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Syntheses of the Uranium Complexes $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ and $[U\{C(Ph)(NSiMe_3)_2\}_2\{\mu_3\text{-}BH_4\}_2]$. Determination of Hydrogen Positions by Single-Crystal X-ray and Neutron Diffraction

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The complex $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ (**1**) is formed in the reaction between the hydride complex $[U\{N(SiMe_3)_2\}_3(H)]$ and $B(C_6F_5)_3$, and H_2 is evolved. The X-ray [$C_{36}H_{53}BF_{15}N_3Si_6U\cdot 3.5C_6D_6$, triclinic, space group $P\bar{1}$, $Z = 2$, 90 K, $a = 14.065(1)$ Å, $b = 14.496(1)$ Å, $c = 18.759(1)$ Å, $\alpha = 82.898(1)°$, $\beta = 74.415(1)°$, $\gamma = 62.919(1)°$] and neutron structure [$C_{36}H_{53}BF_{15}N_3Si_6U\cdot 3.5C_6D_6$, triclinic, space group $P\bar{1}$, $Z = 2$, 20 K, $a = 13.993(1)$ Å, $b = 14.484(1)$ Å, $c = 18.720(1)$ Å, $\alpha = 82.810(1)°$, $\beta = 74.200(1)°$, $\gamma = 63.054(1)$E] of compound **1**, which crystallizes with 3.5 molecules of C_6D_6 per asymmetric unit, show the electron deficiency of the uranium atom to be effectively compensated by the formation of multicenter bonds between U and three Si−CH_2 units of the amido ligands. The reaction of the uranium complex $[U\{C(Ph)(NSiMe_3)_2\}_2(Cl)_2]$ with $[Na(BH_4)]$ gives the complex $[U\{C(Ph)(NSiMe_3)_2\}_2\{\mu_3\text{-}BH_4\}_2]$ (**2**). The X-ray structure of **2** [$C_{26}H_{54}B_2N_4Si_4U$, monoclinic, space group $C2/c$, $Z = 4$, 90 K, $a = 21.613(1)$ Å, $b = 9.233(1)$ Å, $c = 18.132(1)$ Å, $\beta = 98.804(1)°$] proves unequivocally the μ_3 coordination of the BH_4 moieties. In both single-crystal X-ray structure determinations, all hydrogen and deuterium atoms could be located and isotropically refined, including those which are directly coordinated to the uranium. The reliability of the refined hydrogen and deuterium positions for compound **1** is confirmed by comparison of the X-ray and neutron structure determinations. The ability to locate the hydrogen and deuterium positions in these uranium compounds by single-crystal X-ray diffraction is due to good crystal quality, the measurement of data at low temperature, and the use of image plate technology for data collection.

Introduction

In single-crystal diffraction, the structure factors are directly related to the distribution of scattering matter in the unit cell which in the case of X-rays is the electron distribution, time-averaged over the vibrational modes of the solid.[1] As hydrogen atoms in heavy-atom structures contribute only a small fraction to the overall electron density and are quite often involved in extensive thermal motion, the reliable determination of hydrogen atoms by X-ray experiments is often quite difficult if not impossible.[2] In contrast, neutrons are scattered by atomic nuclei and neutron scattering amplitudes are not a regular function of atomic number, and therefore neutron diffraction gives information that often complements that obtained from X-ray diffraction.[3] The location of hydrogen and deuterium atoms by neutron diffraction is much easier because the scattering is higher relative to that of other atoms than is the case for X-rays. Two excellent reviews on this subject have been written by Bau[4] and Teller.[5] Among the difficulties encountered if one wishes to use neutron diffraction, however, are the requirement for larger crystals and the limited availability of time at sources with sufficient neutron flux.

In this work we show that X-ray diffraction is well capable of unveiling hydrogen positions unequivocally in uranium-containing compounds if some basic criteria are met. The elucidation and comparison of the X-ray and neutron structures of the compound $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ (**1**) and the X-ray structure of the compound $[U\{C(Ph)(NSiMe_3)_2\}_2\{\mu_3\text{-}BH_4\}_2]$ (**2**) are discussed in detail, with focus on the determination of hydrogen atom positions and crystallographic evidence for U−C−Si multicenter bonds.

Results and Discussion

Synthesis of $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ (1). The hydride complex $[U\{N(SiMe_3)_2\}_3(H)]$ (**3**) was first prepared by Andersen et al.[6] in 1981. Thermolysis of **3** gives the metallacycle $[\overline{U\{N(SiMe_3)_2\}\{-N(SiMe_3)Si(Me)_2C}(H)_2]$ (**4**) and H_2.[7] The compounds **3**, **4**, and H_2 are in dynamic equilibrium as indicated in Scheme 1. Exposure of a solution

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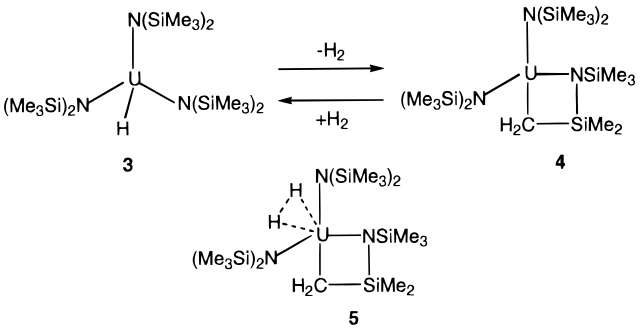
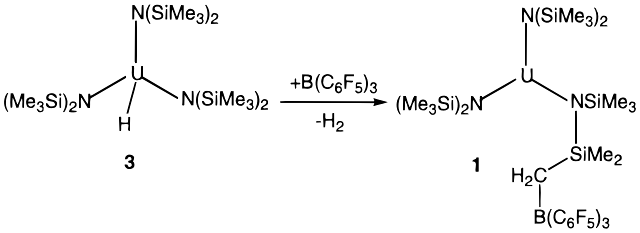
Scheme 1



Scheme 2



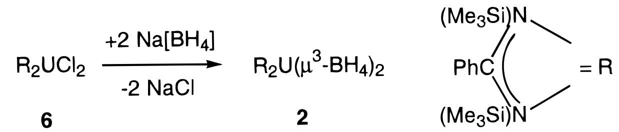
of compound **3** to 1 bar of deuterium in a noncoordinating solvent at room temperature leads to a rapid H/D exchange of all 55 hydrogen atoms of **3**.[8]

However, if the deuteration experiment is performed in the presence of a coordinating solvent such as tetrahydrofuran, no hydrogen−deuterium exchange is observed. This result suggests that in the equilibrium **3** $\rightleftarrows$ **4** there is an intermediate species **5**, in which two H atoms or a μ_2-bonded H_2 molecule occupy a coordination site on the uranium (Scheme 1). In the presence of a coordinating solvent, the H_2 ligand may be replaced by a solvent molecule, and thus the hydrogen−deuterium exchange would be inhibited.[9]

We have shown that the treatment of **3** with $B(C_6F_5)_3$ in pentane affords almost quantitatively the U(IV) complex $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ (**1**) as a pale yellow powder, highly sensitive to air and moisture and unstable above 40 °C (Scheme 2). Only very broad ^{1}H and no ^{13}C NMR signals can be recorded at room temperature for a solution of **1** in C_6D_6, indicating compound **1** to be highly fluxional in solution. At lower temperature, ^{1}H NMR signals appear which are unassignable due to their broadness. To establish the structure of compound **1**, single-crystal X-ray and neutron diffraction experiments were carried out. Of particular interest was the question of whether the product **1** contained a uranium-bonded hydrogen as proposed for compound **5**. This was thought to be likely as the evolution of hydrogen gas during the synthesis of **1** was never observed experimentally.

Synthesis of $[U\{C(Ph)(NSiMe_3)_2\}_2\{\mu_3\text{-}BH_4\}_2]$ (2). In the reaction of the bis[(trimethylsilyl)benzamidinato]uranium complex $[U\{C(Ph)(NSiMe_3)_2\}_2(Cl)_2]$ (**6**) with sodium borohydride, compound $[U\{C(Ph)(NSiMe_3)_2\}_2\{\mu_3\text{-}BH_4\}_2]$ (**2**) is formed in 75% yield (Scheme 3) as a bright green compound which is readily soluble in hydrocarbon solvents. NMR spectroscopy shows it to be fluxional in solution. At 50 °C, both amidinato ligands are equivalent and show internal C_{2v} symmetry as indicated by signals for one phenyl ring and one $SiMe_3$ group in the ^{1}H NMR spectrum. Upon cooling, the $SiMe_3$ signal broadens, and at −45 °C, coalescence is observed. At −70 °C, the dynamic process is slow on the NMR time scale, resulting in two sharp signals for the methyl hydrogen atoms. These NMR observations suggest the fluxional process to be a rotation of the amidinato ligands around their C_2 axis with a rotation barrier of $\Delta G^{\ddagger} = 37$ kJ mol^{-1}.[10] The BH_4 groups show a broad signal in the ^{1}H NMR spectra at ca. 34 ppm, independent of temperature. The infrared spectrum of **2** shows three bands at 2509, 2209, and 2139 cm^{-1} consistent with a μ_3 coordination of the BH_4 ligands.[11] The bands agree very well with those observed for the isostructural complex $[U(Cp)_2(\mu_3\text{-}BH_4)_2]$; however, the μ_3 coordination of this compound could only be assigned by infrared data.[12] To determine unequivocally the coordination type of the BH_4 moieties in **2**, a single-crystal X-ray diffraction experiment was carried out.

Scheme 3



X-ray and Neutron Crystal Structures of $[U\{N(SiMe_3)_2\}_2\{N(SiMe_3)(SiMe_2CH_2B(C_6F_5)_3)\}]$ (1). Extremely air-sensitive crystals of compound **1** suitable for single-crystal X-ray and neutron diffraction experiments were grown from deuterated benzene. Crystals from a C_6H_6 solution or other solvents were never obtained. Compound **1** crystallizes in the centrosymmetric space group $P\bar{1}$ with 1 molecule of **1** and 3.5 molecules of C_6D_6 per asymmetric unit. The high ratio of included solvent in the crystal shows that the C_6D_6 molecules play an important role in the stabilization of the crystal lattice, presumably by enabling efficient packing and thus contributing significantly to the lattice energy. This might indicate that the failure to grow crystals from C_6H_6 is due to subtle differences in the physical and chemical characteristics of hydrogen and deuterium.

The X-ray and neutron diffraction experiments were undertaken at 90 and 20 K, respectively, and in both cases, all 157 atoms were included in unrestrained full-matrix least-squares calculations, as summarized in Table 1. For all atoms heavier than deuterium, the coordinates of the X-ray and neutron refinement show only very small differences. Larger differences are to be expected for the refined positions of hydrogen and deuterium atoms because the involvement of their single electron in C−H or C−D bonds shifts the center of gravity of the electron density toward the bonding partner. As a result, least-squares refinement of hydrogen and deuterium positions from X-ray data gives apparent C−H and C−D bonds that are about 0.1 Å shorter than those from neutron diffraction, which determines the true nuclear position.[3] Table 2 gives a complete list of all C−H and C−D bond lengths observed in compound **1**. The average C−H and C−D bond lengths for the X-ray data are 0.96 Å and for the neutron data are 1.09 Å.

In the X-ray refinement the minimum (−1.72 e Å^{-3}) and maximum residual electron densities (1.10 e Å^{-3}) occur at distances of 0.78 and 1.04 Å from the uranium, respectively.

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Table 1. X-ray and Neutron Crystallographic Data for **1** and **2**

	1	**1**	**2**
wavelength (Å)	Mo Kα, 0.710 69	neutron, 1.5394(1)	Mo Kα, 0.710 69
temperature (K)	90	20	90
empirical formula	$C_{36}H_{53}BF_{15}N_3Si_6U + 3.5\ (C_6D_6)$	$C_{36}H_{53}BF_{15}N_3Si_6U + 3.5\ (C_6D_6)$	$C_{26}H_{54}B_2N_4Si_4U$
formula weight	1230.17 + 294.52	1230.17 + 294.52	794.74
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	14.065(1)	13.993(1)	21.613(1)
b (Å)	14.496(1)	14.484(1)	9.233(1)
c (Å)	18.759(1)	18.720(1)	18.132(1)
α (deg)	82.898(1)	82.810(2)	90
β (deg)	74.415(1)	74.200(2)	98.804(2)
γ (deg)	62.919(1)	63.054(2)	90
volume (Å^3)	3279.9	3254.2	3575.7
Z	2	2	4
ρ_{calcd} (g cm^{-3})	1.544	1.556	1.476
μ (cm^{-1})	25.33	2.00	44.563
R^a	0.024	0.075	0.017
$R_w{}^b$	0.027	0.070	0.019

[a] $R = \sum||F_o| - |F_c||\sum|F_o|$. [b] $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Both peaks lie on well-defined negative and positive ripples spherically surrounding the U atom. These ripples in the difference Fourier map which are only expected to be found in close vicinity of heavy atoms are caused by insufficient compensation of series termination errors in the F_o and F_c Fourier maps.[13] If two H atoms or a μ_2-bonded H_2 molecule were present, they would be expected within a distance of 1.5–3.0 Å from the uranium atom.[14] The nine most intense local maxima within this region in a difference map exhibit peak heights between 0.35 and 0.51 e Å^{-3}, but none of these are found close to positions which H atoms could occupy. Peak heights of 0.5–0.8 e Å^{-3} are expected at positions for missing hydrogen atoms, as evidenced by examining difference maps after several refinement cycles and using an unbiased weighting scheme after having removed arbitrarily chosen carbon-bonded H atoms of **1**. Thus, the X-ray data suggest but cannot prove the absence of a μ_2-H_2 ligand. In contrast, the neutron data show clearly that there is no such ligand. Because the moduli of the hydrogen and deuterium scattering lengths are of the same order as those of the other atoms, the refinement parameters would give strong indications of missed H or D atoms even if these atoms were disordered or fluxional.[15] For example, after the removal of H110 and D930, refinement results are $\Delta\rho_{min} = -6.4$ f Å^{-3} (f = fermi) at the position of H110, $\Delta\rho_{max} = 10.0$ f Å^{-3} at the position of D930, R factors larger than 0.1, and negative displacement factors for the boron and one of the carbon atoms. The difference Fourier map obtained with the correct structure of **1** is flat without ripples ($\Delta\rho_{max} = 0.9$ f Å^{-3}, $\Delta\rho_{min} = -1.0$ f Å^{-3}) and shows no minima which might be associated with missing hydrogen atoms.

In Figure 1 are shown the X-ray and neutron structures of compound **1** in the crystal. The bulky $(Me_3Si)_2N$ and C_6F_5 ligands surround the center of the molecule almost spherically and shield the uranium and boron atoms very effectively. The large number of C–H and C–F bonds at the surface of the molecule give it a hydrophobic character. The three amido ligands are bonded directly to uranium by strong U–N bonds of length ca. 2.2 Å (Table 3). The boron atom is tetrahedrally coordinated by four carbon atoms at distances of ca. 1.6 Å. Complex **1** formally has a structure with a positive charge on uranium and a negative charge on boron.

A close examination of the coordination sphere around the uranium atom reveals that the electron deficiency at uranium is efficiently compensated by donation of electron density from the Si–C bonds (Figure 2a–c): The uranium atom, which is pyramidally coordinated by the three amido ligands, lies 0.7 Å above the plane of N1, N2, and N3 with N–U–N angles of 110.1(1), 111.8(1), and 109.7(1)° (Table 4). All three nitrogen atoms exhibit trigonal planar coordination as evidenced by sums of angles around N1, N2, and N3 of 359.6, 359.2, and 359.9°. Each amido ligand has one of its six Si–CH_2 entities located in close proximity to the uranium atom with U–Si distances of ca. 3.17 Å, U–C distances of ca. 2.87 Å, and U–H distances of ca. 2.70 Å. The U–C distances here are some 15% longer than typical U–C hydrocarbyl distances which occur between 2.41 and 2.55 Å. These coordinated N–Si–CH_2 moieties, the atoms of which are indicated by black circles in Figure 2a,b, are related by local C_3 pseudosymmetry with the uranium atom lying on the 3-fold axis and the Si–CH_2 units pointing toward the U from the side opposite the N atoms. The formation of multicenter bonds between the Si–C bonds and uranium is suggested not only by the short U–Si and U–C distances but also by analysis of bond lengths and angles. The three Si–C bonds close to the uranium exhibit bond lengths of 1.896(2), 1.905(2), and 1.908(2) Å. Due to a reduction of bonding by formation of multicenter bonds, these Si–C bonds are significantly longer than the 15 remaining, noncoordinating Si–C bonds, which are in the range 1.853(3)–1.875(2) Å with an average of 1.864 Å.[16] The close proximity of the coordinating Si–C bonds to the U atom requires major angle distortions. The N–Si–C angles close to uranium are 104.0(1), 104.8(1), and 105.9(1)° in comparison to the 15 remaining N–Si–C angles in the range 108.6(1)–114.9(1)° (average 111.5°). The U–N1–Si10, U–N2–Si20, and U–N3–Si30 angles of 106.0(1), 107.8(1), and 105.2(2)° are much smaller than the corresponding U–N1–Si11, U–N2–Si21, and U–N3–Si31 angles of 131.2(1), 130.7(1), and 131.4(1)°. Figure 3c, which depicts one of the three uranium-coordinating Si–CH_2 units, shows, in detail, that the Si–C and the two C–H bonds (indicated by black bonds) cap the uranium like an umbrella. These C–H

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Table 2. Hydrogen−Carbon and Deuterium−Carbon Bond Lengths (Å) for **1**[a]

C(11)−H(110)	1.03(2) 1.11(1)	C(11)−H(111)	1.00(3) 1.122(9)	C(12)−H(120)	0.99(3) 1.10(1)
C(12)−H(121)	1.00(3) 1.12(1)	C(12)−H(122)	1.01(3) 1.09(1)	C(13)−H(130)	1.03(2) 1.09(1)
C(13)−H(131)	0.98(4) 1.10(1)	C(13)−H(132)	0.94(4) 1.09(1)	C(14)−H(140)	1.00(3) 1.11(1)
C(14)−H(141)	0.99(4) 1.13(1)	C(14)−H(142)	0.98(4) 1.10(1)	C(15)−H(150)	0.93(4) 1.15(1)
C(15)−H(151)	0.94(5) 1.05(1)	C(15)−H(152)	0.95(4) 1.10(1)	C(16)−H(160)	1.05(3) 1.08(1)
C(16)−H(161)	0.95(4) 1.09(1)	C(16)−H(162)	0.99(3) 1.09(1)	C(21)−H(210)	0.93(4) 1.09(1)
C(21)−H(211)	1.06(3) 1.12(1)	C(21)−H(212)	0.89(3) 1.09(1)	C(22)−H(220)	0.89(5) 1.09(1)
C(22)−H(221)	0.99(4) 1.09(1)	C(22)−H(222)	0.94(5) 1.11(1)	C(23)−H(230)	1.01(4) 1.11(1)
C(23)−H(231)	0.93(3) 1.06(1)	C(23)−H(232)	0.98(4) 1.13(1)	C(24)−H(240)	0.94(5) 1.10(1)
C(24)−H(241)	1.06(4) 1.08(1)	C(24)−H(242)	0.92(4) 1.08(1)	C(25)−H(250)	0.95(4) 1.08(1)
C(25)−H(251)	0.95(4) 1.12(1)	C(25)−H(252)	0.96(4) 1.08(1)	C(26)−H(260)	0.97(4) 1.10(1)
C(26)−H(261)	1.09(4) 1.10(1)	C(26)−H(262)	0.96(4) 1.09(1)	C(31)−H(310)	1.00(3) 1.13(1)
C(31)−H(311)	0.97(3) 1.10(1)	C(31)−H(312)	0.86(3) 1.09(1)	C(32)−H(320)	0.91(3) 1.10(1)
C(32)−H(321)	0.97(4) 1.10(1)	C(32)−H(322)	0.95(3) 1.12(1)	C(33)−H(330)	0.95(4) 1.08(1)
C(33)−H(331)	0.98(3) 1.09(1)	C(33)−H(332)	0.93(3) 1.10(1)	C(34)−H(340)	0.88(4) 1.13(1)
C(34)−H(341)	0.97(4) 1.03(1)	C(34)−H(342)	0.88(4) 1.11(1)	C(35)−H(350)	0.97(4) 1.07(1)
C(35)−H(351)	1.01(4) 1.11(1)	C(35)−H(352)	0.98(3) 1.07(1)	C(36)−H(360)	1.01(3) 1.07(1)
C(36)−H(361)	0.93(4) 1.06(1)	C(36)−H(362)	1.00(4) 1.10(1)	C(70)−D(700)	0.91(3) 1.094(5)
C(71)−D(710)	0.88(4) 1.085(5)	C(72)−D(720)	1.00(3) 1.084(5)	C(73)−D(730)	0.98(3) 1.090(5)
C(74)−D(740)	0.93(3) 1.086(5)	C(75)−D(750)	0.92(4) 1.095(5)	C(80)−D(800)	1.06(4) 1.086(5)
C(81)−D(810)	0.97(5) 1.088(5)	C(82)−D(820)	1.08(5) 1.089(5)	C(83)−D(830)	0.95(4) 1.095(6)
C(84)−D(840)	0.59(7) 1.101(6)	C(85)−D(850)	0.79(5) 1.101(6)	C(90)−D(900)	0.92(4) 1.104(5)
C(91)−D(910)	0.97(4) 1.098(5)	C(92)−D(920)	1.06(4) 1.078(5)	C(93)−D(930)	0.93(5) 1.095(5)
C(94)−D(940)	0.95(4) 1.102(6)	C(95)−D(950)	0.86(4) 1.103(6)	C(97)−D(970)	0.99(4) 1.092(5)
C(98)−D(980)	0.88(4) 1.096(5)	C(99)−D(990)	0.93(4) 1.101(6)		

[a] For each bond length, the first-row figures are based on X-ray and the second-row figures on neutron data.

bonds might also contribute electron density to the uranium,[17] but their bond lengths are not accurate enough to prove any expected elongation. Large angles Si20−C21−H210, Si20−C21−H211, Si30−C31−H310, and Si30−C31−H311 of 118.0(6), 115.5(6), 115.7(6), and 117.6(5)°, respectively, indicate that these bonds are strongly affected by the coordination. Compensation of electron deficiency of metal atoms by formation of metal−Si−C multicenter bonds is a well-known feature in lanthanide and actinide chemistry.[18] There are two reliable X-ray crystal structures of monomeric uranium(IV) compounds with $N(SiMe_3)_2$ ligand(s). They have the general formula $[RU\{N(SiMe_3)_2\}_3]$ with R = S-2,6-$Me_2C_6H_3$[19] and O-2,6-$tBu_2C_6H_3$.[20] Both structures exhibit Si−C bonds in close proximity to the uranium as in compound **1**. However the effects of bond length and angle distortions due to U−Si−C multicenter bond formation are far less developed in these compounds because the ligand R (mentioned above) missing in **4** contributes electron density to the metal. Compound **1** is the first structurally characterized uranium(IV) compound whose only ligands are three amido groups.

The structure of the 3.5 independent benzene molecules per asymmetric unit in crystals of compound **1** are depicted in Figure 3a,b for the X-ray and the neutron data, respectively. The

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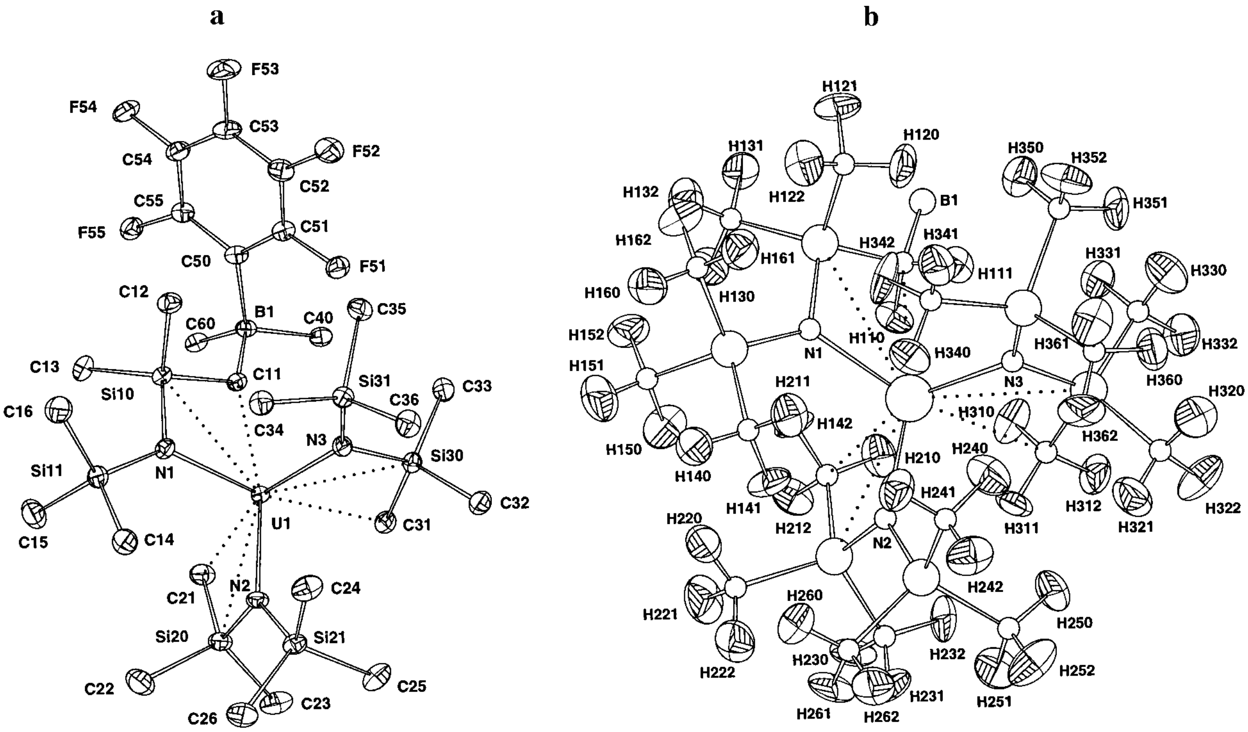

Figure 1. Structure of compound **1** in the crystal for (a) the X-ray (ellipsoids at 50% probability; H atoms and parts of the C_6F_5 rings omitted for clarity) and (b) the neutron experiment (ellipsoids for hydrogens only, at 30% probability; the three C_6F_5 ligands are omitted). Both structures are shown from the same view with the same numbering scheme; however, some labels are omitted for clarity.

Table 3. Selected Bond Lengths (Å) for **1**[a]

U(1)−N(1)	2.186(2) 2.195(4)	U(1)−N(2)	2.196(2) 2.200(4)	U(1)−N(3)	2.214(2) 2.205(4)
U(1)−H(110)	2.42(2) 2.563(8)	U(1)−H(111)	2.64(4) 2.687(8)	U(1)−H(210)	2.80(3) 2.870(8)
U(1)−H(211)	2.70(3) 2.752(8)	U(1)−H(310)	2.77(3) 2.768(8)	U(1)−H(311)	2.72(3) 2.787(8)
U(1)−C(11)	2.858(2) 2.869(5)	U(1)−C(21)	2.912(2) 2.927(5)	U(1)−C(31)	2.872(2) 2.876(6)
U(1)−Si(10)	3.167(1) 3.179(6)	U(1)−Si(20)	3.195(1) 3.205(6)	U(1)−Si(30)	3.156(1) 3.143(6)
Si(10)−C(11)	1.908(2) 1.912(7)	Si(20)−C(21)	1.896(2) 1.901(7)	Si(30)−C(31)	1.905(2) 1.916(7)
Si(10)−C(12)	1.866(2) 1.849(7)	Si(10)−C(13)	1.869(2) 1.868(7)	Si(11)−C(14)	1.867(2) 1.869(7)
Si(11)−C(15)	1.864(3) 1.897(7)	Si(11)−C(16)	1.865(3) 1.861(8)	Si(20)−C(22)	1.853(3) 1.858(7)
Si(20)−C(23)	1.866(3) 1.856(7)	Si(21)−C(24)	1.863(2) 1.867(7)	Si(21)−C(25)	1.866(3) 1.855(7)
Si(21)−C(26)	1.860(3) 1.870(7)	Si(30)−C(32)	1.862(2) 1.868(7)	Si(30)−C(33)	1.858(2) 1.868(7)
Si(31)−C(34)	1.865(3) 1.849(8)	Si(31)−C(35)	1.868(2) 1.894(7)	Si(31)−C(36)	1.875(2) 1.872(7)
Si(10)−N(1)	1.768(2) 1.778(6)	Si(11)−N(1)	1.751(2) 1.735(6)	Si(20)−N(2)	1.746(2) 1.752(6)
Si(21)−N(2)	1.757(2) 1.751(6)	Si(30)−N(3)	1.743(2) 1.736(6)	Si(31)−N(3)	1.757(2) 1.764(7)
C(11)−B(1)	1.688(3) 1.688(6)	C(40)−B(1)	1.666(3) 1.639(6)	C(50)−B(1)	1.654(3) 1.664(6)
C(60)−B(1)	1.657(3) 1.640(6)				

[a] For each bond length, the first-row figures are based on X-ray and the second-row figures on neutron data.

second half of one of the C_6D_6 molecules is generated by a crystallographic center of inversion. The benzene molecules are packed in a complicated way, and there is no indication of disorder at 20 or 90 K. The anisotropic displacement parameters of the carbon atoms C80−C85 of the X-ray data indicate an in-plane libration of one of the benzene molecules which pivots near C81.[21] Due to this anisotropic vibration, which is no longer evident in the 20 K neutron structure, an unreasonably short C84−D840 bond length of 0.59(7) Å is found.[11]

X-ray Crystal Structure of [U{C(Ph)(NSiMe$_3$)$_2$}$_2${μ_3-BH$_4$}$_2$] (2). The structure of the compound [U{C(Ph)-

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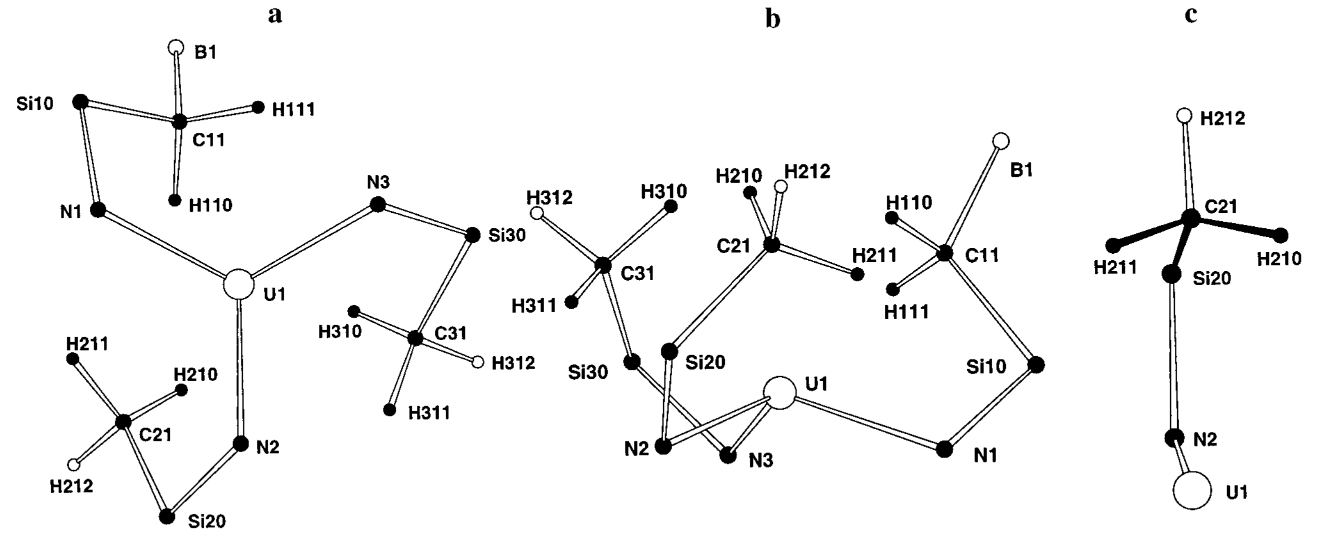

Figure 2. The coordination sphere around the uranium atom of **1** from different views (a, b). All black-colored atoms are bonded to the uranium atom by strong covalent (N) or weaker multicenter bonds (Si, C, H). The bonds of the coordinating Si−CH$_2$ entities cap the uranium atom like an umbrella as demonstrated in part c.

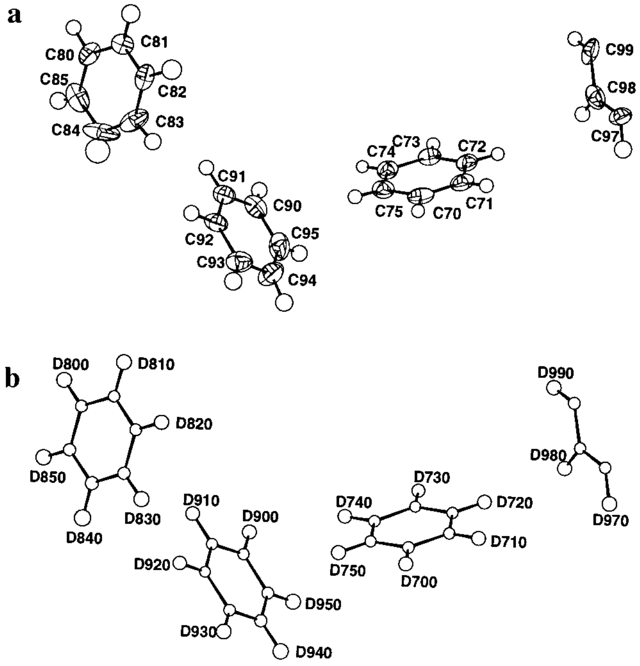

Figure 3. Structure of the 3.5 molecules of C$_6$D$_6$ per asymmetric unit included in crystals of compound **1** for (a) the X-ray (carbon atoms labeled) and (b) the neutron experiment (deuterium atoms labeled). Ellipsoids are drawn at 50% (C atoms of the X-ray experiment) and 20% probability (C atoms of the neutron experiment and all D atoms). The numbering scheme is the same for both structure determinations. The second half of the benzene molecule C97, C98, and C99 is generated by a crystallographic center of inversion.

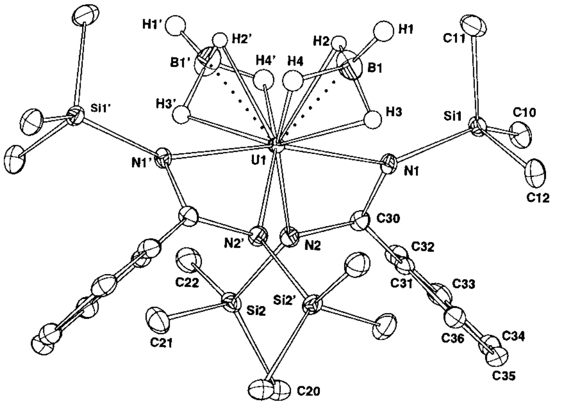

Figure 4. Structure of compound **2** in the crystal (boron-bonded H atoms at 20% probability; all other ellipsoids at 50% probability; phenyl and methyl H atoms omitted for clarity). The molecule exhibits crystallographic *C*$_2$ symmetry with the uranium atom lying on the *C*$_2$ axis.

(NSiMe$_3$)$_2$}$_2${μ_3-BH$_4$}$_2$] (**2**) has been determined by single-crystal X-ray diffraction (Table 1). Compound **2** crystallizes in space group *C*2/*c* with half a molecule per asymmetric unit and with the uranium atom lying on a crystallographic *C*$_2$ axis (Figure 4). Although occupying a special position, the uranium still contributes to the structure factors of all reflection classes.[22] The BH$_4$ moiety is bonded to the uranium atom as a tridentate ligand. Three hydrogen atoms are found in a bridging position with μ-H−B bond lengths of 1.08(2), 1.11(3), and 1.12(3) Å, μ-H−U bond lengths of 2.26(3), 2.27(3), and 2.31(3) Å, and U−μ-H−B angles of ca. 93.3(2), 91.9(2), and 89.4(2)°. The remaining hydrogen atom is terminally bonded to the boron atom [B−H1 = 1.10(3) Å], pointing directly away from the uranium atom [U−B−H1 = 176(2)°]. These values are comparable—after allowing for the artifactual shift of H atoms observed with X-rays—to those found in the neutron structure of [U(BH$_4$)$_4$] for the tridentately bound BH$_4$ groups with μ-H−B bond lengths of ca. 1.23(4) Å, μ-H−U bond lengths of ca. 2.34(2) Å, a U−μ-H−B angle of ca. 99(1)°, and a distance of 1.24(4) Å between uranium and the terminally bonded hydrogen atom.[23] The bidentate benzamidinato ligand exhibits two slightly different U−N bond lengths of U−N1 = 2.420(2) and U−N2 = 2.373(2) Å. The coordination geometry around the uranium atom can be described as strongly distorted octahedral with both N1 atoms on axial positions [N1−U−N1 = 166.4°] and both N2 atoms and BH$_4$ units occupying equatorial vertexes. [B1−U−N2 = 90.6°, N2−U1−N2 = 91.6°, B1−U1−B1 = 109.5°). The recorded data for the X-ray experiment are of high quality. All hydrogen atoms could be found in difference maps without difficulty and could be refined isotropically without the need

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Table 4. Selected Bond Angles (deg) for **1**[a]

Si(10)−C(11)−H(110)	110(2)	B(1)−C(11)−H(110)	110(2)
	110.8(5)		103.1(5)
Si(10)−C(11)−H(111)	110(2)	B(1)−C(11)−H(111)	105(2)
	108.7(5)		103.8(5)
H(110)−C(11)−H(111)	100(2)	Si(20)−C(21)−H(210)	121(2)
	109.8(7)		118.0(6)
Si(20)−C(21)−H(211)	117(2)	Si(20)−C(21)−H(212)	105(2)
	115.5(6)		106.5(6)
Si(30)−C(31)−H(310)	116(2)	Si(30)−C(31)−H(311)	114(2)
	115.7(6)		117.6(5)
Si(30)−C(31)−H(312)	101(2)	N(1)−U(1)−N(2)	110.11(7)
	105.2(5)		109.5(2)
N(1)−U(1)−N(3)	111.83(6)	N(2)−U(1)−N(3)	109.68(6)
	111.8(1)		109.9(1)
N(1)−Si(10)−C(11)	103.96(8)	N(1)−Si(10)−C(12)	109.73(9)
	104.0(3)		109.7(3)
N(1)−Si(10)−C(13)	112.1(1)	N(1)−Si(11)−C(14)	110.2(1)
	111.3(3)		110.4(3)
N(1)−Si(11)−C(15)	110.4(1)	N(1)−Si(11)−C(16)	112.3(1)
	110.6(3)		113.5(4)
N(2)−Si(20)−C(21)	104.82(9)	N(2)−Si(20)−C(22)	114.9(1)
	104.9(3)		114.7(3)
N(2)−Si(20)−C(23)	113.1(1)	N(2)−Si(21)−C(24)	109.63(9)
	113.2(3)		109.8(4)
N(2)−Si(21)−C(25)	110.8(1)	N(2)−Si(21)−C(26)	110.7(1)
	111.7(4)		110.5(4)
N(3)−Si(30)−C(31)	105.9(1)	N(3)−Si(30)−C(32)	114.2(1)
	106.1(3)		114.0(3)
N(3)−Si(30)−C(33)	113.66(9)	N(3)−Si(31)−C(34)	109.3(1)
	114.7(4)		111.3(4)
N(3)−Si(31)−C(35)	108.6(1)	N(3)−Si(31)−C(36)	112.4(1)
	108.1(4)		112.4(4)
U(1)−N(1)−Si(10)	105.99(8)	U(1)−N(1)−Si(11)	131.15(9)
	105.8(2)		131.8(2)
U(1)−N(2)−Si(20)	107.75(8)	U(1)−N(2)−Si(21)	130.65(9)
	107.9(2)		130.2(3)
U(1)−N(3)−Si(30)	105.17(8)	U(1)−N(3)−Si(31)	131.4(1)
	105.2(2)		131.1(2)
Si(10)−N(1)−Si(11)	122.5(1)	Si(20)−N(2)−Si(21)	120.84(9)
	122.2(3)		121.0(3)
Si(30)−N(3)−SI(31)	123.3(1)	C(75)−C(70)−D(700)	120(2)
	123.5(3)		119.8(4)
C(70)−C(71)−D(710)	121(2)	C(71)−C(72)−D(720)	118(2)
	120.6(4)		119.4(4)
C(72)−C(73)−D(730)	119(2)	C(73)−C(74)−D(740)	120(2)
	119.4(4)		119.7(4)
C(75)−C(74)−D(740)	120(2)	C(74)−C(75)−D(750)	119(2)
	119.5(4)		120.6(4)

[a] For each angle, the first-row figures are based on X-ray and the second-row figures on neutron data.

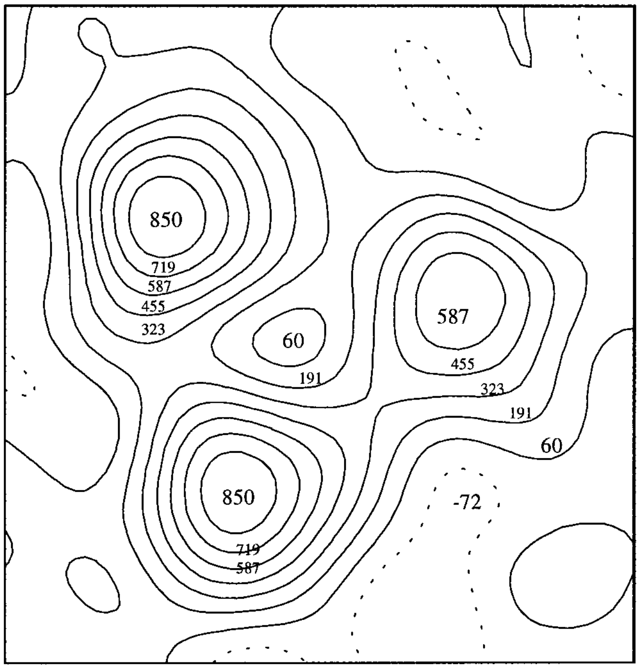

Figure 5. Contour map from a difference Fourier synthesis of a plane which passes through the positions of the hydrogen atoms H2, H3, and H4 of compound **2** after removing H2, H3, and H4 and fully refining the remaining structure fragment. Numbers are differences of electron density (0.001 e Å^{-3}).

for restraints. To confirm the location of the refined hydrogen atom positions in **2**, the bridging hydrogen atoms H2, H3, and H4 were removed and complete, unbiased full refinement on the remaining structure fragment **2′** was performed. Figure 5 shows a contour map from a difference Fourier synthesis of a section of **2′** which contains the positions of H2, H3, and H4 of **2**.[24] The missing hydrogen atoms are clearly recognizable as well-shaped maxima. These three maxima are among the four highest peaks in a difference map over the whole asymmetric unit and are thus very easy to find. A comparison of *R* factors and the residual electron densities of structure **2′** ($R = 0.019$, $R_w = 0.021$, $\Delta\rho_{min} = -1.33$ e Å^{-3}, $\Delta\rho_{max} = 0.91$ e Å^{-3}) and **2** ($R = 0.017$, $R_w = 0.019$, $\Delta\rho_{min} = -1.32$ e Å^{-3}, $\Delta\rho_{max} = 0.89$ e Å^{-3}) reveals no significant differences. In **2** and **2′** the lowest minima in the negative electron density in the difference maps are found in a ripple around the U atom at a distance of around 0.8 Å and one ripple of positive residual electron density at a distance of approximately 1.3 Å from the uranium atom. As already shown for compound **1**, these ripples, caused by insufficient compensation of series termination errors, determine the magnitude of the minimum and maximum residual electron density in final difference maps. Unambiguous determination of the bridging hydrogen atoms at a distance of 2.3 Å from the uranium atom is possible because at this distance the effects of badly compensated termination errors are negligible.

Conclusions

In this work we have shown that it is possible to find hydrogen positions in uranium-containing molecular compounds by single-crystal X-ray diffraction, including those hydrogen atoms directly coordinating the uranium. Such hydrogen locations are widely considered to be unreliable due to the comparatively small scattering factor of hydrogen. Series termination errors in Fourier maps further complicate the location of hydrogen atoms in close proximity to heavy atoms. To overcome these physical limitations, four crucial conditions must be met: First, the crystals used for the X-ray diffraction experiment must be of good "crystallographic" quality, i.e., exhibit a not too large mosaicity and have the right size and shape (e.g., nearly spherical) to give sharp reflections which do not suffer from large anisotropic absorption and spot shape effects. Second, the data set has to be recorded at low temperature, to reduce the effects of dynamic processes and prevent crystal decay during the X-ray exposure. Third, an X-ray diffractometer is needed which is able to determine the reflection intensity with very high accuracy because in crystal structures where the heavy atoms contribute intensity to all reflections the positions of hydrogen atoms are determined by very small contributions to the reflection intensities. For this study an image plate diffractometer was used. The image plate technology is able to supply data of sufficiently high quality because of the high dynamic range of the image plates, the possibility of rapid data collection, and the restricted motion of the crystal in the cold stream. Fourth, chemical knowledge

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(24) Leech, M. A. *Fourier-Viewer*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1997.

about the expected number and position of the hydrogen atoms is needed to some extent. In the case of compound **1**, the X-ray data could only suggest but not prove the absence of uranium-bonded hydrogen atoms whereas, for compound **2**, the location of the boron-bonded hydrogen atoms was easily possible on the basis of detailed chemical knowledge of the exact composition of **2**. Clearly, neutron diffraction experiments are necessary for the reliable determination of hydrogen atom positions in many cases. The intention of this paper is to show that once the structure of a compound has been determined by neutron diffraction, X-ray diffraction experiments can then be used to determine hydrogen positions for related compounds, albeit with lower accuracy.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of pure argon or in an inert-atmosphere box under nitrogen. Standard Schlenk-line techniques were used throughout. All solvents were dried and distilled prior to use, and all chemicals were used as supplied by Aldrich Chemical Co. Infrared spectra were recorded on a 6020 Galaxy series FT-IR instrument. NMR spectra were recorded on a Varian Unity 500 spectrometer, referenced to TMS. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory in Oxford.

[U{N(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)(SiMe$_2$CH$_2$B(C$_6$F$_5$)$_3$)}] (1). To a stirred solution of 0.72 g (1.0 mmol) of [U{N(SiMe$_3$)$_2$}$_3$(H)][4] (**3**) in 20 mL of pentane at 25 °C was added a solution of 0.51 g (1.0 mmol) of B(C$_6$F$_5$)$_3$[25] in 30 mL of pentane. Upon addition, the color changed immediately from dark brown to pale yellow along with the formation of a precipitate. No gas evolution was observed. The reaction mixture was stirred for 1 h, and the volatiles were removed under reduced pressure. After trituration with pentane at 0 °C, the yellow powder was washed with two portions of 20 mL of pentane (0 °C) and then dried. Yield: 0.98 g (0.8 mmol), 80%. Anal. Calcd for $C_{36}H_{53}BF_{15}N_3Si_6U$: C, 35.1; H, 4.4; N, 3.4; B, 0.9; U, 19.3. Found: C, 34.7; H, 4.4; N, 3.2; B, 0.8; U, 19.5. IR (CsI, cm^{-1}): 2960 (w), 1641 (w), 1514 (s), 1460 (vs), 1257 (s), 976 (s), 844 (vs), 611 (m). ^{1}H NMR (500 MHz, toluene-d_8, −30 °C): $\delta = 30, 20, 9, 0, -10, -19, -22$ ppm; all signals broad.

[U{C(Ph)(NSiMe$_3$)$_2$}$_2${μ_3-BH$_4$}$_2$] (2). To a stirred solution of 0.84 g (1.0 mmol) of [U{C(Ph)(NSiMe$_3$)$_2$}$_2$(Cl)$_2$][26] (**6**) in 30 mL of 1,2-dimethoxyethane was added a slight excess of NaBH$_4$ (0.10 g, 2.5 mmol). The reaction mixture was stirred for 36 h to produce a light green solution. Volatiles were removed under reduced pressure, and the green residue was extracted with 40 mL of toluene. After removal of the NaCl by filtration, the solvent was evaporated to dryness and the green crystalline product was washed twice with 20 mL portions of pentane and then dried. Yield: 0.60 g (0.8 mmol), 75%. Anal. Calcd for $C_{26}H_{54}B_2N_4Si_4U$: C, 39.3; H, 6.9; N, 7.1; B, 2.7. Found: C, 39.4; H, 7.1; N, 7.2; B, 2.6. IR (CsI, cm^{-1}): 2960 (w), 2509 (w), 2139 (w), 1402 (s), 1251 (s), 1186 (w), 976 (s), 850 (vs), 763 (s), 705 (s). ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): $\delta = 32.7$ (m, 8H, BH$_4$), 10.4 (s, 4H, C$_6$H$_5$), 8.6 (s, 4H, C$_6$H$_5$), 8.0 (s, 2H, C$_6$H$_5$), 0.31 (s, 36H, SiMe$_3$) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): $\delta = 158$ (C$_6$H$_5$), 132.6 (C$_6$H$_5$), 128.7 (C$_6$H$_5$), 125.6 (s, C$_6$H$_5$), 2.8 (s, SiMe$_3$) ppm. ^{11}B NMR (160 MHz, C$_6$D$_6$): $\delta = -45$ (s, BH$_4$) ppm.

X-ray Crystallographic Studies. Single crystals of compound **1** suitable for X-ray diffraction were grown from a concentrated solution in deuterated benzene at room temperature by slowly cooling to 3 °C. Single crystals of compound **2** were obtained from a concentrated solution in diethyl ether by slow cooling to −30 °C. The crystals used for the diffraction studies were taken out of the mother liquid just before the experiment and immersed in highly viscous perfluoropolyether under argon to prevent loss of solvent and to exclude oxygen. To minimize absorption effects, the crystals were cut to approximately cubic shape,-(0.4 × 0.4 × 0.5 mm for **1** and 0.2 × 0.2 × 0.2 mm for **2**). They were mounted on glass fibers and placed in a cold stream of nitrogen (90 K). Crystals of **1** tended to crack during cooling, but eventually a crystal was found which survived without damage. The data were collected on an Enraf Nonius DIP2020 image plate diffractometer with graphite-monochromated Mo Kα radiation (50 kV, 35 mA) using a 0.9 mm collimator. A distance of 75 mm between the image plate and the crystal was chosen. Eighty-five frames for **1** and 90 frames for **2** with a rotation angle of 2° were recorded in 2° steps to cover an overall rotation of 170 and 180°. All rotations were performed around the ω axis perpendicular to the direction of the X-ray beam ($\kappa = 0°$, $n = 0°$). The exposure time for each frame was 900 s recorded at a speed of 0.4° min^{-1} and three repetitions. The images were processed with the DENZO and SCALEPACK software[27] in space groups *P*1 and *C*2 for **1** and **2**, respectively. Corrections for Lorentz and polarization effects were performed. A total of 12 827 independent reflections were measured for **1** ($\theta_{\max} = 26.7°$) and 3572 intensities were collected for **2** ($\theta_{\max} = 26.7°$). Of these, there are 12 188 and 3490 unique reflections with $I > 2\sigma(I)$ which were used in the solution and refinement of 1045 and 276 parameters, respectively. All further crystallographic calculations were carried out using the CRYSTALS program package.[28] The crystal structures were solved by direct methods[29] and refined without any restraints by the full-matrix least-squares method against *F*. In both structure determinations, all hydrogen and deuterium atoms were easily located in difference Fourier maps and refined isotropically. All other atoms were refined anisotropically without any restraints. Final difference Fourier syntheses showed peak heights up to 1.10−1.72 e Å^{-3} for **1** and 0.89−1.32 e Å^{-3} for **2**. Further details are summarized in Table 1. The CAMERON program was used to produce all crystallographic figures.[30]

Neutron Crystallograhic Studies. Large single crystals of compound **1** were obtained from C$_6$D$_6$ as follows: Typically a saturated solution was prepared at room temperature. The solution was filtered and slowly cooled over several days to 3 °C. This yielded crystals with volumes not greater than 0.5 mm^3, which were used as seeds, if single, in a fresh solution. By repetition of this procedure, five crystals were grown with volumes up to 6 mm^3. These were carefully stored separately in mother liquor at 15 °C for up to 3 months without decomposition. The crystal used for the neutron diffraction experiment was sealed in a glass capillary. It was held in position by glass wool. Toward the mounting end of the glass capillary, the glass wool was soaked with mother liquid in order to prevent solvent loss from the crystal. The tube was glued to an Al pin and sealed in a Displex cryorefrigerator[31] on the thermal-beam instrument D19 at ILL equipped with a 4° × 64° position-sensitive detector.[32] The crystal was cooled at 0.6 °C/min while the strong −1,2,0 reflection was monitored. An increase in mosaic was observed. Because of the relatively weak diffraction and large unit cell, the rather long wavelength 1.539 Å was chosen for maximum intensity. The reflections to a 2θ value of 50° were then measured with ω scans in equatorial geometry, and higher angle data to 55.7° were recorded with normal-beam geometry (ILL programs Hklgen and Mad). The unit cell dimensions were calculated from 1519 strong reflections at 1.5394(2) Å (ILL program Rafd19). Bragg intensities were integrated in 3-D using the ILL program

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Retreat.[33] These 5401 independent intensities were corrected for attenuation by the cylindrical heat shields and by the crystal itself with the program D19abs, based on the ILL version of the CCSL system.[34] The positions of the atoms obtained from the X-ray diffraction experiment were used as the starting model for the full-matrix least-squares refinement against F using CRYSTALS. After extensive tests refining various sets of parameters, the H, B, N, and U atoms were included in the refinement with anisotropic displacement parameters. All other atoms were refined with isotropic displacement parameters in order to keep the ratio of observations to refined parameters to an acceptable level (4596 unique reflections with $I > 2\sigma(I)$ for the refinement of 919 parameters). A final difference Fourier synthesis showed peak heights up to 0.93−1.02 e Å^{-3}. Further details are summarized in Table 1. The CAMERON program was used to produce all crystallographic figures.[28]

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Supporting Information Available: Crystallographic files, in CIF format, for the structure determinations of [U{N(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)(SiMe$_2$CH$_2$B(C$_6$F$_5$)$_3$)}] (X-ray), [U{N(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)(SiMe$_2$CH$_2$B(C$_6$F$_5$)$_3$)}] (neutron), and [U{C(Ph)(NSiMe$_3$)$_2$}$_2${μ_3-BH$_4$}$_2$] are available on the Internet only. Access information is given on any current masthead page.

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