrogen atoms are omitted for clarity.

**Figure S63.** Selected NBOs of 4Np. a) Np-C_{BIPM} σ-bond, b) Np-C_{NHC} σ-bond.
**Figure S64.** Selected NBOs of 5Np. a) Np-C\textsubscript{BIPM} \(\sigma\)-bond, b) Np-C\textsubscript{BIPM} \(\pi\)-bond.

**Figure S65.** Selected NBOs of 6Np. a) Np-C\textsubscript{BIPM} \(\sigma\)-bond, b) Np-C\textsubscript{BIPM} \(\pi\)-bond, c) Np-C\textsubscript{NHC} \(\sigma\)-bond, d) Np-C\textsubscript{NHC} \(\sigma\)-bond.

**Figure S66.** Selected NBOs of 4U. a) U-C\textsubscript{BIPM} \(\sigma\)-bond, b) U-C\textsubscript{NHC} \(\sigma\)-bond.
Figure S67. Selected NBOs of 5U. a) U-C_{BIPM} σ-bond, b) U-C_{BIPM} π-bond.

Figure S68. Selected NBOs of 6U. a) U-C_{BIPM} σ-bond, b) U-C_{BIPM} π-bond, c) U-C_{NHC} σ-bond, d) U-C_{NHC} σ-bond.

Figure S69. Selected NBOs of 4Ce. a) Ce-C_{BIPM} σ-bond, b) Ce-C_{NHC} σ-bond.
Figure S70. Selected NBOs of 5Ce. a) Ce-C_{BIPM} σ-bond, b) Ce-C_{BIPM} π-bond.

Figure S71. Selected NBOs of 6Ce. a) Ce-C_{BIPM} σ-bond, b) Ce-C_{BIPM} π-bond, c) Ce-C_{NHC} σ-bond, d) Ce-C_{NHC} σ-bond.

Figure S72. Selected NBOs of 4Pm. a) Pm-C_{BIPM} σ-bond, b) Pm-C_{NHC} σ-bond.
Figure S73. Selected NBOs of $5\text{Pm}$. a) Pm-C$_{\text{BIPM}}$ $\sigma$-bond, b) Pm-C$_{\text{BIPM}}$ $\pi$-bond.

Figure S74. Selected NBOs of $6\text{Pm}$. a) Pm-C$_{\text{BIPM}}$ $\sigma$-bond, b) Pm-C$_{\text{BIPM}}$ $\pi$-bond, c) Pm-C$_{\text{NHC}}$ $\sigma$-bond, d) Pm-C$_{\text{NHC}}$ $\sigma$-bond.

Table S8. Final coordinates and energy for a single point energy calculation of geometry optimized $4\text{Np}$.

|   |   |   |   |
|---|---|---|---|
| 1.C | 3.631314 | -0.615213 | -3.403553 |
| 2.C | 3.111201 | 2.397281 | -3.575070 |
| 3.C | 2.162714 | -4.116339 | -3.106081 |
| 4.C | -3.667199 | 0.232367 | -2.763600 |
| 5.C | 2.038314 | -7.083148 | -2.472335 |
| 6.C | -0.601119 | 4.191248 | -2.631498 |
| 7.C | 0.071648 | 3.086050 | -2.101225 |
| 8.C | 1.201468 | -6.045214 | -1.800176 |
| 9.C | -3.201120 | -2.679628 | -1.911860 |
| 10.C | -0.872326 | 5.300246 | -1.824976 |
|   |   |   |   |
|---|---|---|---|
| 11.C | 0.408223 | -3.932624 | -1.355642 |
| 12.C | 4.926269 | 1.194232 | -1.392243 |
| 13.C | 0.290173 | -6.156532 | -0.780960 |
| 14.C | 0.470999 | 3.078183 | -0.755071 |
| 15.C | -0.494670 | 5.291248 | -0.476346 |
| 16.C | -0.184632 | 7.352221 | 0.024017 |
| 17.C | -4.731629 | -0.813203 | 0.088794 |
| 18.C | -3.119016 | 2.422805 | 0.026706 |
| 19.C | -3.828150 | 3.614763 | 0.061404 |
| 20.C | 0.160788 | 4.181978 | 0.061404 |
| 21.C | -0.494670 | 5.291248 | -0.476346 |
| 22.C | -0.184632 | 7.352221 | 0.024017 |
| 23.C | -4.731629 | -0.813203 | 0.088794 |
| 24.C | 3.160907 | 3.534942 | 0.950868 |
| 25.C | 2.679346 | 2.216096 | 0.996883 |
| 26.C | -3.786707 | 4.275121 | 1.438075 |
| 27.C | 3.282647 | 1.296653 | 1.874821 |
| 28.C | 4.199119 | 3.936754 | 1.797285 |
| 29.C | -2.314108 | 2.556027 | 2.305333 |
| 30.C | -3.020327 | 3.746516 | 2.485154 |
| 31.C | -1.767111 | -0.638848 | 2.369959 |
| 32.C | 4.321499 | 1.701371 | 2.714243 |
| 33.C | 4.776331 | 3.024644 | 2.685649 |
| 34.C | -0.843713 | -1.585593 | 2.848074 |
| 35.C | -3.012557 | -0.521192 | 3.012451 |
| 36.C | -1.155192 | -2.383449 | 3.952460 |
| 37.C | -3.323664 | -1.324796 | 4.113219 |
| 38.C | -2.395107 | -2.256240 | 4.588465 |
| 39.H | 4.526569 | -0.451169 | -0.025997 |
| 40.H | 2.276590 | 2.222665 | -4.270050 |
| 41.H | 4.026461 | 2.523331 | -4.176521 |
| 42.H | 2.794075 | -0.857549 | -4.072459 |
| 43.H | 2.401936 | -4.853270 | -3.880043 |
| 44.H | 1.817211 | -7.160301 | -3.548063 |
| 45.H | -4.197984 | -0.346748 | -3.535582 |
| 46.H | 1.690022 | -3.250613 | -3.587040 |
| 47.H | -0.904215 | 4.184883 | -3.693347 |
| 48.H | -2.753476 | 0.626696 | -3.229722 |
| 49.H | 3.842641 | -1.481254 | -2.756707 |
| 50.H | 2.924040 | 3.346491 | -3.050353 |
| 51.H | -4.318989 | 1.073480 | -2.483010 |
| 52.H | 3.112962 | -6.870397 | -2.365975 |
| 53.H | 0.291577 | 2.223457 | -2.729709 |
| 54.H | 3.089835 | -3.805716 | -2.603124 |
| 55.H | -2.334107 | -2.877568 | -2.559715 |
| 56.H | -4.108163 | -2.874668 | -2.507240 |
| 57.H | 1.850282 | -8.066709 | -2.026133 |
| 58.H | -1.382817 | 6.169976 | -2.242900 |
| 59.H | 5.776015 | 1.197889 | -2.095187 |
| 60.H | -3.193751 | -3.399853 | -1.081319 |
| 61.H | -3.140123 | 1.924879 | -0.939655 |
| 62.H | 4.957254 | 2.134964 | -0.823353 |
### Table S9. Final coordinates and energy for a single point energy calculation of geometry optimized 5Np.

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| 63.H | -4.409490 | 4.026416  | -0.618262 |
| 64.H | -5.642516 | -1.117597 | -0.631596 |
| 65.H | 0.355923  | -8.247262 | -0.353973 |
| 66.H | 5.078042  | 0.363239  | -0.686603 |
| 67.H | -1.259118 | -7.538609 | -0.178763 |
| 68.H | -0.714301 | 6.149190  | 0.160389  |
| 69.H | -4.907157 | 0.199485  | 0.304130  |
| 70.H | -1.377149 | -3.474002 | 0.442641  |
| 71.H | -1.998783 | -5.142331 | 0.486489  |
| 72.H | 2.729770  | 4.253657  | 0.254763  |
| 73.H | -4.608873 | -1.497687 | 0.763953  |
| 74.H | -0.017092 | -7.244527 | 1.058611  |
| 75.H | 0.438727  | 4.179268  | 1.115621  |
| 76.H | -4.342459 | 5.203494  | 1.580963  |
| 77.H | -0.605992 | -4.671556 | 1.511037  |
| 78.H | 2.969207  | 0.250329  | 3.127620  |
| 79.H | 0.773167  | 0.413736  | 1.888243  |
| 80.H | 4.557295  | 4.966385  | 1.757714  |
| 81.H | 0.125466  | -1.711805 | 2.358459  |
| 82.H | -3.742989 | 0.205847  | 2.658222  |
| 83.H | -1.720893 | 2.152366  | 3.127620  |
| 84.H | -2.975658 | 4.261639  | 3.445870  |
| 85.H | 4.781142  | 0.975227  | 3.386144  |
| 86.H | 5.584839  | 3.340501  | 3.346985  |
| 87.H | -0.421044 | -3.103994 | 4.315961  |
| 88.H | -4.292978 | -1.216011 | 4.601611  |
| 89.H | -2.635818 | -2.878716 | 5.452142  |
| 90.I | -0.190172 | -0.996210 | -4.175239 |
| 91.I | 2.691841  | -2.532431 | 0.816460  |
| 92.N | 1.234846  | -4.690505 | -2.141137 |
| 93.N | 1.908097  | 0.706462  | -1.353878 |
| 94.N | -0.181553 | -4.861526 | -0.543743 |
| 95.N | -1.718709 | -0.460507 | -0.535008 |
| 96.Np | 0.536569  | -1.263146 | -1.149496 |
| 97.P | 1.353593  | 1.606171  | -0.114823 |
| 98.P | -1.389040 | 0.331712  | 0.849304  |
| 99.Si | 3.339953  | 0.946162  | -2.384888 |
| 100.Si | -3.269856 | -0.897820 | -1.291322 |

Energy: \(-590.12253057\) eV
|   |   |   |   |   |
|---|---|---|---|---|
| 9.C | 4.226375 | -2.441306 | -1.855803 |
| 10.C | -1.460028 | -3.719389 | -1.795167 |
| 11.C | -4.130923 | 3.020391 | -1.669508 |
| 12.C | -1.162809 | -2.348048 | -1.704838 |
| 13.C | 5.651709 | 0.985491 | -1.023489 |
| 14.C | 2.392232 | -4.698633 | -0.927746 |
| 15.C | -1.935100 | 2.225862 | -0.983132 |
| 16.C | -3.281237 | 2.498633 | -0.864032 |
| 17.C | 2.817819 | -4.227318 | -0.365291 |
| 18.C | -0.047036 | 5.322945 | -0.162568 |
| 19.C | -0.234919 | -0.034298 | -0.103806 |
| 20.C | -0.378450 | -2.741080 | 1.042390 |
| 21.C | 5.144054 | 0.837718 | 1.310045 |
| 22.C | -1.687763 | -3.088554 | 1.422320 |
| 23.C | 0.690792 | -3.164364 | 1.846982 |
| 24.C | -1.691533 | 1.662731 | 1.826566 |
| 25.C | 1.460922 | 4.374799 | 2.348619 |
| 26.C | 4.193256 | 0.183986 | 2.285420 |
| 27.C | -1.950654 | 2.906391 | 1.427144 |
| 28.C | -2.192380 | 0.501198 | 2.431909 |
| 29.C | -1.916605 | -3.842113 | 2.578159 |
| 30.C | 0.463903 | -3.913967 | 3.005427 |
| 31.C | 1.934899 | 0.362598 | 3.075816 |
| 32.C | -0.841989 | -4.255624 | 3.374615 |
| 33.C | -2.944894 | 0.577236 | 3.609135 |
| 34.C | -2.692193 | 2.984794 | 3.608923 |
| 35.C | -3.195734 | 1.818954 | 4.200589 |
| 36.H | -3.453261 | -3.685907 | 4.564980 |
| 37.H | -2.927924 | -1.250859 | 4.414902 |
| 38.H | 2.490519 | -3.807063 | 4.114143 |
| 39.H | -1.924850 | 3.170580 | 4.267180 |
| 40.H | 1.761707 | -2.181802 | 4.028853 |
| 41.H | -4.312091 | 3.676795 | 3.721718 |
| 42.H | 0.796454 | -3.615265 | 3.596723 |
| 43.H | -2.512080 | -5.262821 | 2.876458 |
| 44.H | 4.322857 | -1.522984 | 2.456881 |
| 45.H | 4.824622 | -3.221542 | 2.354017 |
| 46.H | -1.479493 | -0.401768 | 2.577658 |
| 47.H | -0.417440 | 2.257578 | 2.531703 |
| 48.H | 5.177345 | 0.837726 | 1.999479 |
| 49.H | 2.924810 | 5.431766 | 1.555456 |
| 50.H | -5.171836 | 3.234942 | 1.421143 |
| 51.H | 2.742538 | 4.040647 | 1.447565 |
| 52.H | -0.230431 | 5.176248 | 1.237463 |
| 53.H | -1.056414 | -4.416649 | 1.060059 |
| 54.H | 6.568074 | 0.380823 | 0.943582 |
| 55.H | 4.668238 | -2.259691 | 0.864032 |
| 56.H | 5.888366 | 2.052392 | 0.892432 |
| 57.H | 1.370548 | -5.077186 | -0.773617 |
| 58.H | 3.211226 | 5.246325 | -0.218477 |
| 59.H | 0.378073 | 6.330523 | -0.022970 |
| 60.H | 2.889002 | -4.678792 | 0.054621 |
Table S1. Final coordinates and energy for a single point energy calculation of geometry optimized 6Np.

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| 1.C  | -0.048534 | 0.121039 | -5.264749 |
| 2.C  | -3.695479 | -2.792197 | -4.247650 |
| 3.C  | -3.239542 | -3.000127 | -4.031832 |
| 4.C  | 1.041495 | 2.668623 | -3.991770 |
| 5.C  | 2.700376 | 0.120164 | -4.001133 |
| 6.C  | -4.326914 | -1.683210 | -3.676438 |
| 7.C  | -3.084375 | 3.563983 | -3.169775 |
| 8.C  | -1.594290 | -2.094475 | -3.265405 |
| 9.C  | -2.471923 | 2.311681 | -3.070969 |
| 10.C | -3.593319 | -0.779351 | -2.902373 |
| 11.C | -2.214922 | -0.967335 | -2.702850 |
| 12.C | -3.333549 | 4.318289 | -2.017780 |
| 13.C | 6.100848 | 3.606504 | -1.801743 |

Energy: \(-546.51288965\) eV
|   |   |   |   |   |
|---|---|---|---|---|
|14.C | -2.104387 | 1.786284 | -1.819341 |
|15.C | -2.599567 | -5.447148 | -1.363063 |
|16.C | 3.342754 | 5.382348 | -1.288176 |
|17.C | 4.746025 | 3.190269 | -1.336975 |
|18.C | 5.353467 | 0.754143 | -1.202150 |
|19.C | 3.609165 | 3.924081 | -1.121620 |
|20.C | -1.243305 | -5.217395 | -1.113421 |
|21.C | -3.553135 | -4.525125 | -0.918294 |
|22.C | -2.978101 | 3.804537 | -0.766821 |
|23.C | 3.100711 | 1.717025 | -0.664324 |
|24.C | 3.342754 | 5.382348 | -1.288176 |
|25.C | 4.746025 | 3.190269 | -1.336975 |
|26.C | 5.353467 | 0.754143 | -1.202150 |
|27.C | 3.609165 | 3.924081 | -1.121620 |
|28.C | -1.243305 | -5.217395 | -1.113421 |
|29.C | -3.553135 | -4.525125 | -0.918294 |
|30.C | -2.978101 | 3.804537 | -0.766821 |
|31.C | 3.100711 | 1.717025 | -0.664324 |
|32.C | 3.342754 | 5.382348 | -1.288176 |
|33.C | 4.746025 | 3.190269 | -1.336975 |
|34.C | 5.353467 | 0.754143 | -1.202150 |
|35.C | 3.609165 | 3.924081 | -1.121620 |
|36.C | -1.243305 | -5.217395 | -1.113421 |
|37.C | -3.553135 | -4.525125 | -0.918294 |
|38.C | -2.978101 | 3.804537 | -0.766821 |
|39.C | 3.100711 | 1.717025 | -0.664324 |
|40.C | 3.342754 | 5.382348 | -1.288176 |
|41.C | 4.746025 | 3.190269 | -1.336975 |
|42.C | 5.353467 | 0.754143 | -1.202150 |
|43.C | 3.609165 | 3.924081 | -1.121620 |
|44.C | -1.243305 | -5.217395 | -1.113421 |
|45.C | -3.553135 | -4.525125 | -0.918294 |
|46.C | -2.978101 | 3.804537 | -0.766821 |
|47.C | 3.100711 | 1.717025 | -0.664324 |
|48.C | 3.342754 | 5.382348 | -1.288176 |
|49.C | 4.746025 | 3.190269 | -1.336975 |
|50.C | 5.353467 | 0.754143 | -1.202150 |
|51.C | 3.609165 | 3.924081 | -1.121620 |
|52.C | -1.243305 | -5.217395 | -1.113421 |
|53.C | -3.553135 | -4.525125 | -0.918294 |
|54.C | -2.978101 | 3.804537 | -0.766821 |
|55.C | 3.100711 | 1.717025 | -0.664324 |
|56.C | 3.342754 | 5.382348 | -1.288176 |
|57.C | 4.746025 | 3.190269 | -1.336975 |
|58.C | 5.353467 | 0.754143 | -1.202150 |
|59.C | 3.609165 | 3.924081 | -1.121620 |
|60.C | -1.243305 | -5.217395 | -1.113421 |
|61.C | -3.553135 | -4.525125 | -0.918294 |
|62.C | -2.978101 | 3.804537 | -0.766821 |
|63.C | 3.100711 | 1.717025 | -0.664324 |
|64.C | 3.342754 | 5.382348 | -1.288176 |
|65.C | 4.746025 | 3.190269 | -1.336975 |
|66.C | 5.353467 | 0.754143 | -1.202150 |
|   |   |   |   |   |
|---|---|---|---|---|
| 66.H | 2.913622 | -6.338459 | -1.909349 |
| 67.H | 2.542578 | 5.567065 | -2.021868 |
| 68.H | 4.243831 | 5.893459 | -1.648516 |
| 69.H | -0.491467 | -5.926546 | -1.465122 |
| 70.H | -4.612555 | -4.692365 | -1.120970 |
| 71.H | 6.878923 | 3.389563 | -1.053791 |
| 72.H | 4.825406 | 0.190568 | -1.022072 |
| 73.H | 0.218170 | 3.896202 | -0.220499 |
| 74.H | 0.218170 | 3.896202 | -0.220499 |
| 75.H | 0.218170 | 3.896202 | -0.220499 |
| 76.H | 0.218170 | 3.896202 | -0.220499 |
| 77.H | 0.218170 | 3.896202 | -0.220499 |
| 78.H | 0.218170 | 3.896202 | -0.220499 |
| 79.H | 0.218170 | 3.896202 | -0.220499 |
| 80.H | 0.218170 | 3.896202 | -0.220499 |
| 81.H | 0.218170 | 3.896202 | -0.220499 |
| 82.H | 0.218170 | 3.896202 | -0.220499 |
| 83.H | 0.218170 | 3.896202 | -0.220499 |
| 84.H | 0.218170 | 3.896202 | -0.220499 |
| 85.H | 0.218170 | 3.896202 | -0.220499 |
| 86.H | 0.218170 | 3.896202 | -0.220499 |
| 87.H | 0.218170 | 3.896202 | -0.220499 |
| 88.H | 0.218170 | 3.896202 | -0.220499 |
| 89.H | 0.218170 | 3.896202 | -0.220499 |
| 90.H | 0.218170 | 3.896202 | -0.220499 |
| 91.H | 0.218170 | 3.896202 | -0.220499 |
| 92.H | 0.218170 | 3.896202 | -0.220499 |
| 93.H | 0.218170 | 3.896202 | -0.220499 |
| 94.H | 0.218170 | 3.896202 | -0.220499 |
| 95.H | 0.218170 | 3.896202 | -0.220499 |
| 96.H | 0.218170 | 3.896202 | -0.220499 |
| 97.H | 0.218170 | 3.896202 | -0.220499 |
| 98.H | 0.218170 | 3.896202 | -0.220499 |
| 99.H | 0.218170 | 3.896202 | -0.220499 |
| 100.H | 0.218170 | 3.896202 | -0.220499 |
| 101.H | 0.218170 | 3.896202 | -0.220499 |
| 102.H | 0.218170 | 3.896202 | -0.220499 |
| 103.H | 0.218170 | 3.896202 | -0.220499 |
| 104.H | 0.218170 | 3.896202 | -0.220499 |
| 105.H | 0.218170 | 3.896202 | -0.220499 |
| 106.H | 0.218170 | 3.896202 | -0.220499 |
| 107.H | 0.218170 | 3.896202 | -0.220499 |
| 108.H | 0.218170 | 3.896202 | -0.220499 |
| 109.H | 0.218170 | 3.896202 | -0.220499 |
| 110.H | 0.218170 | 3.896202 | -0.220499 |
| 111.H | 0.218170 | 3.896202 | -0.220499 |
| 112.H | 0.218170 | 3.896202 | -0.220499 |
| 113.H | 0.218170 | 3.896202 | -0.220499 |
| 114.H | 0.218170 | 3.896202 | -0.220499 |
| 115.H | 0.218170 | 3.896202 | -0.220499 |
| 116.H | 0.218170 | 3.896202 | -0.220499 |
| 117.H | 0.218170 | 3.896202 | -0.220499 |
Table S11. Final coordinates and energy for a single point energy calculation of geometry optimized 4U.

|   |   |   |   |
|---|---|---|---|
| 1.C | 3.674010 | -0.620054 | -3.335940 |
| 2.C | 3.147983 | 2.393310 | -3.569636 |
| 3.C | 2.183696 | -4.147115 | -3.130358 |
| 4.C | -3.674347 | 0.218353 | -2.749594 |
| 5.C | 2.020290 | -7.105829 | -2.480321 |
| 6.C | -0.593936 | 4.218591 | -2.617204 |
| 7.C | 0.089781 | 3.113471 | -2.100694 |
| 8.C | 1.197212 | -6.057498 | -1.811219 |
| 9.C | -3.167836 | -2.683013 | -1.906551 |
| 10.C | -0.899926 | 5.303141 | -1.790593 |
| 11.C | 0.432372 | -3.929847 | -1.374984 |
| 12.C | 4.935931 | 1.259344 | -1.340019 |
| 13.C | 0.290549 | -6.153592 | -0.788523 |
| 14.C | 0.465140 | 3.082904 | -0.748763 |
| 15.C | -0.546828 | 5.270243 | -0.436714 |
| 16.C | -0.190772 | -7.338213 | -0.020843 |
| 17.C | -4.741100 | -0.833385 | -0.079572 |
| 18.C | -3.097274 | 2.455659 | 0.032061 |
| 19.C | -3.803400 | 3.647934 | 0.222838 |
| 20.C | 0.121428 | 4.162078 | 0.086664 |
| 21.C | -1.060983 | -4.505331 | 0.541092 |
| 22.C | 0.341530 | 0.574540 | 0.875018 |
| 23.C | -2.359984 | 1.890772 | 1.079947 |
| 24.C | 3.155751 | 3.561728 | 0.955349 |
| 25.C | 2.684786 | 2.239629 | 1.006521 |
| 26.C | -3.772353 | 4.291255 | 1.461942 |
| 27.C | 3.299824 | 1.327006 | 1.883367 |
| 28.C | 4.201365 | 3.971961 | 1.788843 |
| 29.C | -2.308118 | 2.560632 | 2.317067 |
| 30.C | -3.013984 | 3.749213 | 2.506811 |
| 31.C | -1.755474 | -0.619669 | 2.387305 |
| 32.C | 4.342548 | 1.741914 | 2.713639 |
| 33.C | 4.791864 | 3.065895 | 2.673863 |
| 34.C | -0.825237 | -1.554590 | 2.877139 |
| 35.C | -3.008111 | -0.516255 | 3.017912 |
| 36.C | -1.138032 | -2.351937 | 3.981595 |
| 37.C | -3.321211 | -1.322674 | 4.115917 |
| 38.C | -2.386516 | -2.240562 | 4.603120 |
| 39.H | 4.572838 | -0.491280 | -3.959388 |
| 40.H | 2.312060 | 2.204522 | -4.258268 |
| 41.H | 4.058831 | 2.514186 | -4.176458 |
| 42.H | 2.835185 | -0.865904 | -4.001298 |
| 43.H | 2.373239 | -4.873862 | -3.928267 |
| 44.H | 1.793125 | -7.187377 | -3.554481 |

Energy: -704.34159680 eV
|   |     |     |     |
|---|-----|-----|-----|
| 45 | H   | -4.235879 | -0.350841 | -3.505775 |
| 46 | H   | 1.738674  | -3.248487 | -3.576850 |
| 47 | H   | -0.879872 | 4.230913  | -3.670161 |
| 48 | H   | -2.758264 | 0.580796  | -3.234969 |
| 49 | H   | 3.862060  | -1.470149 | -2.662364 |
| 50 | H   | 2.959130  | 3.348442  | -3.058669 |
| 51 | H   | -4.296096 | 1.079894  | -2.465799 |
| 52 | H   | 3.096889  | -6.899868 | -2.381492 |
| 53 | H   | 0.333385  | 2.267005  | -2.744241 |
| 54 | H   | 3.132648  | -3.888950 | -2.638351 |
| 55 | H   | -2.293929 | -2.846293 | -2.553870 |
| 56 | H   | -4.064797 | -2.903805 | -2.506218 |
| 57 | H   | 1.826828  | -8.085309 | -2.026706 |
| 58 | H   | -1.419553 | 6.172431  | -2.197656 |
| 59 | H   | 5.803802  | 1.268008  | -2.018239 |
| 60 | H   | -3.136936 | -3.407603 | -1.081652 |
| 61 | H   | -3.111440 | 1.969669  | -0.942262 |
| 62 | H   | 4.931186  | 2.209913  | -0.790988 |
| 63 | H   | -4.377292 | 4.073336  | -0.601965 |
| 64 | H   | -5.652902 | -1.139336 | -0.616072 |
| 65 | H   | 0.339242  | -8.240779 | -0.347895 |
| 66 | H   | 5.084766  | 0.446767  | -0.614614 |
| 67 | H   | -1.268069 | -7.515913 | -0.166124 |
| 68 | H   | -0.795074 | 6.109569  | 0.214827 |
| 69 | H   | -4.916179 | 0.179539  | 0.309607 |
| 70 | H   | -1.343709 | -3.451908 | 0.444155 |
| 71 | H   | -1.970846 | -5.119557 | 0.508225 |
| 72 | H   | 2.712620  | 4.277271  | 0.262811 |
| 73 | H   | -4.614156 | -1.513464 | 0.774438 |
| 74 | H   | -0.015281 | -7.224191 | 1.059812 |
| 75 | H   | 0.379960  | 4.139534  | 1.146035 |
| 76 | H   | -4.330140 | 5.217091  | 1.613804 |
| 77 | H   | -0.559702 | -6.467063 | 1.508398 |
| 78 | H   | 2.995869  | 0.276934  | 1.893378 |
| 79 | H   | 0.800413  | 0.350402  | 1.839659 |
| 80 | H   | 4.555917  | 5.002777  | 1.740885 |
| 81 | H   | 0.149666  | -1.676389 | 2.396035 |
| 82 | H   | -3.744569 | 0.201315  | 2.656422 |
| 83 | H   | -1.720086 | 2.146402  | 3.137983 |
| 84 | H   | -2.976916 | 4.252315  | 3.474866 |
| 85 | H   | 4.811181  | 1.021449  | 3.385412 |
| 86 | H   | 5.607415  | 3.387377  | 3.324003 |
| 87 | H   | -0.398189 | -3.061373 | 4.355800 |
| 88 | H   | -4.297693 | -1.227356 | 4.593489 |
| 89 | H   | -2.629423 | -2.865880 | 5.463939 |
| 90 | I   | -0.175466 | -1.024675 | -4.192073 |
| 91 | I   | 2.672709  | -2.548243 | 0.801434 |
| 92 | N   | 1.246887  | -4.704332 | -2.160216 |
| 93 | N   | 1.945280  | 0.716529  | -1.340441 |
| 94 | N   | -0.167496 | -4.851966 | -0.554914 |
| 95 | N   | -1.735361 | -0.473124 | -0.512606 |
| 96 | U   | 0.516204  | -1.266010 | -1.159631 |
Table S12. Final coordinates and energy for a single point energy calculation of geometry optimized 5U.

|   |       |       |       |
|---|-------|-------|-------|
| 1 | C     | -2.814376 | -3.327769 | -3.765774 |
| 2 | C     | -2.536224 | -1.959980 | -3.676505 |
| 3 | C     | 1.798893  | -3.166123 | -3.523557 |
| 4 | C     | -2.310575 | 2.994329  | -3.262276 |
| 5 | C     | -2.280285 | -4.210389 | -2.820916 |
| 6 | C     | -3.656935 | 3.245701  | -2.970873 |
| 7 | C     | -1.726955 | -1.474403 | -2.646243 |
| 8 | C     | -1.462227 | 2.486764  | -2.277069 |
| 9 | C     | 4.210759  | -2.448103 | -1.811610 |
|10 | C     | -1.466625 | -3.726383 | -1.792796 |
|11 | C     | -4.149792 | 2.977003  | -1.691628 |
|12 | C     | -1.181191 | -2.353319 | -1.698516 |
|13 | C     | 5.676154  | 0.986805  | -1.003525 |
|14 | C     | 2.367773  | -4.713548 | -0.925304 |
|15 | C     | -1.947804 | 2.220168  | -0.983626 |
|16 | C     | -3.301850 | 2.464214  | -0.703339 |
|17 | C     | 2.804097  | 4.216794  | -0.335926 |
|18 | C     | -0.053549 | 5.311617  | -0.163833 |
|19 | C     | -0.258333 | -0.040057 | -0.094695 |
|20 | C     | -0.395235 | -2.745713 | 1.056945 |
|21 | C     | 5.176740  | 0.789319  | 1.325088 |
|22 | C     | -1.706167 | -3.078782 | 1.441646 |
|23 | C     | 0.672487  | -3.175473 | 1.860300 |
|24 | C     | -1.708133 | 1.656866  | 1.843198 |
|25 | C     | 1.433407  | 4.361787  | 2.365395 |
|26 | C     | 4.202816  | 0.158782  | 2.291695 |
|27 | C     | -1.999296 | 2.902968  | 2.425453 |
|28 | C     | -2.152460 | 0.490682  | 2.483763 |
|29 | C     | -1.939696 | -3.822084 | 2.602596 |
|30 | C     | 0.440125  | -3.914652 | 3.024695 |
|31 | C     | 1.940053  | 0.377925  | 3.049964 |
|32 | C     | -0.867272 | -4.239858 | 3.398996 |
|33 | C     | -2.879922 | 0.565036  | 3.676331 |
|34 | C     | -2.718603 | 2.979024  | 3.620744 |
|35 | C     | -3.164995 | 1.808884  | 4.247132 |
|36 | H     | -3.449762 | -3.706189 | -4.568561 |
|37 | H     | -2.955256 | -1.266953 | -4.407913 |
|38 | H     | 2.472187  | -3.827705 | -4.091048 |
|39 | H     | -1.916670 | 3.197100  | -4.259656 |
|40 | H     | 1.794829  | -2.182601 | -4.015711 |
|41 | H     | -4.317970 | 3.650127  | -3.739580 |
|42 | H     | 0.784497  | -3.582613 | -3.587112 |

Energy: -589.14704475 eV
|   |   |   |   |   |
|---|---|---|---|---|
| 43.H | -2.499390 | -5.277996 | -2.882872 |
| 44.H | 4.315308  | -1.520971  | -2.395653  |
| 45.H | 4.820894  | -3.216966  | -2.310382  |
| 46.H | -1.514450 | -0.406976  | -2.564699  |
| 47.H | -0.412513 | 2.295794   | -2.515882  |
| 48.H | 5.208509  | 0.858296   | -1.985549  |
| 49.H | 2.909786  | -5.439403  | -1.551538  |
| 50.H | -5.198601 | 3.168948   | -1.456632  |
| 51.H | 2.741425  | 4.018445   | -1.415874  |
| 52.H | -0.211975 | 5.169605   | -1.242133  |
| 53.H | -1.058940 | -4.21956   | -1.057308  |
| 54.H | 6.591774  | 0.380882   | -0.926506  |
| 55.H | 4.636656  | -2.280590  | -0.811473  |
| 56.H | 5.912010  | 2.050630   | -0.847416  |
| 57.H | 1.345084  | -5.093461  | -0.790689  |
| 58.H | 3.182685  | 5.241873   | -0.200331  |
| 59.H | 0.364058  | 5.134817   | -0.010384  |
| 60.H | 2.849557  | -4.703334  | 0.063644   |
| 61.H | 3.565864  | 3.540730   | 0.087083   |
| 62.H | -1.042311 | 5.288711   | 0.317129   |
| 63.H | -3.700119 | 2.260257   | 0.290834   |
| 64.H | -2.550226 | -2.765067  | 0.824164   |
| 65.H | 6.177746  | 0.346882   | 1.465464   |
| 66.H | 5.244022  | 1.878768   | 1.492022   |
| 67.H | 1.690715  | -2.936294  | 1.548929   |
| 68.H | -1.673656 | 3.823760   | 1.939252   |
| 69.H | -1.921500 | -0.447721  | 2.037160   |
| 70.H | 1.812440  | 5.385990   | 2.506692   |
| 71.H | 4.206321  | -0.942029  | 2.204259   |
| 72.H | 2.188996  | 3.669349   | 2.766318   |
| 73.H | -2.962178 | -4.082756  | 2.882918   |
| 74.H | 0.526525  | 4.252218   | 2.976129   |
| 75.H | 0.975037  | 0.773202   | 2.720384   |
| 76.H | 4.484388  | 0.434347   | 3.322640   |
| 77.H | 1.860702  | -0.707593  | 3.211526   |
| 78.H | 1.282131  | -4.250008  | 3.633833   |
| 79.H | 2.262784  | 0.878869   | 3.975899   |
| 80.H | -3.227165 | -0.351486  | 4.156819   |
| 81.H | -2.938005 | 3.953290   | 4.061449   |
| 82.H | -1.050296 | -4.825212  | 4.302054   |
| 83.H | -3.735299 | 1.868932   | 5.175828   |
| 84.I | 2.501727  | 1.357519   | -3.494981  |
| 85.N | 1.530067  | -1.795556  | -0.822574  |
| 86.N | 0.624849  | 2.367522   | 0.258128   |
| 87.U | 2.045354  | 0.560348   | -0.546590  |
| 88.O | 4.710522  | 0.537946   | -0.017328  |
| 89.O | 2.887498  | 0.666321   | 1.990015   |
| 90.P | -0.062571 | -1.663208  | -0.407587  |
| 91.P | -0.776553 | 1.506163   | 0.251501   |
| 92.Si | 2.403328  | -3.005009  | -1.744870  |
| 93.Si | 1.130818  | 4.011207   | 0.526577   |

Energy: \(-545.42819150\) eV
Table S13. Final coordinates and energy for a single point energy calculation of geometry optimized 6U.

|   |    x       |    y       |    z       |
|---|------------|------------|------------|
| 1.C | -0.035049  | 0.153730   | -5.272355  |
| 2.C | -3.693264  | -2.780967  | -4.261174  |
| 3.C | -2.325013  | -2.990381  | -4.060168  |
| 4.C | 1.055577   | 2.690866   | -3.982476  |
| 5.C | 2.712799   | 0.135718   | -4.020222  |
| 6.C | -4.319746  | -1.677622  | -3.674029  |
| 7.C | -3.090753  | 3.558141   | -3.161642  |
| 8.C | -1.582515  | -2.091584  | -3.292167  |
| 9.C | -2.458389  | 2.315126   | -3.072513  |
| 10.C| -3.578612  | -0.779809  | -2.900211  |
| 11.C| -2.198031  | -0.969095  | -2.715197  |
| 12.C| -3.372349  | 4.289588   | -2.002257  |
| 13.C| 6.080324   | 3.608369   | -1.784171  |
| 14.C| -2.098410  | 1.777789   | -1.823364  |
| 15.C| -2.608964  | -5.489239  | -1.312722  |
| 16.C| 3.352558   | 5.414934   | -1.239694  |
| 17.C| 4.720476   | 3.203171   | -1.323274  |
| 18.C| 5.299818   | 0.761536   | -1.214316  |
| 19.C| 3.593584   | 3.949118   | -1.101168  |
| 20.C| -1.250178  | -5.251104  | -1.083932  |
| 21.C| -3.559494  | -4.562694  | -0.871372  |
| 22.C| -3.025238  | 3.763613   | -0.753844  |
| 23.C| 3.046123   | 1.739865   | -0.684051  |
| 24.C| -2.398427  | 2.516026   | -0.669411  |
| 25.C| -0.843152  | -4.098150  | -0.406956  |
| 26.C| 1.241185   | 3.427619   | -0.363904  |
| 27.C| -3.154615  | -3.411152  | -0.191437  |
| 28.C| -1.791839  | -3.171968  | 0.055791   |
| 29.C| -1.017297  | -0.263085  | -0.039897  |
| 30.C| 4.525613   | 0.257499   | 2.317349   |
| 31.C| -2.510381  | -1.441375  | 2.232113   |
| 32.C| 2.107225   | 0.886909   | 2.190327   |
| 33.C| -3.023342  | -0.166130  | 2.509691   |
| 34.C| 2.687989   | -3.004911  | 2.887665   |
| 35.C| -0.097249  | 1.891675   | 2.808917   |
| 36.C| -2.975365  | -2.530445  | 2.990500   |
| 37.C| 0.106130   | -4.549098  | 3.104812   |
| 38.C| -3.942916  | 0.028456   | 3.545473   |
| 39.C| -3.895859  | -2.341389  | 4.024195   |
| 40.C| 3.276298   | 1.560724   | 4.069240   |
| 41.C| 1.998746   | 2.037971   | 4.192769   |
| 42.C| -4.374791  | -1.058316  | 4.312457   |
| 43.C| 0.409870   | -1.863784  | 4.557786   |
| 44.C| 4.447815   | 1.667692   | 4.986026   |
| 45.C| 1.354011   | 2.834011   | 5.276947   |
| 46.H | 0.388857   | 0.575847   | -6.197489  |
| 47.H | 0.024458   | -0.940631  | -5.348578  |
| 48.H | -1.101482  | 0.416552   | -5.247344  |
| 49.H | 1.355906   | 2.954248   | -5.009039  |
| 50.H | -4.270496  | -3.479344  | -4.869927  |
|   |   |   |   |
|---|---|---|---|
| 51. H | 3.079626 | 0.392393 | -5.026488 |
| 52. H | -1.832589 | -3.857152 | -4.504189 |
| 53. H | -3.367466 | 3.956102 | -4.139797 |
| 54. H | -5.388675 | -1.510983 | -3.821132 |
| 55. H | 2.753244 | -0.956319 | 3.906416 |
| 56. H | -2.254527 | 1.755590 | -3.986580 |
| 57. H | 0.089807 | 3.175504 | -3.781441 |
| 58. H | 1.803689 | 3.116168 | -3.298358 |
| 59. H | 3.405876 | 0.570539 | -3.288487 |
| 60. H | -0.514054 | -2.253959 | -3.141734 |
| 61. H | 6.353540 | 3.118443 | -2.731488 |
| 62. H | -4.077487 | 0.078748 | -2.448151 |
| 63. H | -3.867821 | 5.259786 | -2.072538 |
| 64. H | 6.116648 | 4.691966 | -1.950877 |
| 65. H | 5.741660 | 0.767101 | -2.219806 |
| 66. H | -2.927130 | -6.391616 | -1.837911 |
| 67. H | 2.576859 | 5.630532 | -1.990991 |
| 68. H | 4.270980 | 5.921528 | -1.559779 |
| 69. H | -0.500862 | -5.964945 | -1.431523 |
| 70. H | -4.621033 | -4.736576 | -1.056913 |
| 71. H | 6.860433 | 3.358014 | -1.048464 |
| 72. H | 4.758435 | -0.183575 | -1.082377 |
| 73. H | 0.866317 | 4.187545 | -1.059691 |
| 74. H | 6.110258 | 0.828617 | -0.473892 |
| 75. H | 3.031435 | 5.873051 | -0.291717 |
| 76. H | 0.590024 | 2.549769 | -0.448022 |
| 77. H | 0.218666 | -3.912281 | -0.232094 |
| 78. H | -3.254206 | 4.321855 | 0.156576 |
| 79. H | -3.905647 | -2.696661 | 0.156153 |
| 80. H | -2.134720 | 2.082810 | 0.297049 |
| 81. H | 1.199741 | 3.821348 | 0.661771 |
| 82. H | 4.262366 | -0.339320 | 1.436508 |
| 83. H | 3.009137 | -3.539135 | 1.983090 |
| 84. H | 5.256432 | 1.026369 | 2.027337 |
| 85. H | -0.404286 | 1.362230 | 1.895593 |
| 86. H | 0.181820 | -5.104525 | 2.159716 |
| 87. H | -2.702363 | 0.668490 | 1.884869 |
| 88. H | -2.627670 | -3.538066 | 2.761586 |
| 89. H | -0.270338 | 2.971009 | 2.685175 |
| 90. H | 3.208062 | -2.037896 | 2.906275 |
| 91. H | 4.982601 | -0.409340 | 3.059676 |
| 92. H | -0.945291 | -4.565208 | 3.421806 |
| 93. H | 3.022923 | -3.578073 | 3.766304 |
| 94. H | 0.680555 | -5.102195 | 3.864611 |
| 95. H | -0.705737 | 1.525617 | 3.645928 |
| 96. H | -4.332569 | 1.028321 | 3.748003 |
| 97. H | -4.245176 | -3.199226 | 4.601982 |
| 98. H | 5.299449 | 2.182400 | 4.514442 |
| 99. H | 0.921450 | -0.889521 | 4.574845 |
| 100. H | -0.669187 | -1.684082 | 4.666122 |
| 101. H | 0.981551 | 3.803399 | 4.910232 |
| 102. H | -5.092892 | -0.910162 | 5.121039 |
|   |   |   |   |
|---|---|---|---|
| 103.H | 4.800732 | 0.677340 | 5.313623 |
| 104.H | 0.745693 | -2.435702 | 5.436886 |
| 105.H | 0.500347 | 2.301033 | 5.723166 |
| 106.H | 4.174064 | 2.233526 | 5.884631 |
| 107.H | 2.073664 | 3.037144 | 6.079090 |
| 108.I | 3.260680 | -2.677005 | -1.081559 |
| 109.N | 0.344381 | 0.317221 | -2.229544 |
| 110.N | 4.365274 | 1.872050 | -1.062827 |
| 111.N | 2.599844 | 3.040961 | -0.719732 |
| 112.N | 0.279901 | 1.901169 | 1.551439 |
| 113.N | 3.316535 | 0.870408 | 2.850997 |
| 114.N | 1.313375 | 1.616743 | 3.046139 |
| 115.U | 1.442512 | -0.359441 | -0.056351 |
| 116.P | -1.192186 | 0.163609 | -1.666645 |
| 117.P | -1.212842 | -1.648043 | 0.918473 |
| 118.Si | 0.964970 | 0.803380 | -3.795933 |
| 119.Si | 0.814685 | -2.795072 | 2.955922 |

Energy: $-703.49454966$ eV

**Table S14.** Final coordinates and energy for a single point energy calculation of geometry optimized $4\text{Ce}$. 

|   |   |   |   |
|---|---|---|---|
| 1.C | 2.142813 | 1.961351 | -4.079856 |
| 2.C | 3.534023 | 2.033725 | -3.966477 |
| 3.C | -0.270371 | -2.540865 | -3.881371 |
| 4.C | 4.187693 | -1.771723 | -2.776384 |
| 5.C | 1.345517 | 1.945069 | -2.931115 |
| 6.C | 4.130610 | 2.063128 | -2.699577 |
| 7.C | -0.973479 | 4.519418 | -2.658264 |
| 8.C | 5.334630 | -1.678475 | -1.984337 |
| 9.C | 2.921966 | -1.643110 | -2.194911 |
| 10.C | 0.716559 | -4.456146 | -1.699854 |
| 11.C | -2.190907 | 3.603669 | -1.769925 |
| 12.C | 1.935780 | 1.992297 | -1.658157 |
| 13.C | 3.338858 | 2.028093 | -1.550575 |
| 14.C | -3.31627 | 3.602510 | -0.914001 |
| 15.C | 5.212552 | -1.440245 | -0.608860 |
| 16.C | 2.788797 | -1.429661 | -0.817877 |
| 17.C | 3.949523 | -1.311677 | -0.029352 |
| 18.C | -5.660239 | 0.729631 | -0.055249 |
| 19.C | -1.101880 | 5.186672 | 0.338864 |
| 20.C | -4.101115 | -1.082973 | 0.591912 |
| 21.C | 2.449463 | 4.138268 | 0.680918 |
| 22.C | 0.836434 | 0.375372 | 0.616763 |
| 23.C | 1.552164 | 3.118057 | 1.037131 |
| 24.C | -6.227661 | -1.224989 | 1.451431 |
| 25.C | -7.652860 | -0.857022 | 1.723143 |
| 26.C | 2.039242 | -3.463831 | 1.458479 |
| 27.C | 1.253903 | -2.297755 | 1.466125 |
| 28.C | 2.936683 | 5.020550 | 1.650497 |
| 29.C | -3.124334 | -3.050844 | 1.753917 |
|   |       |       |       |
|---|-------|-------|-------|
|30. C| -5.512932 | -2.286484 | 1.947670 |
|31. C| 1.117628 | 3.024346 | 2.372270 |
|32. C| 2.051271 | -4.321026 | 2.562793 |
|33. C| -5.963398 | -3.374571 | 2.871732 |
|34. C| 0.472370 | -2.014917 | 2.601297 |
|35. C| 2.522945 | 4.903263 | 2.980651 |
|36. C| 1.604201 | 3.909067 | 3.335824 |
|37. C| 1.279071 | -4.026266 | 3.706121 |
|38. C| 0.490266 | -2.870871 | 3.706121 |
|39. H| 1.671281 | 1.925356 | -5.062779 |
|40. H| 4.156021 | 2.061644 | -4.863051 |
|41. H| -0.638901 | -3.388772 | -4.481827 |
|42. H| -0.887608 | -1.663816 | -4.124757 |
|43. H| 0.760478 | -2.339700 | -4.205918 |
|44. H| 4.273035 | -1.943003 | -3.850303 |
|45. H| -1.283677 | 3.834275 | -3.461140 |
|46. H| 0.260152 | 1.897805 | -3.016301 |
|47. H| -1.466423 | 5.489296 | -2.835142 |
|48. H| 6.322820 | -1.784194 | -2.435469 |
|49. H| 2.032383 | -1.700930 | -2.817134 |
|50. H| 5.216431 | 2.107936 | -2.605400 |
|51. H| 0.438145 | -5.282949 | -2.374555 |
|52. H| 0.112395 | 4.677675 | -2.745577 |
|53. H| -2.435763 | 4.339588 | -2.553019 |
|54. H| 1.778835 | -4.230175 | -1.876726 |
|55. H| -2.944724 | -2.802966 | -1.830574 |
|56. H| -3.679217 | 2.888572 | -1.675578 |
|57. H| -3.822188 | 4.569577 | -1.114065 |
|58. H| 0.610961 | -4.821013 | -0.667088 |
|59. H| -2.292556 | -4.113126 | -0.800702 |
|60. H| -5.062700 | 0.791134 | -0.974136 |
|61. H| 3.813115 | 2.035898 | -0.568880 |
|62. H| 6.104081 | -1.358233 | 0.014695 |
|63. H| -3.665608 | 3.268722 | 0.081636 |
|64. H| 2.772694 | 4.249303 | -0.353755 |
|65. H| -6.719271 | 0.762291 | -0.335248 |
|66. H| -1.717538 | 6.070898 | 0.102967 |
|67. H| -0.050731 | 5.508782 | 0.368437 |
|68. H| -5.430472 | 1.581734 | 0.600659 |
|69. H| 2.652909 | -3.703127 | 0.590204 |
|70. H| 3.864755 | -1.126834 | 1.043110 |
|71. H| -7.938062 | 0.075721 | 1.224594 |
|72. H| -8.344835 | -1.641644 | 1.381306 |
|73. H| -2.260303 | -2.788646 | 1.138391 |
|74. H| -1.380934 | 4.842117 | 1.346334 |
|75. H| 3.640290 | 5.802330 | 1.361340 |
|76. H| -3.376207 | -4.100647 | 1.559328 |
|77. H| 1.092985 | 0.466815 | 1.673042 |
|78. H| -6.771254 | -3.975164 | 2.425808 |
|79. H| -7.821211 | -0.713369 | 2.801189 |
|80. H| 2.670990 | -5.218429 | 2.540178 |
|81. H| -0.159688 | -1.123579 | 2.635206 |
82.H  -2.853522  -2.924763  2.809963
83.H  -5.144218  -4.059057  3.122186
84.H   0.368946   2.281693  2.657981
85.H  -6.343688  -2.959134  3.817150
86.H   2.907404   5.589648  3.737067
87.H   1.256006   3.823245  4.366133
88.H   1.294424  -4.692182  4.555604
89.H  -0.113445  -2.626238  4.581466
90.Ce  -1.786697   0.140749  -0.247271
91.I   -3.027644  0.308189  -3.137636
92.I  -2.330884   0.982451  2.795835
93.N  -0.115887  -1.586189  -0.998688
94.N  -0.686012   2.29952   -0.610743
95.N  -5.351768  -0.526612   0.616566
96.N  -4.232850  -2.178616  1.401420
97.P   0.843758   1.952501  -0.189410
98.P   1.139034  -1.220515  -0.028419
99.Si  -0.426487  -2.986272  2.049808
100.Si  3.859645  -0.954625

Energy: -588.15415491 eV

Table S15. Final coordinates and energy for a single point energy calculation of geometry optimized 5Ce.

1.C   0.697623  -1.035128  -5.036294
2.C   0.536350   3.429408  -4.151900
3.C   3.543276  -0.826166  -3.894586
4.C  -0.407350   4.291654  -3.577575
5.C   0.985833   2.312408  -3.442861
6.C   1.801396  -3.303871  -3.354373
7.C  -2.573587  -0.675027  -2.531001
8.C  -2.343047  -4.349677  -2.229926
9.C  -3.037101  -3.006284  -2.205045
10.C  -0.903077   4.025295  -2.297696
11.C   0.491223   2.035721  -2.157536
12.C  -0.458674   2.899834  -1.594671
13.C  -0.841610  -5.727754  -0.980880
14.C   3.330461   2.372034  -0.959785
15.C   4.652991   2.675137  -0.615803
16.C   2.820835   1.078710  -0.760463
17.C   5.478274   1.692810  -0.060796
18.C   3.656921   0.983111  -0.194377
19.C   4.973523   0.403018   0.153150
20.C   0.136672   0.226863   0.143970
21.C  -4.709107   1.275123  -1.013625
22.C  -3.535136   0.525706   1.135429
23.C  -4.685789   2.655307  -1.242394
24.C  -2.321128   1.139683   1.481221
25.C  -3.481148   3.278403   1.591330
26.C  -2.307088   2.527841  -1.706506
27.C  -1.910154  -4.222523   2.354357
|   |   |   |   |
|---|---|---|---|
| 28.C | 1.476373 | 0.741334 | 3.057092 |
| 29.C | 0.072992 | 0.734472 | 3.047075 |
| 30.C | -3.325502 | -1.913149 | 3.763097 |
| 31.C | 2.174668 | 1.139798 | 4.199993 |
| 32.C | -0.622552 | 1.141718 | 4.199068 |
| 33.C | -0.378330 | -2.570483 | 4.380319 |
| 34.C | 1.476624 | 1.545675 | 5.342446 |
| 35.C | 0.076416 | 1.548744 | 5.339196 |
| 36.H | 1.103273 | -1.539280 | 5.929364 |
| 37.H | 0.627879 | 0.039231 | 5.260168 |
| 38.H | 0.924988 | 3.631537 | 5.151222 |
| 39.H | -0.326159 | -1.407700 | 4.877733 |
| 40.H | 3.920468 | -1.314857 | 4.807887 |
| 41.H | 2.231240 | -3.769570 | 4.255868 |
| 42.H | -0.753297 | 5.168919 | 4.127661 |
| 43.H | 3.601825 | 0.261488 | 4.052889 |
| 44.H | 1.734750 | 1.659628 | 3.890754 |
| 45.H | -3.023095 | -0.694499 | 3.536024 |
| 46.H | -3.675885 | -2.917448 | 3.101861 |
| 47.H | -1.796240 | -4.487740 | 3.180306 |
| 48.H | 0.780280 | -3.709872 | 3.248205 |
| 49.H | 4.226421 | -1.071894 | 3.068381 |
| 50.H | 2.392611 | -3.638367 | 2.487454 |
| 51.H | -3.097458 | -5.151121 | 2.136660 |
| 52.H | -1.732888 | 0.024781 | 2.510532 |
| 53.H | -3.325402 | -0.373137 | 1.786218 |
| 54.H | -0.345595 | -6.037258 | 1.913570 |
| 55.H | -1.636487 | 4.693528 | 1.842626 |
| 56.H | -3.674106 | -2.903524 | 1.307725 |
| 57.H | 2.699079 | 3.149271 | -1.392106 |
| 58.H | 5.036064 | 3.682469 | -0.786560 |
| 59.H | -1.625743 | -6.452392 | -0.712696 |
| 60.H | -0.848518 | 2.678883 | -0.600301 |
| 61.H | -0.096356 | -5.658766 | -0.180968 |
| 62.H | 6.510747 | 1.929118 | 0.202561 |
| 63.H | 3.278678 | -0.913355 | -0.029158 |
| 64.H | 5.607821 | -0.371160 | 0.588164 |
| 65.H | -5.646433 | 0.779522 | -0.753612 |
| 66.H | -3.547922 | -0.554110 | 0.985866 |
| 67.H | -5.603182 | 3.240683 | 1.159291 |
| 68.H | -2.622769 | -4.280543 | 1.517279 |
| 69.H | -3.458096 | 4.352508 | 1.782674 |
| 70.H | -0.948789 | -4.652025 | 2.028182 |
| 71.H | -1.376539 | 3.022586 | 1.990091 |
| 72.H | 2.015646 | 0.442006 | 2.157398 |
| 73.H | -2.290725 | -4.865002 | 3.165099 |
| 74.H | -4.152587 | -2.002421 | 3.041904 |
| 75.H | -3.303232 | -0.870167 | 4.113330 |
| 76.H | 0.593982 | -2.880210 | 3.966007 |
| 77.H | 3.265610 | 1.139463 | 4.192862 |
| 78.H | -1.713321 | 1.149732 | 4.206512 |
| 79.H | -3.569538 | -2.548810 | 4.630085 |
Table S16. Final coordinates and energy for a single point energy calculation of geometry optimized 6Ce.

|   |   |   |   |   |
|---|---|---|---|---|
| 1.C | -0.580992 | -0.703151 | -4.771780 |
| 2.C | 2.154303 | -1.923480 | -4.466717 |
| 3.C | -5.771553 | -2.203170 | -4.037133 |
| 4.C | -4.217350 | 0.353048 | -3.634161 |
| 5.C | -0.281364 | -3.458041 | -3.508749 |
| 6.C | -4.654304 | -2.055414 | -3.057947 |
| 7.C | 4.784613 | 0.626567 | -2.827408 |
| 8.C | 5.905300 | 0.013656 | -2.256488 |
| 9.C | -4.091818 | -2.963858 | -2.198569 |
| 10.C | 3.502351 | 0.300690 | -2.380078 |
| 11.C | -4.406223 | -4.404217 | -1.961813 |
| 12.C | -2.957756 | -0.972587 | -1.931220 |
| 13.C | 5.737372 | -0.913762 | -1.222387 |
| 14.C | 3.522629 | 4.051522 | -1.162932 |
| 15.C | 3.321902 | -0.644689 | -1.357244 |
| 16.C | 4.833459 | 3.852316 | -0.715998 |
| 17.C | 2.355177 | -3.768435 | -1.015396 |
| 18.C | 4.454504 | -1.236194 | -0.770155 |
| 19.C | 2.406210 | -5.098903 | -0.591874 |
| 20.C | 2.470132 | 3.333386 | -0.589150 |
| 21.C | -2.231076 | -2.867170 | -0.500540 |
| 22.C | 1.763504 | -2.778601 | -0.211277 |
| 23.C | -4.804741 | 1.769186 | -0.131206 |
| 24.C | 5.086865 | 2.924081 | 0.300192 |
| 25.C | 1.857614 | -5.465717 | 0.643554 |
| 26.C | 2.713984 | 2.407660 | 0.439142 |
| 27.C | -2.165859 | 4.423283 | 0.618874 |
| 28.C | 0.982654 | -0.066744 | 0.466741 |
| 29.C | 4.035168 | 2.202610 | 0.872262 |
| 30.C | 1.230642 | -3.156509 | 1.029303 |
| 31.C | -3.006512 | 0.489776 | 1.029079 |
| 32.C | 1.269062 | -4.489258 | 1.454587 |

Energy: $-544.683538$ eV
|   |       |       |       |
|---|-------|-------|-------|
| 33.C| 0.470495 | 5.182727 | 1.884005 |
| 34.C| -4.982599 | 0.794332 | 2.179685 |
| 35.C| -6.366092 | 1.303841 | 2.413613 |
| 36.C| -1.800690 | -0.812556 | 2.775505 |
| 37.C| -4.152027 | 0.057079 | 2.983303 |
| 38.C| 1.719586 | 1.373586 | 2.930134 |
| 39.C| -1.473610 | 3.337988 | 3.369342 |
| 40.C| 2.222505 | 2.489146 | 3.621814 |
| 41.C| 1.494431 | 0.188183 | 3.644298 |
| 42.C| -4.355353 | -0.493292 | 4.356025 |
| 43.C| 2.458582 | 2.431261 | 4.997437 |
| 44.C| 1.721190 | 0.126583 | 5.023632 |
| 45.C| 2.195694 | 1.252450 | 5.706294 |
| 46.H| -0.575521 | -1.180993 | -5.765597 |
| 47.H| 1.977909 | -2.485980 | -5.399152 |
| 48.H| -5.449602 | -1.973693 | -5.064572 |
| 49.H| -0.213426 | 0.328007 | -4.882852 |
| 50.H| -4.161098 | 0.147843 | -4.710877 |
| 51.H| 2.592197 | -0.953114 | -4.742254 |
| 52.H| -0.177558 | -3.947715 | -4.491359 |
| 53.H| -6.146610 | -3.233731 | -4.031218 |
| 54.H| -1.625346 | -0.647376 | -4.431119 |
| 55.H| -6.618673 | -1.539818 | -3.800962 |
| 56.H| 2.915342 | -2.468813 | -3.889754 |
| 57.H| -5.215940 | 0.747674 | -3.400086 |
| 58.H| 4.907745 | 1.357936 | -3.627575 |
| 59.H| -3.457621 | 1.104681 | -3.388446 |
| 60.H| -1.355940 | -3.408160 | -3.276756 |
| 61.H| -5.224068 | -4.725926 | -2.617918 |
| 62.H| 6.906577 | 0.260107 | -2.614948 |
| 63.H| 0.205471 | -4.100893 | -2.759986 |
| 64.H| 2.629848 | 0.769282 | -2.835593 |
| 65.H| -3.540099 | -5.050045 | -2.173365 |
| 66.H| 3.314876 | 4.770134 | 1.957444 |
| 67.H| 2.790619 | -3.497016 | -1.976859 |
| 68.H| 5.656350 | 4.416753 | -1.159342 |
| 69.H| 2.877439 | -5.851207 | -1.226721 |
| 70.H| -4.717569 | -4.594366 | 0.922836 |
| 71.H| 6.606859 | -1.392659 | -0.768374 |
| 72.H| 1.447303 | 3.495382 | 0.932419 |
| 73.H| -4.016078 | 1.907001 | -0.876851 |
| 74.H| -2.025179 | -3.916672 | -0.734997 |
| 75.H| -5.635561 | 1.214690 | -0.588435 |
| 76.H| -1.269176 | -2.341759 | -0.482327 |
| 77.H| -1.844832 | 4.698170 | -0.397090 |
| 78.H| 4.335789 | 1.963332 | 0.034715 |
| 79.H| -5.160338 | 2.759331 | 0.181304 |
| 80.H| 6.107483 | 2.758358 | 0.648809 |
| 81.H| -2.717271 | -2.800977 | 0.482072 |
| 82.H| -2.987875 | 3.698529 | 0.523328 |
| 83.H| 1.898900 | -6.505168 | 0.974666 |
| 84.H| -2.573831 | 5.321477 | 1.110484 |
Table S17. Final coordinates and energy for a single point energy calculation of geometry optimized 4Pm.

|   | X    | Y    | Z     | Energy: $-702.46114925$ eV |
|---|------|------|-------|-----------------------------|
| 1 | 2.158642 | 1.951814 | -4.068778 |
| 2 | 3.549251  | 2.028929  | -3.951553  |
| 3 | -0.292632  | -2.530232  | -3.882126  |
| 4 | 4.148356  | -1.750601  | -2.783419  |
| 5 | 1.358639  | 1.931028  | -2.922178  |
| 6 | 4.142310  | 2.057618  | -2.682966  |
| 7 | -0.927715  | 4.525101  | -2.662732  |
| 8 | 5.298054  | -1.658769  | -1.995325  |
| 9 | 2.884690  | -1.630036  | -2.196192  |
| 10 | 0.695321  | -4.434328  | -1.695053  |
| 11 | -2.216908  | -3.609328  | -1.790045  |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12.C | 1.944921 | 1.978153 | -1.647130 |
| 13.C | 3.347682 | 2.017382 | -1.536023 |
| 14.C | -3.321702 | 3.613835 | 0.971906 |
| 15.C | 5.180281 | -1.430312 | -0.617925 |
| 16.C | 2.755322 | -1.426995 | -0.817302 |
| 17.C | 3.919000 | -1.310530 | -0.032709 |
| 18.C | -5.566991 | 0.746832 | 0.002010 |
| 19.C | -1.108812 | 5.164669 | 0.340056 |
| 20.C | -4.024841 | -1.095045 | 0.602256 |
| 21.C | 2.464223 | 4.115405 | 0.702781 |
| 22.C | 0.824254 | 0.372984 | 0.631085 |
| 23.C | 1.547865 | 3.107886 | 1.046173 |
| 24.C | 2.755322 | -1.426995 | -0.817302 |
| 25.C | 3.919000 | -1.310530 | -0.032709 |
| 26.C | -5.566991 | 0.746832 | 0.002010 |
| 27.C | -1.108812 | 5.164669 | 0.340056 |
| 28.C | -4.024841 | -1.095045 | 0.602256 |
| 29.C | 2.464223 | 4.115405 | 0.702781 |
| 30.C | 0.824254 | 0.372984 | 0.631085 |
| 31.C | 1.547865 | 3.107886 | 1.046173 |
| 32.C | 2.755322 | -1.426995 | -0.817302 |
| 33.C | 3.919000 | -1.310530 | -0.032709 |
| 34.C | -5.566991 | 0.746832 | 0.002010 |
| 35.C | -1.108812 | 5.164669 | 0.340056 |
| 36.C | -4.024841 | -1.095045 | 0.602256 |
| 37.C | 2.464223 | 4.115405 | 0.702781 |
| 38.C | 0.824254 | 0.372984 | 0.631085 |
| 39.H | 1.689820 | 1.915737 | 5.052960 |
| 40.H | 4.173499 | 2.060807 | 0.002010 |
| 41.H | -0.644529 | -3.388052 | -4.478596 |
| 42.H | -0.921843 | -1.664713 | -4.135586 |
| 43.H | 0.736546 | -2.315146 | -4.202824 |
| 44.H | 4.229858 | -1.913736 | -3.858804 |
| 45.H | -1.228019 | 3.850673 | -3.478353 |
| 46.H | 0.273793 | 1.881385 | -3.009642 |
| 47.H | -1.414534 | 5.498594 | -2.835808 |
| 48.H | 6.284708 | -1.756942 | -2.451117 |
| 49.H | 1.993123 | -1.685847 | -2.815316 |
| 50.H | 5.227695 | 2.105630 | -2.585950 |
| 51.H | 0.423712 | -5.261765 | -2.371814 |
| 52.H | 0.159905 | 4.679586 | -2.730838 |
| 53.H | -2.440936 | -4.347554 | -2.577134 |
| 54.H | 1.756919 | -4.202677 | -1.867653 |
| 55.H | -2.977038 | -2.816285 | -1.857861 |
| 56.H | -3.662703 | 2.891696 | -1.727825 |
| 57.H | -3.793246 | 4.584344 | -1.199006 |
| 58.H | 0.587845 | -4.801304 | -0.663147 |
| 59.H | -2.324697 | -4.120897 | -0.822971 |
| 60.H | -5.018451 | 0.807716 | -0.946388 |
| 61.H | 3.819523 | 2.024130 | -0.553253 |
| 62.H | 6.073943 | -1.348475 | 0.002608 |
| 63.H | -3.682347 | 3.302189 | 0.021232 |
|   | x   | y   | z   |   |   |   |
|---|-----|-----|-----|---|---|---|
| 64.H | 2.800371 | 4.224398 | -0.327720 |
| 65.H | -6.636474 | 0.827976 | -0.217168 |
| 66.H | -1.720841 | 6.051036 | 0.103351 |
| 67.H | -0.058430 | 5.485812 | 0.392160 |
| 68.H | -5.268206 | 1.572324 | 0.663707 |
| 69.H | 2.653752 | -3.689664 | 0.597092 |
| 70.H | 3.838229 | -1.132518 | 1.041021 |
| 71.H | -7.879829 | 0.032829 | 1.202327 |
| 72.H | -8.265571 | -1.683519 | 1.405920 |
| 73.H | -2.186274 | -2.800832 | 1.133698 |
| 74.H | -3.302968 | -4.126514 | 1.519419 |
| 75.H | -7.879829 | 0.032829 | 1.202327 |
| 76.H | -8.265571 | -1.683519 | 1.405920 |
| 77.H | -2.186274 | -2.800832 | 1.133698 |
| 78.H | -3.302968 | -4.126514 | 1.519419 |
| 79.H | -7.745385 | -0.712474 | 2.798550 |
| 80.H | 2.692653 | -5.200347 | 2.549693 |
| 81.H | -0.209079 | -1.155357 | 2.626562 |
| 82.H | -2.794523 | -2.975284 | 2.797458 |
| 83.H | -5.088689 | -4.118405 | 3.064802 |
| 84.H | 0.332955 | 2.287377 | 2.650672 |
| 85.H | -6.266816 | -3.017311 | 3.794412 |
| 86.H | 2.913504 | 5.549648 | 3.768457 |
| 87.H | 1.223393 | 3.811376 | 4.373227 |
| 88.H | 1.299804 | 4.695237 | 4.559441 |
| 89.H | -0.145669 | -2.655928 | 4.576136 |
| 90.Pm | -1.789036 | 0.165254 | -0.255490 |
| 91.I | -3.031848 | 0.289144 | -3.107415 |
| 92.I | -2.352833 | 1.005847 | 2.767821 |
| 93.N | -0.154350 | -1.573805 | -0.989930 |
| 94.N | -0.679865 | 2.289979 | -0.623327 |
| 95.N | -5.273789 | -0.533742 | 0.632971 |
| 96.N | -4.160877 | -2.202609 | 1.392512 |
| 97.P | 0.842991 | 1.942844 | -0.184258 |
| 98.P | 1.105776 | -1.223133 | -0.024466 |
| 99.Si | -0.457447 | -2.970989 | -2.048856 |
| 100.Si | -1.447990 | 3.850977 | -0.973680 |

Energy: -589.23163282 eV

**Table S18.** Final coordinates and energy for a single point energy calculation of geometry optimized 5Pm.
|   |     |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|-----|
|   | C   | C   | C   | C   | C   | C   |
| 11| 0.487061 | 2.037454 | -2.147284 |     |     |     |
| 12| -0.436294 | 2.917328 | -1.565612 |     |     |     |
| 13| -0.800681 | -5.703569 | -0.924632 |     |     |     |
| 14| 3.327725 | 2.351543 | -0.966036 |     |     |     |
| 15| 4.654138 | 2.646989 | -0.629864 |     |     |     |
| 16| 2.811064 | 1.062133 | -0.758324 |     |     |     |
| 17| 5.474662 | 1.662576 | -0.073345 |     |     |     |
| 18| 3.642497 | 0.079200 | -0.190086 |     |     |     |
| 19| 4.962466 | 0.377834 | 0.151118  |     |     |     |
| 20| 0.126180 | 0.205806 | 0.133371  |     |     |     |
| 21| -4.712236 | 1.243674 | 1.000350  |     |     |     |
| 22| -3.535540 | 0.499144 | 1.119274  |     |     |     |
| 23| -4.696281 | 2.621753 | 1.242901  |     |     |     |
| 24| -2.326652 | 1.116394 | 4.166819  |     |     |     |
| 25| -3.495951 | 3.247640 | 1.602161  |     |     |     |
| 26| -2.318820 | 2.502069 | 1.714132  |     |     |     |
| 27| -1.903460 | -4.246624 | 2.380383 |     |     |     |
| 28| 1.486007 | 0.698764 | 3.032850  |     |     |     |
| 29| 0.082813 | 0.718077 | 3.031573  |     |     |     |
| 30| -3.306246 | -1.916084 | 3.774288 |     |     |     |
| 31| 2.198493 | 1.094940 | 4.166819  |     |     |     |
| 32| -0.598545 | 1.145973 | 4.184411  |     |     |     |
| 33| -0.351749 | -2.563609 | 4.369465 |     |     |     |
| 34| 1.514977 | 1.522256 | 5.310418  |     |     |     |
| 35| 0.114975 | 1.549352 | 5.316235  |     |     |     |
| 36| 1.118283 | -1.579036 | -5.934690 |     |     |     |
| 37| 0.647766 | 0.008219 | -5.282797 |     |     |     |
| 38| 0.902076 | 3.637570 | -5.141798 |     |     |     |
| 39| -0.315915 | -1.430114 | -4.891040 |     |     |     |
| 40| 3.933883 | -1.324009 | -4.795112 |     |     |     |
| 41| 2.251160 | -3.795314 | -4.234134 |     |     |     |
| 42| -0.727599 | 5.201879 | -4.084140 |     |     |     |
| 43| 3.601035 | 0.254042 | -4.048311 |     |     |     |
| 44| 1.691099 | 1.642860 | -3.903168 |     |     |     |
| 45| -2.958279 | -0.701711 | -3.566692 |     |     |     |
| 46| -3.602599 | -2.920786 | -3.116038 |     |     |     |
| 47| -1.700758 | -4.464191 | -3.154896 |     |     |     |
| 48| 0.800859 | -3.728798 | -3.221700 |     |     |     |
| 49| 4.225349 | -1.073375 | -3.054269 |     |     |     |
| 50| 2.412006 | -3.635521 | -2.465983 |     |     |     |
| 51| -3.013176 | -5.141780 | -2.135380 |     |     |     |
| 52| -1.700827 | 0.043641 | -2.520421 |     |     |     |
| 53| -3.306331 | -0.361271 | -1.829179 |     |     |     |
| 54| -0.290428 | -6.025752 | -1.845339 |     |     |     |
| 55| -1.583834 | 4.733012 | -1.788195 |     |     |     |
| 56| -3.632179 | -2.899203 | -1.322888 |     |     |     |
| 57| 2.699441 | 3.130346 | -1.400110 |     |     |     |
| 58| 5.043217 | 3.650632 | -0.808963 |     |     |     |
| 59| -1.597914 | -6.417203 | -0.665266 |     |     |     |
| 60| -0.815379 | 2.701302 | -0.565691 |     |     |     |
| 61| -0.069473 | -5.632002 | -0.112494 |     |     |     |
| 62| 6.509834 | 1.892761 | 0.182726  |     |     |     |
Table S19. Final coordinates and energy for a single point energy calculation of geometry optimized 6Pm.

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| 1.C  | -0.561028 | -0.675175 | -4.787529 |
| 2.C  | 2.164760 | -1.926458 | -4.471440 |
| 3.C  | -5.749706 | -2.187347 | -4.039007 |
| 4.C  | -4.183366 | 0.353381 | -3.637742 |
| 5.C  | -0.283647 | -3.433086 | -3.518109 |
| 6.C  | -4.638922 | -2.046106 | -3.051526 |
| 7.C  | 4.808258  | 0.596617  | -2.812938 |
| 8.C  | 5.920349  | -0.018802 | -2.228282 |
| 9.C  | -4.090338 | -2.954974 | -2.184194 |
| 10.C | 3.520478  | 0.283375  | -2.372054 |
| 11.C | -4.419815 | -4.391446 | -1.944518 |
| 12.C | -2.936380 | -0.973957 | -1.923862 |
| 13.C | 5.738558  | -0.935530 | -1.186842 |
| 14.C | 3.525289  | 4.061369  | -1.145863 |
| 15.C | 3.326026  | -0.652441 | -1.342806 |
| 16.C | 4.831404  | 3.872158  | -0.681283 |

Energy: \(-545.84775623\) eV
|   |            |            |            |
|---|------------|------------|------------|
| 17 | 2.335478   | -3.776500  | -1.015407  |
| 18 | 4.450151   | -1.245934  | -0.741820  |
| 19 | 2.387895   | -5.103666  | -0.581614  |
| 20 | 2.471514   | 3.330546   | -0.590791  |
| 21 | -2.227644  | -2.872109  | -0.488440  |
| 22 | 1.751553   | -2.779586  | -0.214609  |
| 23 | -4.786335  | 1.766954   | -0.162617  |
| 24 | 5.079753   | 2.939648   | 0.332269   |
| 25 | 1.850799   | -5.459675  | 0.662119   |
| 26 | 2.709991   | 2.402965   | 0.437187   |
| 27 | -2.170674  | 4.430847   | 0.597768   |
| 28 | 0.977835   | -0.074326  | 0.466991   |
| 29 | 4.026984   | 2.205800   | 0.885901   |
| 30 | 1.227490   | -3.147637  | 1.032814   |
| 31 | -2.982669  | 0.511591   | 1.012168   |
| 32 | 1.270095   | -4.476268  | 1.470001   |
| 33 | 0.473311   | 5.193949   | 1.838176   |
| 34 | -4.964949  | 0.801972   | 2.153195   |
| 35 | -6.353256  | 1.300814   | 2.381663   |
| 36 | -1.771330  | -0.774325  | 2.765158   |
| 37 | -4.130530  | 0.075471   | 2.962683   |
| 38 | 1.713769   | 1.361739   | 2.922591   |
| 39 | -1.458183  | 3.358437   | 3.349521   |
| 40 | 2.196951   | 2.477208   | 3.627998   |
| 41 | 1.522066   | 0.160780   | 3.619524   |
| 42 | -4.332473  | -0.469779  | 4.337633   |
| 43 | 2.447622   | 2.402357   | 5.000118   |
| 44 | 1.764718   | 0.081274   | 4.995100   |
| 45 | 2.220618   | 1.205994   | 5.691501   |
| 46 | -0.555437  | -1.149847  | -5.783022  |
| 47 | 1.989056   | -2.498366  | -5.398186  |
| 48 | -5.412421  | -1.981786  | -5.066683  |
| 49 | -0.187520  | 0.354304   | -4.893123  |
| 50 | -4.127168  | 0.141438   | -4.713083  |
| 51 | 2.615539   | -0.964527  | -4.755194  |
| 52 | -0.195503  | -3.919696  | -4.503644  |
| 53 | -6.147005  | -3.209348  | -4.020203  |
| 54 | -1.605528  | -0.613437  | -4.449546  |
| 55 | -6.584178  | -1.501897  | -3.823242  |
| 56 | 2.916197   | -2.473334  | -3.882867  |
| 57 | -5.180477  | 0.753195   | -3.407105  |
| 58 | 4.942040   | 1.319178   | -3.619268  |
| 59 | -3.421408  | 1.103354   | -3.394389  |
| 60 | -1.354477  | -3.378665  | -3.270423  |
| 61 | -5.251256  | -4.700748  | -2.589250  |
| 62 | 6.925968   | 0.216496   | -2.582028  |
| 63 | 0.209824   | -4.081284  | -2.778229  |
| 64 | 2.654339   | 0.753217   | -2.838236  |
| 65 | -3.565947  | -5.048773  | -2.169467  |
| 66 | 3.322067   | 4.783378   | -1.938480  |
| 67 | 2.764199   | -3.513679  | -1.982227  |
| 68 | 5.654621   | 4.448413   | -1.108173  |
|   |   |   |   |   |
|---|---|---|---|---|
|   |   |   |   |   |
| 69.H | 2.851613 | -5.862141 | -1.214481 |
| 70.H | -4.718962 | -4.579227 | -0.901939 |
| 71.H | 6.601277 | -1.416274 | -0.722136 |
| 72.H | 1.451858 | 3.485654 | -0.946470 |
| 73.H | -3.992743 | 1.914619 | -0.901061 |
| 74.H | -2.018153 | -3.918711 | -0.733175 |
| 75.H | -5.604188 | 1.196529 | -0.623222 |
| 76.H | -1.270225 | -2.341055 | -0.461441 |
| 77.H | -1.856666 | 4.70255 | -0.420585 |
| 78.H | 4.320606 | -1.965994 | 0.067661 |
| 79.H | -5.161267 | 2.751314 | 0.144869 |
| 80.H | 6.096791 | 2.781682 | 0.694442 |
| 81.H | -2.717325 | -2.817916 | 0.493032 |
| 82.H | -2.992569 | 3.705695 | 0.508715 |
| 83.H | 1.894841 | -6.496243 | 1.001798 |
| 84.H | -2.575123 | 5.330554 | 1.090872 |
| 85.H | 1.040369 | 5.395917 | 0.917565 |
| 86.H | 4.231237 | 1.485832 | 1.679988 |
| 87.H | -7.065170 | 0.897109 | 1.645064 |
| 88.H | 0.796749 | -2.362074 | 1.654851 |
| 89.H | -0.100315 | 6.102772 | 2.086012 |
| 90.H | -6.406037 | 2.399194 | 2.327664 |
| 91.H | 0.861540 | -4.742955 | 2.446880 |
| 92.H | -0.960306 | -0.685670 | 2.029869 |
| 93.H | 1.196183 | 5.038830 | 2.651915 |
| 94.H | 2.393336 | 3.407847 | 3.096710 |
| 95.H | -6.702965 | 1.003591 | 3.377616 |
| 96.H | -1.994183 | -1.835359 | 2.945962 |
| 97.H | -2.282062 | 2.630844 | 3.270941 |
| 98.H | 1.199399 | -0.714955 | 3.056318 |
| 99.H | -1.440644 | -0.309947 | 3.702259 |
| 100.H | -1.862389 | 4.275713 | 3.809390 |
| 101.H | -0.699883 | 2.944729 | 4.032196 |
| 102.H | -4.244076 | -1.567242 | 4.362016 |
| 103.H | -5.332099 | -0.211041 | 4.706602 |
| 104.H | -3.599194 | -0.062367 | 5.050157 |
| 105.H | 2.824369 | 3.278980 | 5.529694 |
| 106.H | 1.608897 | -0.861639 | 5.523250 |
| 107.H | 2.412703 | 1.148068 | 6.764492 |
| 108.Pm | -0.975669 | 0.721105 | -0.839191 |
| 109.I | -1.288116 | 2.971272 | -2.992352 |
| 110.N | -3.921976 | -0.856322 | -2.868541 |
| 111.N | 0.557274 | -0.898063 | -2.038357 |
| 112.N | -3.064737 | -2.274759 | -1.518599 |
| 113.N | -0.083148 | 2.323312 | 0.857540 |
| 114.N | -4.241341 | 1.047449 | 0.979212 |
| 115.N | -2.941091 | -0.085171 | 2.242190 |
| 116.P | 1.609678 | -1.022681 | -0.791850 |
| 117.P | 1.281449 | 1.465198 | 1.123910 |
| 118.Si | 0.491353 | -1.698920 | -3.600231 |
| 119.Si | -0.744468 | 3.748657 | 1.634760 |

Energy: $-703.54428584$ eV
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