

Crystallographic characterization of
(C₅H₄SiMe₃)₃U(BH₄)Cory J. Windorff,^{a,b}† Justin N. Cross,^a Brian L. Scott,^a Stosh A. Kozimor^{a*} and William J. Evans^{b*}^aLos Alamos National Laboratory, Los Alamos, New Mexico 87544, USA, and ^bDepartment of Chemistry, University of California, Irvine, California 92697, USA. *Correspondence e-mail: stosh@lanl.gov, wevans@uci.edu

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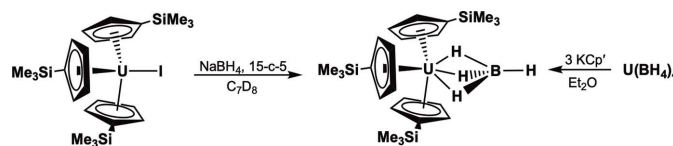
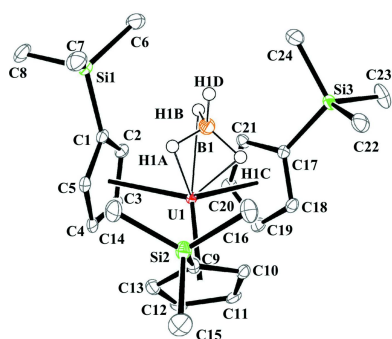
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New syntheses have been developed for the synthesis of (borohydrido- κ^3H)tris[η^5 -(trimethylsilyl)cyclopentadienyl]uranium(IV), [U(BH₄)(C₈H₁₃Si)₃] or Cp'₃U(BH₄) (Cp' = C₅H₄SiMe₃) and its structure has been determined by single-crystal X-ray crystallography. This compound crystallized in the space group $P\bar{1}$ and the structure features three η^5 -coordinated Cp' rings and a κ^3 -coordinated (BH₄)⁻ ligand.

1. Chemical context

Actinide borohydrides have been of interest since the 1940s, owing to their potential volatility and applied use in vapor deposition technologies for the production of thin films (Hoekstra & Katz, 1949; Daly & Girolami, 2010). Uranium borohydride compounds are structurally interesting because the (BH₄)⁻ ligand can coordinate large electropositive cations (such as uranium) in several modes. For example, κ^1 , κ^2 , and κ^3 U–(BH₄) binding has previously been reported (Ephritikhine, 1997). Borohydrides can also achieve high coordination numbers with uranium, *e.g.* the oligomeric 14-coordinate U(BH₄)₄ (Bernstein *et al.*, 1972). Although several cyclopentadienyl uranium borohydrides have been crystallographically characterized (Ephritikhine, 1997), the structure of Cp'₃U(BH₄) (Cp' = C₅H₄SiMe₃), made in 1992 (Berthet & Ephritikhine, 1992), has not been reported. Our interest in Cp' uranium chemistry (MacDonald *et al.*, 2013; Windorff *et al.*, 2017) prompted us to determine the coordination mode of (BH₄)⁻ within the tris-cyclopentadienyl uranium platform using single-crystal X-ray diffraction. Toward this end, we developed new synthetic routes to the Cp'₃U(BH₄) compound.



The Cp'₃U(BH₄) compound was originally synthesized by reacting Cp'₃UH with H₃B–PPh₃ (Berthet & Ephritikhine, 1992). Our attempts to repeat this procedure in toluene and diethyl ether solvents were unsuccessful, potentially because we were uncertain about the details of the reaction. However, we were successful in synthesizing Cp'₃U(BH₄) from Cp'₃UH with H₃B–PPh₃ in hot THF solvent. We also observed Cp'₃U(BH₄) could be prepared in high yield (96%) by reacting

Table 1

A comparison of structural parameters (Å, °) in Cp₃U(BH₄) and other Cp₃UX {X = Cl⁻, I⁻, [Si(SiMe₃)₃]⁻} complexes.

cent = C₅H₄SiMe₃ centroid.

| | Cp ₃ U(BH ₄) | Cp ₃ UCl ^a (Windorff <i>et al.</i> , 2017) | Cp ₃ UI (Windorff <i>et al.</i> , 2017) | Cp ₃ U(η ¹ -CH=CH ₂) (Schock <i>et al.</i> , 1988) | Cp ₃ U[Si(SiMe ₃) ₃] (Réant <i>et al.</i> , 2020) |
|-----------------|-------------------------------------|---|---|---|---|
| U—(cent) | 2.458, 2.490, 2.500 | 2.473 | 2.475, 2.478, 2.480 | 2.481, 2.483, 2.489 | 2.472, 2.478, 2.485 |
| (cent)—U—X | 104.13, 104.14, 104.83 | 100.00 | 97.9, 101.2, 101.6 | 95.1 100.0 100.2 | 96.04, 96.30, 97.65 |
| (cent)—U—(cent) | 113.28, 114.26, 114.26 | 117.00 | 116.1, 116.4, 118.3 | 116.4, 117.2, 120.0 | 118.28, 118.88, 119.08 |

Note: (a) The asymmetric unit contains one Cp' ring, one-third of a chloride atom, and one-third of a uranium atom.

Cp₃UI with NaBH₄ in the presence of 15-crown-5. When this reaction was carried out in toluene at room temperature, the I⁻ ligand was substituted by the (BH₄)⁻ anion. Another method we developed for synthesizing Cp₃U(BH₄) involved reacting U(BH₄)₄ with KCp' (3 equiv.) in diethyl ether. This reaction, where (BH₄)⁻ was substituted by (Cp')⁻, also proceeded in high yield (89%). X-ray quality crystals of Cp₃U(BH₄) formed at 253 K overnight from diethyl ether solutions.

Of our two synthetic routes, we preferred making Cp₃U(BH₄) from Cp₃UI over U(BH₄)₄ because the U(BH₄)₄ starting material was more challenging to isolate in a chemically pure form. Another interesting comparison between the two synthetic methods involved the substitution chemistry. The (Cp')⁻ anion displaced (BH₄)⁻ from U(BH₄)₄ and (BH₄)⁻ displaced I⁻ in Cp₃UI. Hence, we qualitatively concluded that the stability of the U—X bond for molecular compounds dissolved in organic solvents was largest for (Cp')⁻, intermediate for (BH₄)⁻, and lowest for I⁻. The generality of this conclusion is limited, and we acknowledge

the solubility of the other reaction products (such as NaI) might significantly influence the substitution chemistry on uranium.

2. Structural commentary

Single crystal X-ray data from Cp₃U(BH₄) were refined in the triclinic *P* $\bar{1}$ space group with one crystallographically unique molecule in the unit cell, see Fig. 1. The data are of high quality, and electron-density difference peaks consistent with the location and geometry of bridging hydrides were located from a difference-Fourier map with U—H distances of 2.35 (5), 2.35 (5), and 2.36 (5) Å. Although the uncertainty associated with the U—H bonds is relatively high, they are consistent with previously reported bond lengths for actinide(IV) hydride interactions (Ephritikhine, 1997; Daly *et al.*, 2010). Significantly lower uncertainty is associated with the U—B distance at 2.568 (4) Å, which is similar to two of the three U—B distances in [U(BH₄)₃(DME)]₂(μ-O) (DME = 1,2-dimethoxyethane), 2.574 (6), 2.584 (6), and 2.635 (7) Å (Daly *et al.*, 2012). The U—B distance in (C₅H₅)₃U(BH₄) was reported to be 2.48 Å (Zanella *et al.*, 1988), although disorder in that structure prevented a full solution from being obtained. Theoretical calculations on (C₅H₅)₃U(BH₄) in the gas phase and in solution predicted U—B distances of 2.533 and 2.557 Å (Elkechai *et al.*, 2009), which are also consistent with our data. Other (C₅R₅)₂U(BH₄)₂ structures showed similar U—B distances of 2.56 (1) Å for [C₅H₃(SiMe₃)₂]₂U(BH₄)₂ (Blake *et al.*, 1995), 2.58 (3) Å in (C₅Me₅)₂U(BH₄)₂ (Gradoz *et al.*, 1994, Marsh *et al.*, 2002), and 2.553 (1) Å in (PC₄Me₄)₂U(BH₄)₂ (Baudry *et al.*, 1990).

The uranium—(Cp' centroid) distances in Cp₃U(BH₄) range from 2.458–2.500 Å and average 2.48 (2) Å (uncertainty reported as the standard deviation from the mean at 1σ). These uranium—(Cp' centroid) distances compare well with the 2.473 Å analogous metric in Cp₃UCl (Windorff *et al.*, 2017) and other Cp₃UX structures (see Table 1) with average U—(Cp' centroid) distances of 2.478 (3) Å in Cp₃UI (Windorff *et al.*, 2017), 2.484 (4) Å in Cp₃U(η¹-CH=CH₂) (Schock *et al.*, 1988) and 2.478 (7) Å in Cp₃U[Si(SiMe₃)₃] (Réant *et al.*, 2020). The 113.9 (6)° average of (Cp' centroid)—U—(Cp' centroid) angles in Cp₃U(BH₄) is more acute than the 117.0° angle in Cp₃UCl and other Cp₃UX structures, where the average (Cp' centroid)—U—(Cp' centroid) angles were reported as 117 (1)° in Cp₃UI, 112 (2)° in Cp₃U(η¹-

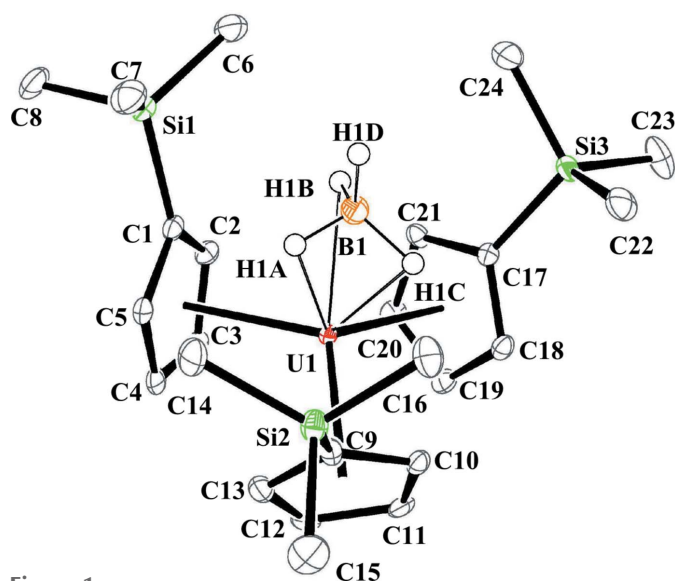


Figure 1

Structure of Cp₃U(BH₄) with atomic displacement parameters drawn at the 50% probability level. Boron-bound hydrogen atoms are represented as isotropic circles. All carbon-bound hydrogen atoms are omitted. Selected structural metrics, U—(Cp' centroid) average 2.48 (2) Å, U—H average 2.35 (1) Å, (Cp' centroid)—U—(Cp' centroid) average 113.9 (6)°, (Cp' centroid)—U—B average 104.4 (4)°, and terminal B—H distance of 1.11 (5) Å.

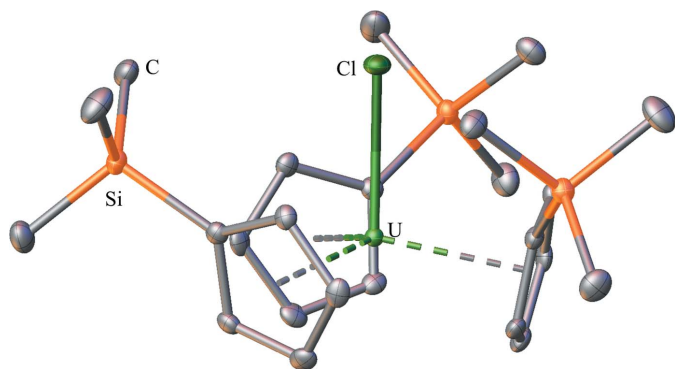


Figure 2
Structure of $\text{Cp}'_3\text{UCl}$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Windorff *et al.*, 2017); the isomorphous thorium complex, $\text{Cp}'_3\text{ThCl}$, is also known (Réant *et al.*, 2020). Hydrogen atoms are omitted for clarity.

$\text{CH}=\text{CH}_2$), and $118.7(4)^\circ$ in $\text{Cp}'_3\text{U}[\text{Si}(\text{SiMe}_3)_3]$. The more acute (Cp' centroid)—U—(Cp' centroid) angles are complemented by a more obtuse average (Cp' centroid)—U—B angle of $104.4(4)^\circ$ in $\text{Cp}'_3\text{U}(\text{BH}_4)$, likely due to the close proximity

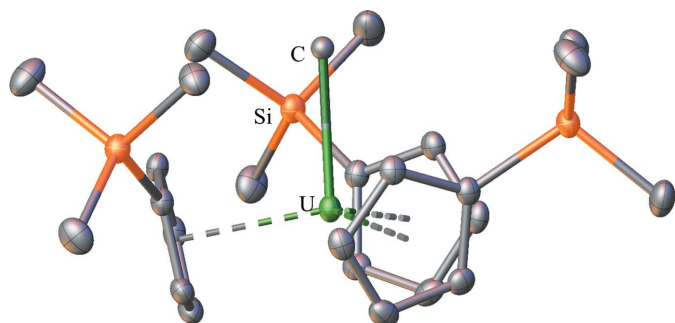


Figure 3
Structure of $\text{Cp}'_3\text{U}(\text{CH}_3)/\text{Cl}$ with only the $(\text{CH}_3)^-$ ligand shown, with atomic displacement parameters drawn at the 50% probability level, except the $-\text{CH}_3$ unit, which has been plotted as an isotropic sphere, as reproduced from the published CIF (Windorff *et al.*, 2017), see the manuscript for further details. Hydrogen atoms are omitted for clarity.

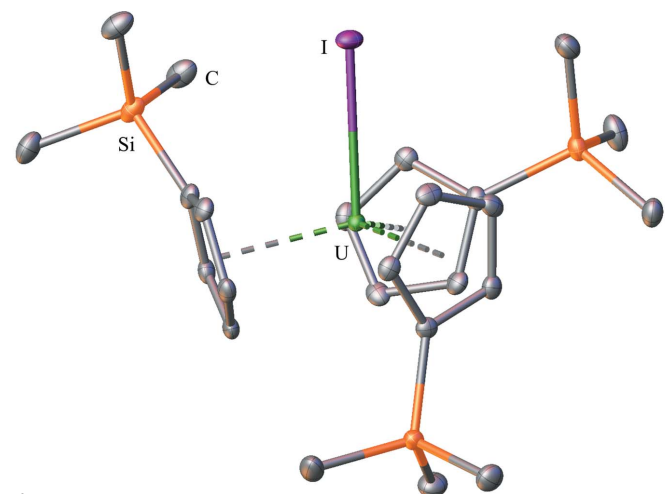


Figure 4
Structure of $\text{Cp}'_3\text{UI}$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Windorff *et al.*, 2017). Hydrogen atoms are omitted for clarity.

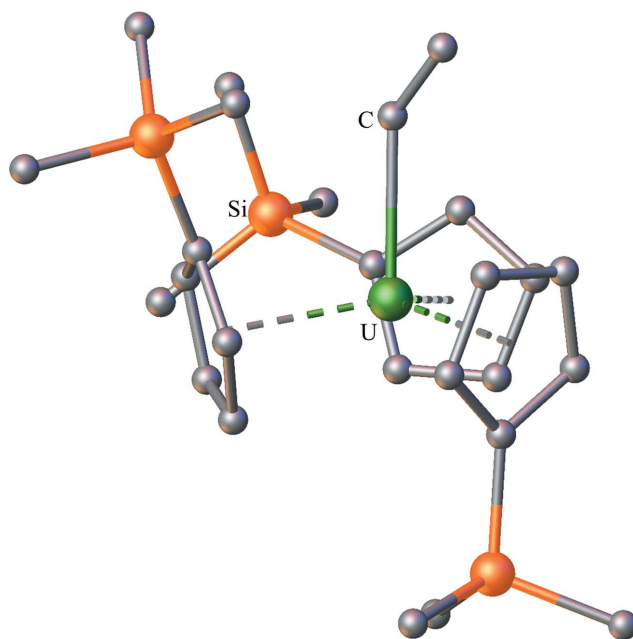


Figure 5
Structure of $\text{Cp}'_3\text{U}(\eta^1\text{-CH}=\text{CH}_2)$ with atomic displacement parameters drawn as isotropic spheres, as reproduced from the CIF (Schock *et al.*, 1988). Hydrogen atoms are omitted for clarity.

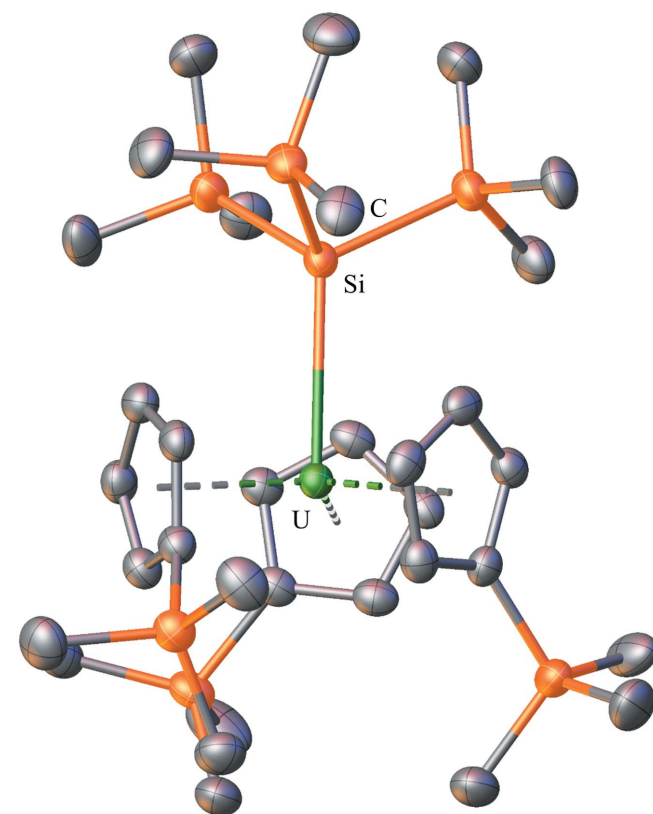


Figure 6
Structure of $\text{Cp}'_3\text{U}[\text{Si}(\text{SiMe}_3)_3]$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Réant *et al.*, 2020); the isomorphous thorium complex, $\text{Cp}'_3\text{Th}[\text{Si}(\text{SiMe}_3)_3]$, is also known (Réant *et al.*, 2020). Hydrogen atoms are omitted for clarity.

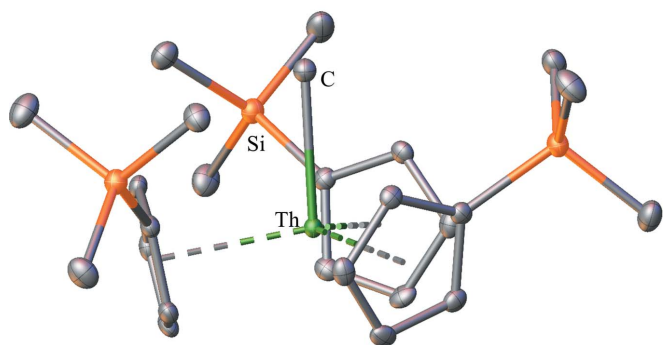


Figure 7
Structure of $\text{Cp}'_3\text{ThCH}_3$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Wedal *et al.*, 2019). Hydrogen atoms are omitted for clarity.

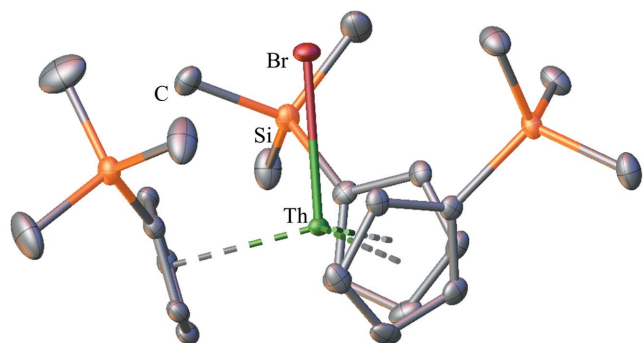


Figure 8
Structure of $\text{Cp}'_3\text{ThBr}$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF in the $P\bar{3}$ space group (Windorff *et al.*, 2017); there is a second report of the same molecule in the $P2_1/c$ space group, featuring the same ligand orientation (Wedal *et al.*, 2019). Hydrogen atoms are omitted for clarity.

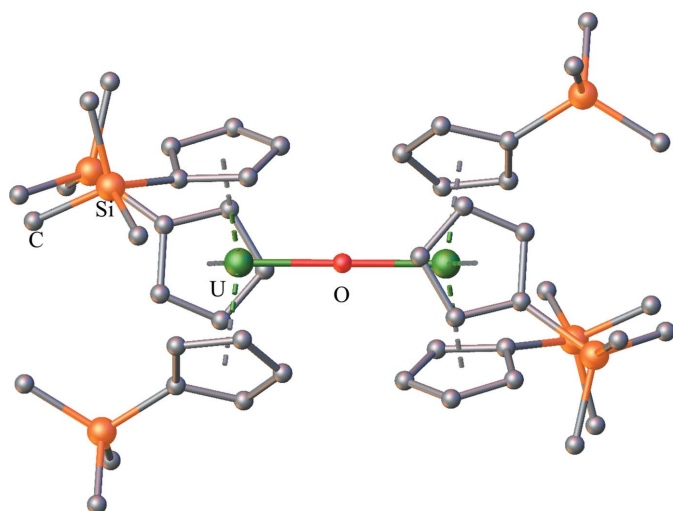


Figure 9
Structure of $(\text{Cp}'_3\text{U})_2(\mu\text{-O})$ with atomic displacement parameters drawn as isotropic spheres, as reproduced from the CIF (Berthet *et al.*, 1991); the isomorphous thorium complex, $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$, is also known (Wedal *et al.*, 2019). Hydrogen atoms are omitted for clarity.

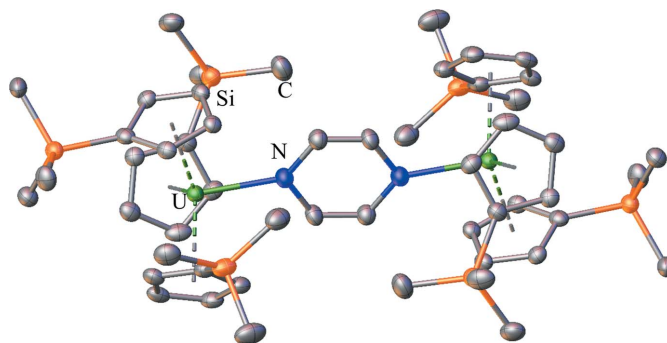


Figure 10
Structure of $(\text{Cp}'_3\text{U})_2[\mu\text{-}(\text{N}_2\text{C}_4\text{H}_4)]$ with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Mehdoui *et al.*, 2004). Hydrogen atoms are omitted for clarity.

of the $(\text{BH}_4)^{1-}$ ligand compared with $(\text{Cp}'\text{ centroid})\text{-U-X}$ angles of 100.0° in $\text{Cp}'_3\text{UCl}$, $100(2)^\circ$ in $\text{Cp}'_3\text{UI}$, $98(3)^\circ$ in $\text{Cp}'_3\text{U}(\eta^1\text{-CH=CH}_2)$, and $96.7(9)^\circ$ in $\text{Cp}'_3\text{U}[\text{Si}(\text{SiMe}_3)_3]$, see Table 1.

An unusual feature of the $\text{Cp}'_3\text{U}(\text{BH}_4)$ structure is that all three of the trimethylsilyl groups are oriented in a single direction towards the $(\text{BH}_4)^{1-}$ unit. This orientation has not been observed in other $\text{Cp}'_3\text{U}(\text{anion})$ and $\text{Cp}'_3\text{U}(\mu\text{-dianion})\text{UCp}'_3$ structures, which are shown in Figs. 2–12. The closest comparison is with the $\text{Cp}'_3\text{UCl}$ structure (Windorff *et al.*, 2017), where all three trimethylsilyl groups are oriented towards the Cl^- unit, but twisted down and away from the chloride towards the meridian. The $\text{Cp}'_3\text{UI}$ (Windorff *et al.*, 2017) and $\text{Cp}'_3\text{U}(\eta^1\text{-CH=CH}_2)$ (Schock *et al.*, 1988) complexes have one trimethylsilyl group pointed away from the anionic ligand. The $\text{Cp}'_3\text{U}[\text{Si}(\text{SiMe}_3)_3]$ complex (Réant *et al.*, 2020) represents the opposite extreme where all of the

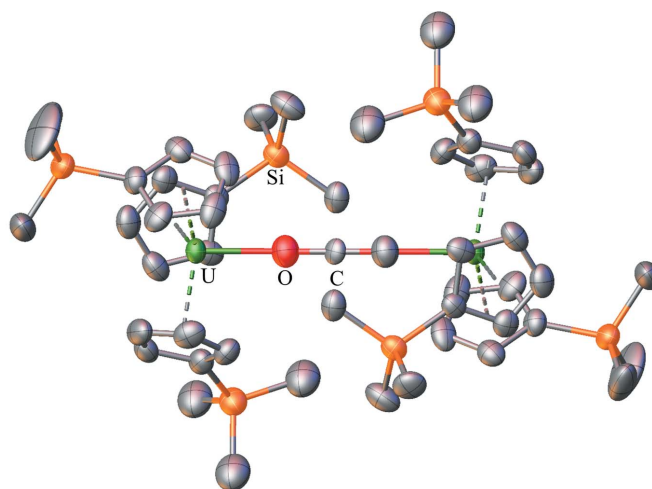


Figure 11
Structure of $(\text{Cp}'_3\text{U})_2(\mu\text{-CCO})$ with atomic displacement parameters drawn at the 50% probability level and disorder in the $(\mu\text{-CCO})^{2-}$ unit displayed in one configuration, as reproduced from the published CIF (Tsoureas & Cloke, 2018). The molecule contains a plane of symmetry, and the unit cell contains two half molecules with the same orientation. For clarity, only one full molecular unit is depicted and hydrogen atoms are omitted for clarity.

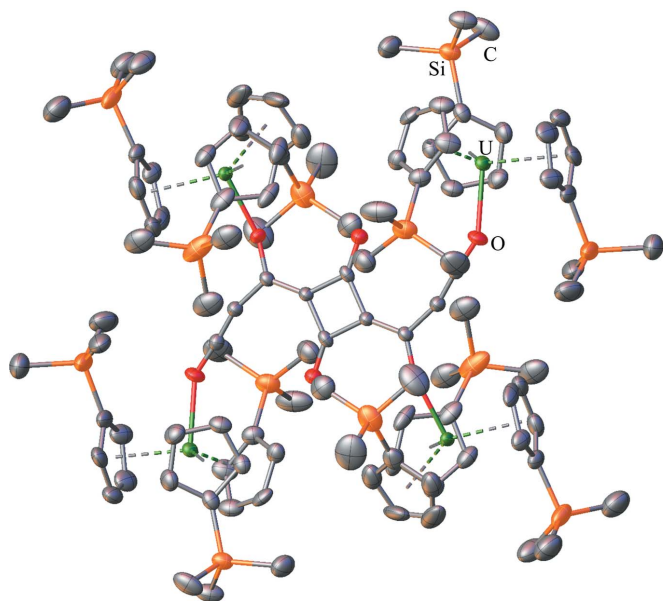


Figure 12
Structure of $(\text{Cp}'_3\text{U})_4(\mu\text{-}L)$ where L = a complex organic structure containing a central cyclobutene-1,3-dione ring, with atomic displacement parameters drawn at the 50% probability level, as reproduced from the published CIF (Tsoureas & Cloke, 2018). Hydrogen atoms and disorder in the $-\text{SiMe}_3$ groups are omitted for clarity.

trimethylsilyl groups are oriented away from the $[\text{Si}(\text{SiMe}_3)_3]^{1-}$ unit. Since $\text{Cp}'_3\text{U}(\text{BH}_4)$ has the smallest mono-anion of the $\text{Cp}'_3\text{U}(\text{anion})$ complexes and the correspondingly smallest $(\text{Cp}' \text{ centroid})-\text{U}-(\text{Cp}' \text{ centroid})$, and the largest $(\text{Cp}' \text{ centroid})-\text{U}-X$ angles, the orientation of the silyl groups could occur due to steric factors. However, it is also possible that some dispersion forces between the $(\text{BH}_4)^-$ and the trimethylsilyl groups could contribute to the orientation (Liptrot *et al.*, 2016). It is interesting to note that in the $\text{Cp}'_3\text{Th}X$ series where $X = \text{Cl}$ (Réant *et al.*, 2020), Br (Windorff *et al.*, 2017), and CH_3 (Wedal *et al.*, 2019), all three trimethylsilyl groups are oriented towards the anion, but twisted down and away from the anion towards the meridian as in $\text{Cp}'_3\text{UCl}$.

3. Supramolecular features

There are no major supramolecular features to report. The molecules pack in an alternating 180° rotation from one another within the unit cell and stack 'head to tail' between the unit cells.

4. Database survey

A search using the Cambridge Structural Database (Version 5.41, March 2020; Groom *et al.*, 2016) for borohydride structures containing η^5 -aromatic five-membered rings bound to uranium showed two classes of complexes. There were the uranium(IV) piano-stool complexes: $(\text{C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$ (DEKVEU and DEKVEU10; Baudry *et al.*, 1985, 1989); $(\text{C}_5\text{Me}_5)\text{U}(\text{BH}_4)(\text{SPS}^{\text{Me}})$ (JOJTIM; Arliguie *et al.*, 2008),

where $\text{SPS}^{\text{Me}} = \text{PC}_5\text{H-3,5-Ph,-2,6-(P(S)Ph}_2\text{)-1-Me}$, a λ^4 -phosphinine with two lateral phosphinosulfide groups, and the tetramethylphosphol (PC_4Me_4) compound $(\text{PC}_4\text{Me}_4)(\text{C}_8\text{H}_8)\text{-U}(\text{BH}_4)(\text{THF})$ (MOBVEE; Cendrowski-Guillaume *et al.*, 2002). There were also uranium(IV) metallocene structures, $(\text{Ring})_2\text{U}(\text{BH}_4)_2$, where $\text{Ring} = \text{C}_5\text{H}_5$ (CPURBH; Zanella *et al.*, 1977), $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ (ZEYZOS; Blake *et al.*, 1995), C_5Me_5 (WIFFOG and WIFFOG01; Gradoz *et al.*, 1994; Marsh *et al.*, 2002), C_9H_7 (VASVUG, $\text{C}_9\text{H}_7 = \text{indenide}$; Rebizant *et al.*, 1989) and PC_4Me_4 (KIJBK, $\text{PC}_4\text{Me}_4 = \text{tetramethylphosphol}$; Baudry *et al.*, 1990). The macrocyclic *trans*-calix[2]benzene[2]-pyrrolide (L) complex $[\text{LU}(\text{BH}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ was also in the database (CUJMEB; Arnold *et al.*, 2015). This last compound features two η^5 -bound $\text{NC}_4\text{H}_2\text{R}_2$ ligands. Also in the database were a few examples of uranium(III) borohydrides, such as the mono borohydride $[(\text{PC}_4\text{Me}_4)_2\text{U}(\text{BH}_4)]_2$ (YEZJES; Gradoz *et al.*, 1994) and the mixed oxidation state piano stool $[\text{Na}(\text{THF})_6][(\text{C}_5\text{Me}_5)\text{U}(\text{BH}_4)_3]_2$ (VAXMUC; Ryan *et al.*, 1989)] complexes.

There are also three dimeric uranium(IV) complexes with Cp'^- ligands, all of the form $(\text{Cp}'_3\text{U})_2(\mu\text{-}X)$ where $X = \text{O}^{2-}$ (SOSXON; Berthet *et al.*, 1991), $(\text{pyrazine})^{2-}$, $(\text{N}_2\text{C}_4\text{H}_4)^{2-}$ (EYERIJ; Mehdoui *et al.*, 2004), and CCO^{2-} (PIKFAT; Tsoureas & Cloke, 2018). There is also the tetrametallic $(\text{Cp}'_3\text{U})_4(\mu\text{-}L)$ (PIKDUL; Tsoureas & Cloke, 2018) where L is a complex organic structure containing a central cyclobutene-1,3-dione ring.

5. Spectroscopic Features

The fully defined $\text{Cp}'_3\text{U}(\text{BH}_4)$ compound was also characterized by ^1H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ multi-nuclear NMR spectroscopy. It was of particular interest to examine the $^{29}\text{Si}\{^1\text{H}\}$ spectrum for comparison with previous studies of silicon-containing paramagnetic uranium complexes (Windorff & Evans, 2014). The ^1H NMR spectrum in C_7D_8 was in good agreement with the literature (Berthet & Ephritikhine, 1992). $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ spectra were also obtained in both C_7D_8 and C_6D_6 , as well as different field strengths, 500 vs 600 MHz for ^1H , to see if any significant solvent or field effects were present. Since the spectra were not dependent on solvent or field strength, only the spectra obtained in C_6D_6 in a 600 MHz field will be discussed here. See Section 6 for full details.

In general, the resonances attributable to the Cp'^- ligands are sharp ($\nu_{1/2} < 50$ Hz) and paramagnetically shifted over a range of δ 9.6 to -22.6 ppm, in the ^1H NMR spectrum, and a $^{29}\text{Si}\{^1\text{H}\}$ resonance at δ -57.4 ppm was observed, typical of other tetravalent uranium complexes (Windorff & Evans, 2014). The resonances attributable to the $(\text{BH}_4)^-$ unit showed considerably more shifting and broadening, resonating at δ -59.5 ($\nu_{1/2} = 300$ Hz) and 79.6 ($\nu_{1/2} = 240$ Hz) in the ^1H and $^{11}\text{B}\{^1\text{H}\}$ spectra, respectively. Since the $(\text{BH}_4)^-$ ligand exhibited a single ^1H NMR resonance whereas two distinct hydride environments are present in the solid state, it appears that the complex is fluxional in solution. This is in line with previous studies (Ephritikhine, 1997).

6. Synthesis and crystallization

6.1. General considerations

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using glovebox techniques under an argon atmosphere. Solvents (THF, Et₂O, toluene, hexane, and pentane) were sparged with UHP argon (Praxair) and dried by passage through columns containing a copper(II) oxide oxygen scavenger (Q-5) and molecular sieves prior to use or stirred over sodium benzophenone ketyl, briefly exposed to vacuum several times to degas and distilled under vacuum. All ethereal solvents were stored over activated 4 Å molecular sieves. Deuterated solvents (Cambridge Isotopes) used for nuclear magnetic resonance (NMR) spectroscopy were dried over sodium benzophenone ketyl, degassed by three freeze-pump-thaw cycles, and distilled under vacuum before use. The ¹H, ¹¹B{¹H}, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra were recorded on a GN 500, Cryo 500 or Bruker Avance 600 spectrometer operating at 500.2 MHz, 160.1 MHz, 125.8 MHz, and 99.1 MHz for the 500 MHz spectrometers, respectively, and 600.1 MHz, 192.6 MHz, 150.9 MHz and 119.2 MHz for the 600 MHz spectrometer, respectively, at 298 K unless otherwise stated. The ¹H and ¹³C{¹H} NMR spectra were referenced internally to solvent resonances, ¹¹B and ²⁹Si{¹H} NMR spectra were referenced externally to BF₃(Et₂O) and SiMe₄, respectively, the ²⁹Si{¹H} spectra were acquired using the INEPT pulse sequence. The 15-crown-5 (Aldrich) reagent was dried over activated molecular sieves and degassed by three freeze-pump-thaw cycles before use. The NaBH₄ (Aldrich) reagent was placed under vacuum (10⁻³ Torr) for 12 h before use. The following compounds were prepared following literature procedures: KCp' (Peterson *et al.*, 2013), U(BH₄)₄ (Schlesinger & Brown, 1953), Cp'₃UI (Windorff *et al.*, 2017).

6.2. Cp'₃U(BH₄) from Cp'₃UI, NaBH₄ and 15-crown-5

Solid NaBH₄ (15 mg, 0.40 mmol) was added to a C₇D₈ (toluene-*d*₈, 0.6 mL) solution of Cp'₃UI (37 mg, 0.048 mmol) in a J-Young NMR tube, an excess of 15-crown-5 (1 drop) was added and the tube was sealed and removed from the glovebox and vortexed (30 s). The NaBH₄ was not fully soluble in C₇D₈ even in the presence of 15-crown-5. After 18 h, NMR spectroscopy showed complete conversion to Cp'₃U(BH₄). The sample was brought back into the glovebox and the volatiles were removed under reduced pressure. The product was then extracted into Et₂O, filtered away from white insoluble solids [presumably Na(15-crown-5)I and excess NaBH₄] and the volatiles were removed under reduced pressure to give Cp'₃U(BH₄) (30 mg, 96%) as a wine-red solid. ¹H NMR (C₇D₈, 500.2 MHz): δ 9.7 (*s*, C₅H₄SiMe₃, 6H), -2.1 (*s*, C₅H₄SiMe₃, 27H), -23.1 (*s*, C₅H₄SiMe₃, 6H), -59.8 (*s*, *br*, *v*_{1/2} = 325 Hz, U-(BH₄), 4H); ¹¹B{¹H} NMR (C₇D₈, 160.1 MHz): δ 79.1 [*s*, *br*, *v*_{1/2} = 230 Hz, U-(BH₄)]; ¹³C{¹H} NMR (C₇D₈, 125.8 MHz): δ 233.1 (C₅H₄SiMe₃), 214.0 (C₅H₄SiMe₃), 185.6 (C₅H₄SiMe₃), 0.4 (C₅H₄SiMe₃); ²⁹Si{¹H} NMR (C₇D₈, 99.1 MHz, INEPT): δ -57.7 (*s*, C₅H₄SiMe₃); ¹H NMR (C₆D₆, 600.1 MHz): δ 9.6 (*s*, C₅H₄SiMe₃, 6H), -2.0 (*s*,

Table 2

Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | [U(BH ₄)(C ₈ H ₁₃ Si) ₃] |
| <i>M</i> _r | 664.69 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 112 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 8.7530 (15), 12.217 (2), 13.657 (2) |
| α , β , γ (°) | 94.159 (3), 96.016 (3), 103.256 (3) |
| <i>V</i> (Å ³) | 1406.6 (4) |
| <i>Z</i> | 2 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 5.91 |
| Crystal size (mm) | 0.88 × 0.62 × 0.17 |
| Data collection | |
| Diffractometer | Bruker D8 Quest with Photon II detector |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.413, 0.747 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 30231, 10686, 9355 |
| <i>R</i> _{int} | 0.055 |
| (sin θ /λ) _{max} (Å ⁻¹) | 0.769 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.037, 0.102, 1.07 |
| No. of reflections | 10686 |
| No. of parameters | 274 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 3.87, -2.72 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), and *SHELXTL2018/3* (Sheldrick, 2008).

C₅H₄SiMe₃, 27H), -22.6 (*s*, C₅H₄SiMe₃, 6H), -59.3 (*s*, *br*, *v*_{1/2} = 300 Hz, U-(BH₄), 4H); ¹¹B{¹H} NMR (C₆D₆, 192.6 MHz): δ 79.6 [*s*, *br*, *v*_{1/2} = 240 Hz, U-(BH₄)]; ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): δ 232.0 (C₅H₄SiMe₃), 214.2 (C₅H₄SiMe₃), 186.5 (C₅H₄SiMe₃), 0.6 (C₅H₄SiMe₃); ²⁹Si{¹H} NMR (C₆D₆, 119.2 MHz, INEPT): δ -57.4 (*s*, C₅H₄SiMe₃).

6.3. Cp'₃U(BH₄) from U(BH₄)₄ and KCp'

An Et₂O (5 mL) solution of KCp' (460 mg, 2.61 mmol) was added to a pale-green solution of U(BH₄)₄ (250 mg, 0.841 mmol), also dissolved in Et₂O (5 mL). White solids precipitated (presumably KBH₄) as the solution quickly turned orange and then slowly changed to dark red (30 min). After stirring the mixture for an additional 12 h, volatiles were removed under reduced pressure, and the product was extracted into hexane leaving white solids behind (presumably KBH₄). Removal of the volatiles under reduced pressure gave Cp'₃U(BH₄) (496 mg, 89%) as a dark wine-red solid. X-ray quality crystals were grown from a concentrated ether solution at 253 K.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Analytical scattering factors neutral atoms were used throughout the analysis. A 3-D

rendering of the molecule can be found at the following web address: <https://submission.iucr.org/jtk/serve/z/Utg9EjfTrqJ-VoXA/zz0000/0/>.

C–H bond distances were constrained to 0.95 Å for cyclopentadienyl C–H moieties, and to 0.98 Å for aliphatic CH₃ moieties, respectively. Methyl torsion angles were not refined but constrained to be staggered. The borohydride H atoms were located from a difference-Fourier map and their positions were freely refined. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C/B})$ with 1.5 for CH₃ and BH₄ and 1.2 for C–H units, respectively.

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supporting information

Acta Cryst. (2021). E77, 383-389 [https://doi.org/10.1107/S2056989021002425]

Crystallographic characterization of $(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}(\text{BH}_4)$

Cory J. Windorff, Justin N. Cross, Brian L. Scott, Stosh A. Kozimor and William J. Evans

Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *APEX3* (Bruker, 2018); data reduction: *SAINTE* (Bruker, 2018); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *SHELXTL2018/3* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL2018/3* (Sheldrick, 2008).

(Borohydrido- κ^3H)tris[η^5 -(trimethylsilyl)cyclopentadienyl]uranium(IV)

Crystal data

$[\text{U}(\text{BH}_4)(\text{C}_8\text{H}_{13}\text{Si})_3]$

$M_r = 664.69$

Triclinic, $P\bar{1}$

$a = 8.7530$ (15) Å

$b = 12.217$ (2) Å

$c = 13.657$ (2) Å

$\alpha = 94.159$ (3)°

$\beta = 96.016$ (3)°

$\gamma = 103.256$ (3)°

$V = 1406.6$ (4) Å³

$Z = 2$

$F(000) = 652$

$D_x = 1.569$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 30231 reflections

$\theta = 2.4$ – 33.1 °

$\mu = 5.91$ mm⁻¹

$T = 112$ K

Plate, red

$0.88 \times 0.62 \times 0.17$ mm

Data collection

Bruker D8 Quest with Photon II detector
diffractometer

Radiation source: $I\mu\text{S}$ 3.0 microfocus

ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\text{min}} = 0.413$, $T_{\text{max}} = 0.747$

30231 measured reflections

10686 independent reflections

9355 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\text{max}} = 33.1$ °, $\theta_{\text{min}} = 2.4$ °

$h = -13$ → 13

$k = -18$ → 18

$l = -20$ → 20

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.102$

$S = 1.07$

10686 reflections

274 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 3.87$ e Å⁻³

$\Delta\rho_{\text{min}} = -2.72$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|-------------|----------------------------------|
| U1 | 0.51249 (2) | 0.16808 (2) | 0.26353 (2) | 0.00963 (4) |
| B1 | 0.8150 (5) | 0.2329 (4) | 0.3009 (4) | 0.0177 (8) |
| H1A | 0.761 (6) | 0.294 (5) | 0.308 (4) | 0.027* |
| H1B | 0.771 (6) | 0.205 (5) | 0.219 (4) | 0.027* |
| H1C | 0.762 (6) | 0.166 (5) | 0.348 (4) | 0.027* |
| H1D | 0.944 (6) | 0.271 (5) | 0.317 (4) | 0.027* |
| Si1 | 0.76504 (13) | 0.39347 (9) | 0.07862 (8) | 0.0156 (2) |
| Si2 | 0.71528 (13) | 0.35432 (9) | 0.54090 (9) | 0.0161 (2) |
| Si3 | 0.79753 (13) | -0.07373 (10) | 0.23562 (8) | 0.0161 (2) |
| C1 | 0.5747 (4) | 0.3269 (3) | 0.1255 (3) | 0.0134 (6) |
| C2 | 0.4548 (4) | 0.2353 (3) | 0.0762 (3) | 0.0142 (7) |
| H2 | 0.467664 | 0.185642 | 0.022485 | 0.017* |
| C3 | 0.3126 (4) | 0.2291 (3) | 0.1192 (3) | 0.0168 (7) |
| H3A | 0.205686 | 0.182752 | 0.090235 | 0.020* |
| C4 | 0.3423 (5) | 0.3169 (3) | 0.1952 (3) | 0.0194 (8) |
| H4A | 0.259820 | 0.343109 | 0.229549 | 0.023* |
| C5 | 0.5036 (5) | 0.3754 (3) | 0.2021 (3) | 0.0170 (7) |
| H5A | 0.551554 | 0.449334 | 0.242324 | 0.020* |
| C6 | 0.8516 (6) | 0.2832 (4) | 0.0182 (4) | 0.0258 (9) |
| H6A | 0.773894 | 0.237713 | -0.034755 | 0.039* |
| H6B | 0.946750 | 0.320007 | -0.009698 | 0.039* |
| H6C | 0.879493 | 0.234315 | 0.067481 | 0.039* |
| C7 | 0.9080 (5) | 0.4833 (4) | 0.1805 (4) | 0.0259 (9) |
| H7A | 0.935861 | 0.435704 | 0.231009 | 0.039* |
| H7B | 1.003659 | 0.521095 | 0.153741 | 0.039* |
| H7C | 0.859331 | 0.540147 | 0.210342 | 0.039* |
| C8 | 0.7126 (6) | 0.4851 (4) | -0.0173 (4) | 0.0284 (10) |
| H8A | 0.637627 | 0.438442 | -0.070950 | 0.043* |
| H8B | 0.664218 | 0.541988 | 0.012768 | 0.043* |
| H8C | 0.808545 | 0.522937 | -0.043833 | 0.043* |
| C9 | 0.5445 (4) | 0.2558 (3) | 0.4617 (3) | 0.0139 (6) |
| C10 | 0.5031 (4) | 0.1358 (3) | 0.4589 (3) | 0.0129 (6) |
| H10A | 0.566960 | 0.090586 | 0.496241 | 0.016* |
| C11 | 0.3457 (4) | 0.0938 (3) | 0.4159 (3) | 0.0148 (7) |
| H11A | 0.280490 | 0.015468 | 0.418243 | 0.018* |
| C12 | 0.2877 (4) | 0.1864 (3) | 0.3859 (3) | 0.0159 (7) |
| H12A | 0.174487 | 0.184244 | 0.363546 | 0.019* |
| C13 | 0.4089 (5) | 0.2856 (3) | 0.4155 (3) | 0.0156 (7) |
| H13 | 0.400650 | 0.360371 | 0.406008 | 0.019* |

| | | | | |
|------|------------|-------------|------------|-------------|
| C14 | 0.7834 (5) | 0.4881 (3) | 0.4818 (4) | 0.0236 (9) |
| H14A | 0.694252 | 0.523095 | 0.467930 | 0.035* |
| H14B | 0.867433 | 0.540488 | 0.526781 | 0.035* |
| H14C | 0.823995 | 0.470669 | 0.419794 | 0.035* |
| C15 | 0.6386 (6) | 0.3890 (4) | 0.6594 (3) | 0.0269 (9) |
| H15A | 0.553651 | 0.428013 | 0.645944 | 0.040* |
| H15B | 0.597529 | 0.319142 | 0.688904 | 0.040* |
| H15C | 0.724665 | 0.438154 | 0.705407 | 0.040* |
| C16 | 0.8764 (5) | 0.2804 (4) | 0.5706 (3) | 0.0226 (8) |
| H16A | 0.965381 | 0.332556 | 0.612059 | 0.034* |
| H16B | 0.836522 | 0.215057 | 0.606193 | 0.034* |
| H16C | 0.911947 | 0.254911 | 0.509097 | 0.034* |
| C17 | 0.6012 (4) | -0.0360 (3) | 0.2171 (3) | 0.0128 (6) |
| C18 | 0.4764 (5) | -0.0648 (3) | 0.2755 (3) | 0.0140 (6) |
| H18 | 0.485999 | -0.088223 | 0.340226 | 0.017* |
| C19 | 0.3343 (4) | -0.0530 (3) | 0.2215 (3) | 0.0153 (7) |
| H19 | 0.232617 | -0.068713 | 0.243279 | 0.018* |
| C20 | 0.3699 (4) | -0.0141 (3) | 0.1306 (3) | 0.0145 (7) |
| H20A | 0.290811 | -0.013775 | 0.072251 | 0.017* |
| C21 | 0.5350 (4) | -0.0017 (3) | 0.1283 (3) | 0.0130 (6) |
| H21A | 0.589324 | 0.009939 | 0.067662 | 0.016* |
| C22 | 0.8854 (5) | -0.0487 (4) | 0.3683 (3) | 0.0238 (9) |
| H22A | 0.904791 | 0.031903 | 0.390761 | 0.036* |
| H22B | 0.811913 | -0.092648 | 0.408388 | 0.036* |
| H22C | 0.985486 | -0.072076 | 0.375288 | 0.036* |
| C23 | 0.7622 (7) | -0.2283 (4) | 0.1955 (4) | 0.0334 (11) |
| H23A | 0.716059 | -0.243268 | 0.125928 | 0.050* |
| H23B | 0.862889 | -0.250933 | 0.203265 | 0.050* |
| H23C | 0.689316 | -0.271505 | 0.236365 | 0.050* |
| C24 | 0.9339 (5) | 0.0070 (4) | 0.1537 (4) | 0.0277 (10) |
| H24A | 0.883975 | -0.008159 | 0.084891 | 0.042* |
| H24B | 0.954902 | 0.088142 | 0.174393 | 0.042* |
| H24C | 1.033665 | -0.016878 | 0.159288 | 0.042* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| U1 | 0.00980 (6) | 0.01025 (6) | 0.00983 (7) | 0.00336 (4) | 0.00194 (4) | 0.00341 (4) |
| B1 | 0.0131 (18) | 0.019 (2) | 0.021 (2) | 0.0041 (15) | 0.0016 (16) | 0.0059 (16) |
| Si1 | 0.0167 (5) | 0.0131 (4) | 0.0176 (5) | 0.0025 (4) | 0.0052 (4) | 0.0052 (4) |
| Si2 | 0.0188 (5) | 0.0123 (4) | 0.0163 (5) | 0.0030 (4) | 0.0004 (4) | 0.0002 (4) |
| Si3 | 0.0160 (5) | 0.0195 (5) | 0.0161 (5) | 0.0099 (4) | 0.0025 (4) | 0.0049 (4) |
| C1 | 0.0143 (15) | 0.0126 (15) | 0.0135 (16) | 0.0032 (12) | 0.0010 (12) | 0.0050 (12) |
| C2 | 0.0163 (16) | 0.0158 (16) | 0.0109 (16) | 0.0038 (13) | 0.0015 (13) | 0.0037 (12) |
| C3 | 0.0140 (16) | 0.0207 (18) | 0.0172 (18) | 0.0051 (13) | 0.0010 (13) | 0.0098 (14) |
| C4 | 0.0163 (17) | 0.0192 (18) | 0.028 (2) | 0.0106 (14) | 0.0061 (15) | 0.0141 (16) |
| C5 | 0.0186 (17) | 0.0148 (16) | 0.0210 (19) | 0.0079 (13) | 0.0051 (14) | 0.0091 (14) |
| C6 | 0.030 (2) | 0.020 (2) | 0.029 (2) | 0.0048 (17) | 0.0154 (19) | 0.0026 (17) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C7 | 0.024 (2) | 0.021 (2) | 0.030 (2) | -0.0006 (16) | 0.0056 (18) | 0.0030 (17) |
| C8 | 0.028 (2) | 0.029 (2) | 0.032 (3) | 0.0063 (18) | 0.0100 (19) | 0.021 (2) |
| C9 | 0.0145 (15) | 0.0117 (15) | 0.0165 (17) | 0.0045 (12) | 0.0024 (13) | 0.0022 (12) |
| C10 | 0.0168 (16) | 0.0122 (15) | 0.0102 (15) | 0.0033 (12) | 0.0028 (12) | 0.0028 (12) |
| C11 | 0.0148 (15) | 0.0169 (16) | 0.0132 (16) | 0.0016 (13) | 0.0061 (13) | 0.0057 (13) |
| C12 | 0.0119 (15) | 0.0236 (18) | 0.0143 (17) | 0.0067 (13) | 0.0046 (13) | 0.0026 (14) |
| C13 | 0.0167 (16) | 0.0175 (17) | 0.0145 (17) | 0.0076 (13) | 0.0025 (13) | 0.0023 (13) |
| C14 | 0.026 (2) | 0.0122 (17) | 0.032 (2) | 0.0031 (15) | 0.0054 (18) | 0.0032 (16) |
| C15 | 0.037 (2) | 0.023 (2) | 0.018 (2) | 0.0031 (18) | 0.0037 (18) | -0.0048 (16) |
| C16 | 0.0228 (19) | 0.0204 (19) | 0.025 (2) | 0.0080 (15) | -0.0036 (16) | 0.0027 (16) |
| C17 | 0.0141 (15) | 0.0125 (15) | 0.0126 (16) | 0.0041 (12) | 0.0025 (12) | 0.0029 (12) |
| C18 | 0.0190 (17) | 0.0126 (15) | 0.0104 (16) | 0.0033 (13) | 0.0025 (13) | 0.0024 (12) |
| C19 | 0.0137 (15) | 0.0127 (15) | 0.0182 (18) | -0.0003 (12) | 0.0032 (13) | 0.0031 (13) |
| C20 | 0.0140 (15) | 0.0176 (16) | 0.0097 (16) | 0.0018 (13) | -0.0030 (12) | -0.0001 (12) |
| C21 | 0.0149 (16) | 0.0140 (15) | 0.0111 (16) | 0.0063 (12) | 0.0007 (12) | -0.0007 (12) |
| C22 | 0.0220 (19) | 0.033 (2) | 0.020 (2) | 0.0142 (17) | 0.0007 (16) | 0.0059 (17) |
| C23 | 0.040 (3) | 0.025 (2) | 0.041 (3) | 0.022 (2) | 0.001 (2) | -0.001 (2) |
| C24 | 0.023 (2) | 0.038 (3) | 0.030 (2) | 0.0164 (19) | 0.0102 (18) | 0.014 (2) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|-----------|
| U1—B1 | 2.568 (4) | C7—H7B | 0.9800 |
| U1—C21 | 2.731 (4) | C7—H7C | 0.9800 |
| U1—C10 | 2.732 (4) | C8—H8A | 0.9800 |
| U1—C20 | 2.733 (4) | C8—H8B | 0.9800 |
| U1—C5 | 2.740 (4) | C8—H8C | 0.9800 |
| U1—C12 | 2.748 (4) | C9—C13 | 1.419 (5) |
| U1—C11 | 2.754 (3) | C9—C10 | 1.424 (5) |
| U1—C4 | 2.755 (4) | C10—C11 | 1.403 (5) |
| U1—C3 | 2.755 (4) | C10—H10A | 1.0000 |
| U1—H1A | 2.35 (5) | C11—C12 | 1.411 (5) |
| U1—H1B | 2.35 (5) | C11—H11A | 1.0000 |
| U1—H1C | 2.36 (5) | C12—C13 | 1.417 (5) |
| B1—H1A | 0.98 (6) | C12—H12A | 1.0000 |
| B1—H1B | 1.15 (6) | C13—H13 | 0.9500 |
| B1—H1C | 1.12 (5) | C14—H14A | 0.9800 |
| B1—H1D | 1.11 (5) | C14—H14B | 0.9800 |
| Si1—C7 | 1.868 (5) | C14—H14C | 0.9800 |
| Si1—C8 | 1.871 (4) | C15—H15A | 0.9800 |
| Si1—C6 | 1.872 (5) | C15—H15B | 0.9800 |
| Si1—C1 | 1.877 (4) | C15—H15C | 0.9800 |
| Si2—C16 | 1.867 (4) | C16—H16A | 0.9800 |
| Si2—C9 | 1.871 (4) | C16—H16B | 0.9800 |
| Si2—C15 | 1.873 (5) | C16—H16C | 0.9800 |
| Si2—C14 | 1.877 (4) | C17—C18 | 1.415 (5) |
| Si3—C22 | 1.867 (5) | C17—C21 | 1.421 (5) |
| Si3—C23 | 1.873 (5) | C18—C19 | 1.420 (5) |
| Si3—C17 | 1.876 (4) | C18—H18 | 0.9500 |

| | | | |
|------------|-------------|------------|-----------|
| Si3—C24 | 1.884 (5) | C19—C20 | 1.402 (5) |
| C1—C2 | 1.418 (5) | C19—H19 | 0.9500 |
| C1—C5 | 1.432 (6) | C20—C21 | 1.421 (5) |
| C2—C3 | 1.420 (5) | C20—H20A | 1.0000 |
| C2—H2 | 0.9500 | C21—H21A | 1.0000 |
| C3—C4 | 1.396 (6) | C22—H22A | 0.9800 |
| C3—H3A | 1.0000 | C22—H22B | 0.9800 |
| C4—C5 | 1.418 (5) | C22—H22C | 0.9800 |
| C4—H4A | 1.0000 | C23—H23A | 0.9800 |
| C5—H5A | 1.0000 | C23—H23B | 0.9800 |
| C6—H6A | 0.9800 | C23—H23C | 0.9800 |
| C6—H6B | 0.9800 | C24—H24A | 0.9800 |
| C6—H6C | 0.9800 | C24—H24B | 0.9800 |
| C7—H7A | 0.9800 | C24—H24C | 0.9800 |
| | | | |
| B1—U1—C21 | 91.29 (14) | C3—C4—H4A | 125.3 |
| B1—U1—C10 | 88.27 (13) | C5—C4—H4A | 125.3 |
| C21—U1—C10 | 121.25 (11) | U1—C4—H4A | 125.3 |
| B1—U1—C20 | 121.42 (14) | C4—C5—C1 | 108.8 (4) |
| C21—U1—C20 | 30.15 (11) | C4—C5—U1 | 75.7 (2) |
| C10—U1—C20 | 116.28 (11) | C1—C5—U1 | 77.6 (2) |
| B1—U1—C5 | 89.68 (13) | C4—C5—H5A | 124.8 |
| C21—U1—C5 | 119.23 (12) | C1—C5—H5A | 124.8 |
| C10—U1—C5 | 119.52 (12) | U1—C5—H5A | 124.8 |
| C20—U1—C5 | 115.78 (12) | Si1—C6—H6A | 109.5 |
| B1—U1—C12 | 128.78 (14) | Si1—C6—H6B | 109.5 |
| C21—U1—C12 | 131.96 (12) | H6A—C6—H6B | 109.5 |
| C10—U1—C12 | 48.97 (11) | Si1—C6—H6C | 109.5 |
| C20—U1—C12 | 104.45 (12) | H6A—C6—H6C | 109.5 |
| C5—U1—C12 | 89.90 (12) | H6B—C6—H6C | 109.5 |
| B1—U1—C11 | 117.73 (13) | Si1—C7—H7A | 109.5 |
| C21—U1—C11 | 113.80 (11) | Si1—C7—H7B | 109.5 |
| C10—U1—C11 | 29.63 (11) | H7A—C7—H7B | 109.5 |
| C20—U1—C11 | 95.57 (11) | Si1—C7—H7C | 109.5 |
| C5—U1—C11 | 118.89 (12) | H7A—C7—H7C | 109.5 |
| C12—U1—C11 | 29.73 (11) | H7B—C7—H7C | 109.5 |
| B1—U1—C4 | 119.54 (13) | Si1—C8—H8A | 109.5 |
| C21—U1—C4 | 115.96 (13) | Si1—C8—H8B | 109.5 |
| C10—U1—C4 | 114.79 (12) | H8A—C8—H8B | 109.5 |
| C20—U1—C4 | 98.00 (13) | Si1—C8—H8C | 109.5 |
| C5—U1—C4 | 29.91 (11) | H8A—C8—H8C | 109.5 |
| C12—U1—C4 | 70.43 (12) | H8B—C8—H8C | 109.5 |
| C11—U1—C4 | 99.66 (12) | C13—C9—C10 | 105.6 (3) |
| B1—U1—C3 | 129.05 (13) | C13—C9—Si2 | 125.9 (3) |
| C21—U1—C3 | 87.02 (12) | C10—C9—Si2 | 126.4 (3) |
| C10—U1—C3 | 134.56 (12) | C11—C10—C9 | 109.8 (3) |
| C20—U1—C3 | 69.70 (12) | C11—C10—U1 | 76.0 (2) |
| C5—U1—C3 | 49.08 (12) | C9—C10—U1 | 77.7 (2) |

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| C12—U1—C3 | 85.59 (12) | C11—C10—H10A | 124.4 |
| C11—U1—C3 | 109.24 (11) | C9—C10—H10A | 124.4 |
| C4—U1—C3 | 29.34 (13) | U1—C10—H10A | 124.4 |
| B1—U1—H1A | 22.4 (14) | C10—C11—C12 | 107.6 (3) |
| C21—U1—H1A | 110.3 (14) | C10—C11—U1 | 74.3 (2) |
| C10—U1—H1A | 88.4 (14) | C12—C11—U1 | 74.9 (2) |
| C20—U1—H1A | 139.8 (14) | C10—C11—H11A | 125.7 |
| C5—U1—H1A | 70.3 (13) | C12—C11—H11A | 125.7 |
| C12—U1—H1A | 115.5 (14) | U1—C11—H11A | 125.7 |
| C11—U1—H1A | 116.7 (14) | C11—C12—C13 | 107.6 (3) |
| C4—U1—H1A | 99.3 (13) | C11—C12—U1 | 75.4 (2) |
| C3—U1—H1A | 116.2 (13) | C13—C12—U1 | 76.6 (2) |
| B1—U1—H1B | 26.5 (14) | C11—C12—H12A | 125.4 |
| C21—U1—H1B | 70.8 (14) | C13—C12—H12A | 125.4 |
| C10—U1—H1B | 113.0 (14) | U1—C12—H12A | 125.4 |
| C20—U1—H1B | 100.0 (14) | C12—C13—C9 | 109.4 (3) |
| C5—U1—H1B | 85.6 (13) | C12—C13—H13 | 125.3 |
| C12—U1—H1B | 154.6 (14) | C9—C13—H13 | 125.3 |
| C11—U1—H1B | 141.1 (13) | Si2—C14—H14A | 109.5 |
| C4—U1—H1B | 113.1 (13) | Si2—C14—H14B | 109.5 |
| C3—U1—H1B | 109.6 (13) | H14A—C14—H14B | 109.5 |
| H1A—U1—H1B | 39.9 (19) | Si2—C14—H14C | 109.5 |
| B1—U1—H1C | 25.8 (13) | H14A—C14—H14C | 109.5 |
| C21—U1—H1C | 90.4 (14) | H14B—C14—H14C | 109.5 |
| C10—U1—H1C | 66.9 (14) | Si2—C15—H15A | 109.5 |
| C20—U1—H1C | 116.7 (13) | Si2—C15—H15B | 109.5 |
| C5—U1—H1C | 112.4 (13) | H15A—C15—H15B | 109.5 |
| C12—U1—H1C | 114.2 (14) | Si2—C15—H15C | 109.5 |
| C11—U1—H1C | 94.8 (13) | H15A—C15—H15C | 109.5 |
| C4—U1—H1C | 140.7 (13) | H15B—C15—H15C | 109.5 |
| C3—U1—H1C | 154.7 (13) | Si2—C16—H16A | 109.5 |
| H1A—U1—H1C | 42.1 (18) | Si2—C16—H16B | 109.5 |
| H1B—U1—H1C | 46.4 (18) | H16A—C16—H16B | 109.5 |
| U1—B1—H1A | 66 (3) | Si2—C16—H16C | 109.5 |
| U1—B1—H1B | 66 (3) | H16A—C16—H16C | 109.5 |
| H1A—B1—H1B | 97 (4) | H16B—C16—H16C | 109.5 |
| U1—B1—H1C | 67 (3) | C18—C17—C21 | 106.5 (3) |
| H1A—B1—H1C | 107 (4) | C18—C17—Si3 | 126.3 (3) |
| H1B—B1—H1C | 110 (4) | C21—C17—Si3 | 125.2 (3) |
| U1—B1—H1D | 174 (3) | C17—C18—C19 | 108.8 (3) |
| H1A—B1—H1D | 108 (4) | C17—C18—H18 | 125.6 |
| H1B—B1—H1D | 115 (4) | C19—C18—H18 | 125.6 |
| H1C—B1—H1D | 118 (4) | C20—C19—C18 | 108.2 (3) |
| C7—Si1—C8 | 109.1 (2) | C20—C19—H19 | 125.9 |
| C7—Si1—C6 | 111.5 (2) | C18—C19—H19 | 125.9 |
| C8—Si1—C6 | 108.4 (2) | C19—C20—C21 | 107.5 (3) |
| C7—Si1—C1 | 110.74 (19) | C19—C20—U1 | 77.0 (2) |
| C8—Si1—C1 | 106.02 (19) | C21—C20—U1 | 74.8 (2) |

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|--------------|-------------|-----------------|------------|
| C6—Si1—C1 | 110.83 (18) | C19—C20—H20A | 125.5 |
| C16—Si2—C9 | 109.96 (19) | C21—C20—H20A | 125.5 |
| C16—Si2—C15 | 107.7 (2) | U1—C20—H20A | 125.5 |
| C9—Si2—C15 | 105.7 (2) | C20—C21—C17 | 109.0 (3) |
| C16—Si2—C14 | 113.1 (2) | C20—C21—U1 | 75.0 (2) |
| C9—Si2—C14 | 111.05 (19) | C17—C21—U1 | 78.9 (2) |
| C15—Si2—C14 | 109.0 (2) | C20—C21—H21A | 124.6 |
| C22—Si3—C23 | 108.2 (2) | C17—C21—H21A | 124.6 |
| C22—Si3—C17 | 111.93 (19) | U1—C21—H21A | 124.6 |
| C23—Si3—C17 | 107.1 (2) | Si3—C22—H22A | 109.5 |
| C22—Si3—C24 | 111.8 (2) | Si3—C22—H22B | 109.5 |
| C23—Si3—C24 | 108.4 (3) | H22A—C22—H22B | 109.5 |
| C17—Si3—C24 | 109.23 (18) | Si3—C22—H22C | 109.5 |
| C2—C1—C5 | 105.6 (3) | H22A—C22—H22C | 109.5 |
| C2—C1—Si1 | 126.1 (3) | H22B—C22—H22C | 109.5 |
| C5—C1—Si1 | 126.4 (3) | Si3—C23—H23A | 109.5 |
| C1—C2—C3 | 109.7 (4) | Si3—C23—H23B | 109.5 |
| C1—C2—H2 | 125.2 | H23A—C23—H23B | 109.5 |
| C3—C2—H2 | 125.2 | Si3—C23—H23C | 109.5 |
| C4—C3—C2 | 107.5 (3) | H23A—C23—H23C | 109.5 |
| C4—C3—U1 | 75.3 (2) | H23B—C23—H23C | 109.5 |
| C2—C3—U1 | 75.9 (2) | Si3—C24—H24A | 109.5 |
| C4—C3—H3A | 125.5 | Si3—C24—H24B | 109.5 |
| C2—C3—H3A | 125.5 | H24A—C24—H24B | 109.5 |
| U1—C3—H3A | 125.5 | Si3—C24—H24C | 109.5 |
| C3—C4—C5 | 108.4 (4) | H24A—C24—H24C | 109.5 |
| C3—C4—U1 | 75.3 (2) | H24B—C24—H24C | 109.5 |
| C5—C4—U1 | 74.4 (2) | | |
| C7—Si1—C1—C2 | -164.8 (3) | Si2—C9—C10—U1 | -128.1 (3) |
| C8—Si1—C1—C2 | 76.9 (4) | C9—C10—C11—C12 | 3.1 (4) |
| C6—Si1—C1—C2 | -40.5 (4) | U1—C10—C11—C12 | -68.1 (3) |
| C7—Si1—C1—C5 | 33.1 (4) | C9—C10—C11—U1 | 71.2 (3) |
| C8—Si1—C1—C5 | -85.2 (4) | C10—C11—C12—C13 | -2.8 (4) |
| C6—Si1—C1—C5 | 157.4 (3) | U1—C11—C12—C13 | -70.5 (3) |
| C5—C1—C2—C3 | 1.5 (4) | C10—C11—C12—U1 | 67.7 (3) |
| Si1—C1—C2—C3 | -163.6 (3) | C11—C12—C13—C9 | 1.6 (4) |
| C1—C2—C3—C4 | 0.3 (4) | U1—C12—C13—C9 | -68.1 (3) |
| C1—C2—C3—U1 | -69.1 (3) | C10—C9—C13—C12 | 0.3 (4) |
| C2—C3—C4—C5 | -2.0 (4) | Si2—C9—C13—C12 | -163.7 (3) |
| U1—C3—C4—C5 | 67.7 (3) | C22—Si3—C17—C18 | -45.2 (4) |
| C2—C3—C4—U1 | -69.7 (3) | C23—Si3—C17—C18 | 73.3 (4) |
| C3—C4—C5—C1 | 3.0 (4) | C24—Si3—C17—C18 | -169.5 (4) |
| U1—C4—C5—C1 | 71.3 (3) | C22—Si3—C17—C21 | 153.2 (3) |
| C3—C4—C5—U1 | -68.3 (3) | C23—Si3—C17—C21 | -88.3 (4) |
| C2—C1—C5—C4 | -2.8 (4) | C24—Si3—C17—C21 | 28.9 (4) |
| Si1—C1—C5—C4 | 162.3 (3) | C21—C17—C18—C19 | 2.5 (4) |
| C2—C1—C5—U1 | 67.2 (2) | Si3—C17—C18—C19 | -161.9 (3) |

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|----------------|------------|-----------------|------------|
| Si1—C1—C5—U1 | -127.7 (3) | C17—C18—C19—C20 | -1.5 (4) |
| C16—Si2—C9—C13 | -172.4 (3) | C18—C19—C20—C21 | 0.0 (4) |
| C15—Si2—C9—C13 | 71.6 (4) | C18—C19—C20—U1 | -69.3 (3) |
| C14—Si2—C9—C13 | -46.5 (4) | C19—C20—C21—C17 | 1.6 (4) |
| C16—Si2—C9—C10 | 26.8 (4) | U1—C20—C21—C17 | 72.3 (3) |
| C15—Si2—C9—C10 | -89.2 (4) | C19—C20—C21—U1 | -70.8 (3) |
| C14—Si2—C9—C10 | 152.7 (3) | C18—C17—C21—C20 | -2.5 (4) |
| C13—C9—C10—C11 | -2.1 (4) | Si3—C17—C21—C20 | 162.1 (3) |
| Si2—C9—C10—C11 | 161.8 (3) | C18—C17—C21—U1 | 67.2 (3) |
| C13—C9—C10—U1 | 68.0 (3) | Si3—C17—C21—U1 | -128.1 (3) |
