SYNTHESIS AND CRYSTAL STRUCTURE OF TRICYCLOPENTADIENYL(CYCLOOCTANE-1,5-DIYL)-URANIUM DIHYDROBORATE

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Summary

Cp_3UCl reacts with Na(HBBN) (BBN = 9-borabicyclo(3.3.1.)nonane) in THF solution to give $Cp_3U(HBBN)$, which is the first complex having a $(BBNH^-)$ ligand attached to a d or f transition metal. The IR spectrum and the X-ray crystal structure show that the boron hydride ligand is coordinated to the uranium through two hydrogen bridges. The geometry around the uranium atom is pseudo-tetrahedral if the η^5-cyclopentadienyl ligand centroids and the boron atom are regarded as vertices.

Coordination of the boron hydride ligands to transition metals gives rise both to bidentate and tridentate structural geometries in which the boron atom is connected to the metal center through two (form **A**) or three (form **B**) bridging hydrogen atoms

(A)   (B)

[1]. The mode of ligation mainly depends on the metal radius and on the steric demands of the other ligands in the molecule. Thus bidentate structures are usually found for d-transition metals, whereas with the larger $5f$-actinide metals boron tridentate coordination is usual [2]. The coordination mode appears to affect the BH_4–M bond strength, since BH_3 removal by Lewis bases has been observed only for d-transition metals (e.g. M = Zr and Hf [3]), and not for M = $5f$ metals (U or

Th). Monosubstituted hydroborate ligands, BH_3R^- (R = alkyl or phenyl group), show the same bonding features as BH_4^- [4,12] when coordinated to actinide ions. Our interest in this field of chemistry led us to investigate the possible formation and the structural properties of species, such as $Cp_3UH_2BR_2$, in which two hydrogen atoms of the BH_4^- anion are replaced by alkyl or phenyl groups. $BH_2R_2^-$ anions are generally unstable, undergoing the following disproportionation [5]:

$$2BH_2R_2^- \rightleftarrows BHR_3^- + BH_3R^-$$

Because of this a type of $BH_2R_2^-$ anion with BHR_2 = 9-borabicyclo(3.3.1)nonane (BBN), which forms stable alkaline M(HBBN) salt (M = Li, Na, K) [6], was
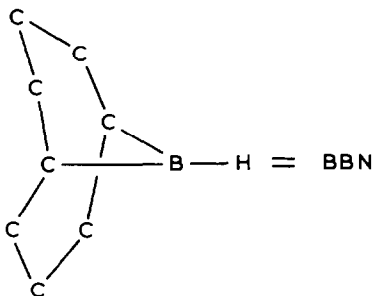
employed in the present study. We describe here the synthesis, spectroscopic properties, and X-ray structural characterization of the complex $Cp_3U(HBBN)$ $(Cp = \eta^5\text{-}C_5H_5)$, which is, to our knowledge, the first complex with a $(HBBN^-)$ ligand attached to a d or f transition metal.

Experimental

All operations were carried out in glove boxes filled with purified nitrogen. Solvents were dried and purified by standard procedures [7].

(9-BBN)$_2$ (Janssen) was used without further purification. UCl_4, TlCp, Cp_3UCl were prepared as described elsewhere [8]. The ^1H and ^{11}B NMR spectra were recorded with a Varian FT80A spectrophotometer; the ^1H chemical shifts are relative to C_6D_5H as internal standard, and the ^{11}B chemical shifts to $BF_3 \cdot OEt_2$ as external standard. Infrared spectra were recorded with a Perkin–Elmer 580B apparatus using Nujol mulls sandwiched between KBr plates in a sealed air-tight O-holders. UV-NIR VIS spectra were recorded with a Cary 17D spectrometer. Elemental analyses were carried out by Dornis U. Kolbe Mikroanalytisches Laboratorium, Mülheim (F.R.G.).

Synthesis of Cp$_3$U(HBBN)

Freshly prepared Na(HBBN) (145 mg, 1 mmole) [6] was added to 468 mg of Cp_3UCl (1 mmole) in 20 ml THF. After 3 h stirring at room temperature the solvent was removed under vacuum and the residue was extracted with toluene. After filtration of the extract (to remove white solid, presumably NaCl, formed during the reaction), the toluene was removed in vacuum to leave a red-brown powder (yield 80%). Anal. Found: C, 49.58; H, 5.52; B, 2.07. $C_{23}H_{31}BU$ calc: C, 49.64; H, 5.57; B,

1.97%. ^{1}H NMR: (T 27°C, δ in ppm) 14.29 (s, 15H), 13.26 (2H), 16.23 (2H), 50.29 (2H), 17.61 (4H), 20.90 (4H), -55 (2H). ^{11}B NMR: (T 27°C, δ in ppm) -55.16 (b); 51°C -53.95 (bt). The product sublimes at 200°C, 10^{-4} mmHg.

Crystal data

Crystals suitable for X-ray determination were obtained by slow evaporation of a toluene solution inside a glove box. Data were collected at room temperature from a crystal mounted on a single-crystal four-circle diffractometer in a random orientation. Crystal data and details of the parameters associated with data collection and structure refinement are given in Table 1. The reduced cell quoted was obtained by use of TRACER [9]. For intensities and background the "three-point" technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections [10] and the absolute scale was established by the Wilson method [11]. Scans showed that crystal absorption effects could not be neglected, and an absorption correction was then applied [12], with maximum and minimum corrections of 1.498 and 1.003. The function minimized during the least-squares refinement was $\Sigma w \, | \Delta(F) |^{2}$. Unit weights were applied since these gave acceptable agreement analyses. Anomalous scattering corrections were included in all structure

TABLE 1

EXPERIMENTAL DETAILS FOR THE X-RAY DIFFRACTION STUDIES ON COMPLEX I.

Formula	$C_{23}H_{31}BU$
M	556.3
Crystal habit	red-brown, irregular thick prisms
Crystal system	orthorhombic
Reflection conditions	$h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$
Space group	$P2_12_12_1$
T (°C) ^{a}	22
a (Å)	20.682(4)
b (Å)	20.284(3)
c (Å)	9.597(4)
V (Å^{3})	4026(2)
Z	8
D_{c} (g cm^{-3})	1.836
Crystal size (mm)	$0.35 \times 0.42 \times 0.50$
μ (cm^{-1})	76.5
Diffractometer	Phillips PW 1100
Radiation	graphite-monochromatized Mo-K_{α} ($\lambda = 0.7107$ Å)
2θ range (°)	6–47
Reflcns measd	$\pm h, k, l$
Unique reflections	6105
Criterion for obsn	$I > 3\sigma(I)$
Unique obsd data	4002
No. of variables	157
Overdetermination ratio	25.5
Max shift/error on last cycle	0.3
$R = \Sigma \| F_{o} | - | F_{c} \| / \Sigma | F_{o} |$	0.054
$R_{w} = [\Sigma w \| F_{o} | - | F_{c} \|^{2} / \Sigma w | F_{o} |^{2}]^{1/2}$	0.062

^{a} Unit cell parameters were obtained by least-squares analysis of the setting angles of 20 carefully centered reflections chosen from diverse regions of reciprocal space.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$)

Molecule A				Molecule B		
Atom	x	y	z	x	y	z
U(1)	1052(1)	608(1)	1466(1)	2839(1)	6536(1)	1725(1)
C(1)	−233(9)	555(8)	695(19)	2536(14)	7817(13)	2438(24)
C(2)	−149(9)	1210(8)	1187(19)	3152(14)	7862(13)	1793(24)
C(3)	261(9)	1546(8)	237(19)	3612(14)	7559(13)	2688(24)
C(4)	430(9)	1099(8)	−843(19)	3279(14)	7327(13)	3885(24)
C(5)	124(9)	487(8)	−559(19)	2614(14)	7486(13)	3731(24)
C(6)	1932(13)	−396(11)	966(25)	1924(7)	5572(10)	2388(22)
C(7)	2292(13)	199(11)	934(25)	2530(7)	5242(10)	2351(22)
C(8)	2098(13)	562(11)	−261(25)	2908(7)	5477(10)	3481(22)
C(9)	1618(13)	190(11)	−968(25)	2537(7)	5952(10)	4216(22)
C(10)	1515(13)	−402(11)	−210(25)	1929(7)	6011(10)	3541(22)
C(11)	958(9)	1709(10)	3123(25)	3904(12)	6719(9)	−21(25)
C(12)	1489(9)	1864(10)	2245(25)	4130(12)	6309(9)	1075(25)
C(13)	2007(9)	1435(10)	2592(25)	3818(12)	5689(9)	954(25)
C(14)	1796(9)	1014(10)	3683(25)	3399(12)	5715(9)	−217(25)
C(15)	1147(9)	1183(10)	4011(25)	3453(12)	6352(9)	−820(25)
B(1)	611(15)	−461(15)	300(32)	1775(20)	6722(20)	3(43)
C(16)	783(17)	−1241(17)	3277(44)	1009(14)	6525(15)	−196(26)
C(17)	140(16)	−1609(17)	2958(34)	608(16)	7149(17)	−22(35)
C(18)	−436(17)	−1386(18)	3819(38)	819(20)	7726(20)	−957(40)
C(19)	−525(16)	−640(19)	3729(37)	1515(17)	7842(17)	−1023(35)
C(20)	78(19)	−267(18)	4152(39)	1933(18)	7257(19)	−1149(40)
C(21)	357(18)	−366(19)	5616(40)	1884(17)	6894(17)	−2585(38)
C(22)	665(20)	−1001(20)	5872(42)	1273(23)	6538(27)	−2749(49)
C(23)	1027(24)	−1317(22)	4673(48)	972(16)	6161(15)	−1566(40)

factor calculations [13]. Scattering factors for neutral atoms were taken from ref. 13a for non-hydrogen atoms and from ref. 14 for H. For the low-angle reflections no correction for secondary extinction was deemed necessary.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was by full-matrix least-squares, first isotropically, then anisotropically for the two independent uranium atoms. During the refinement the cyclopentadienyl rings were constrained to be regular pentagons. Solution and refinement were based on the observed reflections. The hydrogen atoms were fixed in calculated positions (C–H = 1.08 Å, B–H = 1.20 Å) and introduced in refinement as fixed contributors (U_{iso} = 0.10 Å). Since the space group is polar, the chirality of the crystal was examined by inverting all the coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence once again. The resulting R values (R = 0.059, R_w = 0.068) indicated the previous choice to be correct. In the final difference map there were no peaks above the general background. Final atomic fractional coordinates and thermal parameters are quoted in Table 2.

Reaction of Na(HBBN) with "Cp₂UCl₂"

A mixture of 380 mg of UCl_4 (1 mmol) and TlCp 538 mg (2 mmol) in 20 ml THF was stirred for about 2 h, then filtered, and Na(HBBN) (2 mmol) was added to the filtrate. After ca. 5 h stirring at room temperature, ^1H and ^{11}B spectra of the

solution showed the signals due to Cp$_3$U(HBBN) together with others which were not assigned.

Results and discussion

The room temperature reaction of Na(HBBN) with Cp$_3$UCl in THF led cleanly to Cp$_3$U(HBBN):

$$Cp_3UCl + Na(HBBN) \rightarrow Cp_3U(HBBN) + NaCl$$
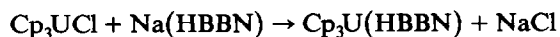
The same reaction between a UCl$_4$/TlCp mixture (1:2 molar ratio), however, produced a solution which showed ^{1}H and ^{11}B NMR signals corresponding to Cp$_3$U(HBBN) and other unassignable peaks.

Cp$_3$U(HBBN) is a thermally stable red brown moderately volatile powder, which is sparingly soluble in THF, benzene, and toluene and insoluble in aliphatic hydrocarbons. It is quite sensitive to oxygen and moisture. Elemental and X-ray crystallographic analyses correspond to the proposed formula C$_{23}$H$_{31}$BU. The infrared spectrum, recorded with a Nujol mull in the range 4000–300 cm^{-1}, shows the bands typical of the Cp groups (1010 and 795 cm^{-1}) as well as strong absorptions at 2030 cm^{-1} and 1280 cm^{-1}; using the criteria established by Marks [15], these bands can be assigned to the B–H$_{bridging}$ stretching for bidentate ligation and to the (BH$_2$)$_b$ deformation modes, respectively; the BH$_2$ deformation would normally be in the range 1100–1200 cm^{-1}; and the wavenumber shift to higher wavenumbers is probably a result of the replacement of two terminal hydrogen atoms by the cyclooctane ring; similar features have been observed for the following tridentate monosubstituted species: Cp$_3$UBH$_4$ (1160 cm^{-1}) and Cp$_3$UBH$_3$Et [4] (1215 cm^{-1}) and U(BH$_4$)$_4$ [16], (1230 cm^{-1}) or (1240 cm^{-1}) [17], and U(BH$_3$CH$_3$)$_4$ [18] (1270 cm^{-1}). Absorptions characteristic of B–H$_{terminal}$ are, of course, absent. Thus from the infrared data it can be inferred that the boron-hydride ligand is coordinated to the uranium atom through two hydrogen bridges.

The ^{1}H NMR spectrum of Cp$_3$U(HBBN) in C$_6$D$_6$ is typical of paramagnetic organometallic uranium compounds with large isotropic shifts [19], and shows all the signals from the various protons, although no unequivocal assignment was possible. Except for a sharp singlet assigned to the Cp protons, the signals are broad singlets, and no clear multiplicity could be observed in double resonance experiments. The signal at −55 ppm, broader (300 Hz) than the others, was assigned to the bridging H because of its anomalous position and the fact that its width corresponds with the sum of the single H–B coupling constants (85–90 Hz). As demonstrated by the IR data and structural analysis (vide infra), the (HBBN)$^-$ group is η^2-bonded to Cp$_3$U moiety, in contrast to the situation in the Cp$_3$UBH$_4$ compound in which the boron hydride is trihapto bonded, so it might at first sight be suggested that the H$_{Cp}$ resonance is at lower field than in Cp$_3$UBH$_4$. Actually the chemical shift for the Cp protons is almost the same as that for Cp$_3$UBH$_4$ (7 ppm upfield from TMS with respect to 6.3 for Cp$_3$UBH$_4$), and this is in accord with the observations by Marks et al. [1,4] that bi- and tri-dentate hydroborate groups share the same number of bonding electron pairs with the metal since the electron density on the metal will be the same for Cp$_3$U(HBBN) and Cp$_3$UBH$_4$, it is reasonable that there should be no appreciable decrease in the shift [20–22]. On the other hand, the shift for H$_{bridging}$ is very different from that for Cp$_3$UBH$_4$ (−55 ppm for
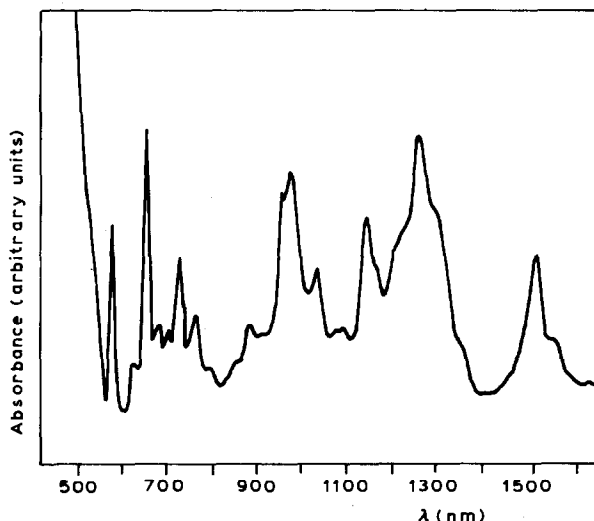
Fig. 1. VIS-NIR spectrum of $(\eta^5\text{-}C_5H_5)_3U(HBBN)$.

Cp$_3$U(HBBN), and 60 ppm for Cp$_3$UBH$_4$) and no [11]B–[1]H coupling could be observed clearly. With our compound the signal is broad, and becomes narrower when the sample is warmed to 50–55°C. Correspondingly, the ^{11}B NMR spectrum shows no coupling with H-bridging at room temperature but at about 50°C it resembles a broad triplet. Unfortunately, because of the low solubility of Cp$_3$U(HBBN) in the solvents used, spectra could not be recorded at low temperature, and it is not clear if, since the molecule is not fluxional, the broadening of the signals is due to magnetic effects. Figure 1 shows the spectrum in the visible and near IR; in the range 500–1600 nm it closely resembles that of Cp$_3$UBH$_4$, and displays broader absorptions than other Cp$_3$UX compounds [20] probably owing to overlap of several bands.

The structure of the Cp$_3$U(HBBN) complex is shown in Fig. 2.

It consists of two crystallographically independent monomeric $(\eta^5\text{-}C_5H_5)_3$-U(HBBN) molecules (A and B) related to each other by a noncrystallographic mirror plane. Their structural parameters are not significantly different within the experimental errors. The geometry around the uranium atoms is as usual for Cp$_3$UX systems in a pseudo-tetrahedral arrangement in which the η^5-bonded cyclopentadienyl ligand centroids (Cp) and the boron atoms form the vertices.

The Cp–U–Cp angles are larger than the tetrahedral value, averaging 115(1)° for both molecules, while the B–U–Cp angles are lower, and are significantly different from each other (Table 3). They are consistent with those observed in other Cp$_3$UX systems [23–25], and reflect the marked rigidity of the Cp$_3$U unit, which retains its geometry whatever the nature of X.

The U–C distances fall in the rather narrow range 2.73(3)–2.79(2) Å for molecule A and 2.71 (2)–2.81(2) Å for molecule B. The average values are 2.76(1) Å for the three Cp rings (molecule A), 2.771(1) for Cp(1) and Cp(3), 2.76(1) for Cp(2) (molecule B). They are in good agreement with those observed in $(\eta^5$-C$_5$H$_5)_3$UCHP(CH$_3$)$_2$(C$_6$H$_5$) [23] where the lengthening with respect to distance found in other Cp$_3$U systems [24,25] is caused by steric crowding.
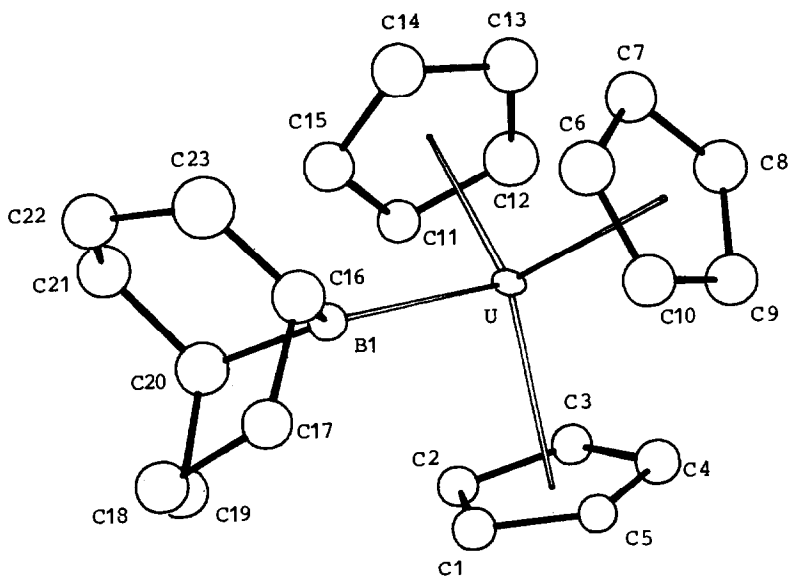
Fig. 2. An ORTEP drawing of the $(\eta^5\text{-}C_5H_5)_3U(HBBN)$ complex (molecule A).

The U–B distances (2.78(3) and 2.78(4) Å for **A** and **B**, respectively) are longer than that in $U(BH_4)_4$ [26] (2.52(1) Å), in which the BH_4 groups forms three B–H $\cdots$ U bridge bonds, but are close to the values observed when these groups provide two hydrogen atoms to the coordination polyhedron of the uranium atom. This, along with the positions of the hydrogen atoms, suggests the same anchoring mode for (HBBN). In fact, although the hydrogen atoms could not be directly located, their tetrahedrally idealized positions are at 2.45 and 2.17 Å for molecule **A**, and 2.45 and 2.21 Å for molecule **B** from uranium. These values are in agreement with those observed in $U(BH_4)_4$, and the apparent asymmetry is consistent with steric crowding of the Cp_3U unit. The 9-borabicyclo(3.3.1)nonane skeleton shows a slightly flattened twin chair conformation similar to that in the 9-BBN dimer and in bicyclo(3.3.1)nonane [27]. The flattening is indicated by the increase in the C(17)–C(16)–C(23) and C(19)–C(20)–C(21) angles above the tetrahedral value (Table 3) and by the distances of boron and C(18) from the C(16),C(17),C(19),C(20) plane (0.88(3), −0.64(4) Å, respectively, for molecule A; −0.78(4), 0.50(4) Å for molecule **B**), and of boron and C(22) from the C(16),C(20),C(21),C(23) plane (0.80(3), −0.39(4) Å, respectively for molecule **A**; −0.86(4), 0.44(5) Å for molecule **B**). This could be due to some repulsion between C(18) and C(22), which are at intermolecular distances of 3.11(5) Å (for both molecules) that are less than the sum of Van der Waals radii. The data clearly show that stable double hydrogen bridged complexes can be formed between Cp_3U^+ cation and a disubstituted hydroborate substituted anion as well with the tridentate anions. The $Cp_3U(HBBN)$ complex shows the characteristic chemico-physical properties of common organometallic tetrahydroborate uranium complexes, namely molecularity, volatility, thermal stability, and resistance to BBN abstraction by Lewis bases [28]. Some distortions of the B–C, C–C bonds and related bond angles in the geometry of the BBN structure of $Cp_3U(HBBN)$ with respect to the BBN dimer are probably due to the replacement

TABLE 3

BOND LENGTHS (Å) AND SELECTED BOND ANGLES (deg) FOR [(η^5-C$_5$H$_5$)$_3$U(HBBN)]

	Mol. A	Mol. B		Mol. A	Mol. B
U(1)–B(1)	2.78(3)	2.78(4)	U(1)–C(11)	2.75(2)	2.79(2)
U(1)–C(1)	2.76(2)	2.76(3)	U(1)–C(12)	2.80(2)	2.78(2)
U(1)–C(2)	2.78(2)	2.77(3)	U(1)–C(13)	2.81(2)	2.76(2)
U(1)–C(3)	2.77(2)	2.78(3)	U(1)–C(14)	2.75(2)	2.75(2)
U(1)–C(4)	2.75(2)	2.77(2)	U(1)–C(15)	2.71(2)	2.78(2)
U(1)–C(5)	2.74(2)	2.76(2)	U(1)–Cp(1) [a]	2.48(2)	2.49(3)
U(1)–C(6)	2.77(2)	2.79(2)	U(1)–Cp(2)	2.47(2)	2.48(2)
U(1)–C(7)	2.74(3)	2.77(2)	U(1)–Cp(3)	2.49(2)	2.50(2)
U(1)–C(8)	2.73(3)	2.73(2)	U(1)–H(1B)	2.45	2.45
U(1)–C(9)	2.75(2)	2.74(2)	U(1)–H(2B)	2.18	2.21
U(1)–C(10)	2.78(2)	2.78(2)			
B(1)–C(16)	1.64(5)	1.65(5)	C(18)–C(19)	1.53(5)	1.46(5)
B(1)–C(20)	1.61(5)	1.58(6)	C(19)–C(20)	1.51(5)	1.47(5)
C(16)–C(17)	1.56(5)	1.52(5)	C(20)–C(21)	1.53(5)	1.56(5)
C(16)–C(23)	1.44(6)	1.51(5)	C(21)–C(22)	1.46(6)	1.46(6)
C(17)–C(18)	1.52(5)	1.54(5)	C(22)–C(23)	1.52(6)	1.50(6)
B(1)–U(1)–Cp(1)	104(2)	106(2)	C(16)–C(17)–C(18)	115(3)	114(3)
B(1)–U(1)–Cp(2)	98(2)	97(2)	C(17)–C(18)–C(19)	111(3)	115(3)
B(1)–U(1)–Cp(3)	108(2)	107(2)	C(18)–C(19)–C(20)	112(3)	117(3)
Cp(1)–U(1)–Cp(2)	116(1)	116(1)	C(19)–C(20)–C(21)	119(3)	114(3)
Cp(1)–U(1)–Cp(3)	114(1)	114(1)	C(19)–C(20)–B(1)	105(3)	112(3)
Cp(2)–U(1)–Cp(3)	115(1)	114(1)	C(21)–C(20)–B(1)	110(3)	106(3)
C(16)–B(1)–C(20)	106(3)	106(3)	C(20)–C(21)–C(22)	116(3)	112(3)
C(17)–C(16)–C(23)	116(3)	118(3)	C(21)–C(22)–C(23)	117(4)	122(4)
C(17)–C(16)–B(1)	104(3)	108(3)	C(22)–C(23)–C(26)	119(4)	113(3)
C(23)–C(16)–B(1)	109(3)	106(3)	U(1)–B(1)–C(16)	140(2)	143(2)
			U(1)–B(1)–C(20)	113(2)	110(2)

[a] Cp(1) = Cp ring C(1)–C(5); Cp(2) = Cp ring C(6)–C(10); Cp(3) = Cp ring C(11)–C(15). The distances are between the uranium atom and the cyclopentadienyl ring centroids.

of the small boron atom by the bigger uranium atom and to the consequent steric and electronic effects. Finally it should be pointed out that no complex with the stoicheiometry Cp$_2$U(HBBN)$_2$, analogous to Cp$_2$U(BH$_4$)$_2$ [29], could be obtained; an important influence here is probably the larger size (based on the cone-packing model) of the potentially bidentate (HBBN)$^-$ anion than of the potentially tridentate BH$_4$$^-$ anion, confirming the validity of the steric criteria recently defined by Li Xing-Fu [30] in analysing the stabilities of the various molecular geometries of lanthanide and actinide complexes.

Acknowledgement

References

1 T.J. Marks and J.R. Kolb, Chem. Rev., 77 (1977) 263.
2 N. Edelstein, Inorg. Chem., 20 (1981) 297.

3   B.D. James, R.K. Nanda and M.G.H. Wallbridge, Inorg. Chem., 6 (1967) 1979.

4   T.J. Marks and J.R. Kolb, J. Am. Chem. Soc. 97 (1975) 27.

5   H.C. Brown, B. Singaram and S. Singaram, J. Organomet. Chem., 239 (1982) 43.

6   R. Koster and G. Seidel, Inorg. Synth., 22 (1983) 198.

7   D.D. Perrin, W.L.F. Armarego and D.R. Perrin in Purification of Laboratory Chemicals, 2nd ed. Pergamon Press, 1980.

8   F. Ossola, G. Rossetto, P. Zanella, G. Paolucci and R.D. Fischer, J. Organomet. Chem., 309 (1986) 55.

9   S.L. Lawton, R.A. Jacobson, "TRACER", a cell reduction program. Ames Laboratory. Iowa State University of Science and Technology, 1965.

10 Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using: "SHELX-76. System of Crystallographic Computer Programs"; G. Sheldrick, University of Cambridge, Cambridge, England, 1976.

11 A.J.C. Wilson, Nature, 150 (1942) 151.

12 A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., A24 (1968) 351.

13 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. IV, 1974, (a) p. 99, (b) p. 149.

14 R.F. Stewart, E.R. Davidson, W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.

15 T.J. Marks, W.J. Kennelly, J.R. Kolb and L.A. Shimp, Inorg. Chem., 11 (1972) 2540.

16 N. Davies, M.G.H. Wallbridge, B.E. Smith and B.D. James, J. Chem. Soc., Dalton Trans., (1973) 162.

17 V.V. Volkov, K.G. Myakishev and Z.A. Grankina, Russ. J. Inorg. Chem., 15 (1970) 1490.

18 R. Shinomoto, E. Gamp, N.M. Edelstein, D.H. Templeton and A. Zalkin, Inorg. Chem., 22 (1983) 2351.

19 W. Jahn, K. Yünlü, W. Oroschin, H.D. Amberger and R.D. Fischer, Inorg. Chim. Acta, 95 (1984) 85.

20 G. Paolucci, G. Rossetto, P. Zanella, K. Yünlü and R.D. Fischer, J. Organomet. Chem., 272 (1984) 363

21 A. Berton, M. Porchia, G. Rossetto and P. Zanella, J. Organomet. Chem., 302 (1986) 351

22 R.D. Fischer in T.J. Marks and I. Fragalà (Eds.), Fundamental and Technological Aspects of Organo-f-Element Chemistry, p. 277 Proceedings of NATO ASI Aquafredda di Maratea, Italy September 1984, D. Reidel Publishing Company, Dordrecht.

23 R.E. Cramer, R.B. Maynard, J.C. Paw and J.W. Gilje, Organometallics, 2 (1983) 1336.

24 K.N. Raymond and C.W. Eigenbrot, Acc. Chem. Res., 13 (1980) 276.

25 P. Zanella, G. Paolucci, G. Rossetto, F. Benetollo, A. Polo, R.D. Fischer and G. Bombieri, J. Chem. Soc., Chem. Commun., (1985) 96.

26 E.R. Bernstein, W.C. Hamilton, T.A. Keiderling, S.J. La Placa, S.J. Lippard and J.J. Mayerle, Inorg. Chem., 11 (1972) 3009.

27 E.L. Osina, V.S. Mastryukov, L.V. Vilkov and N.A. Belikova, J. Chem. Soc., Chem. Commun., (1976) 12.

28 Our unpublished data.

29 P. Zanella, G. De Paoli, G. Bombieri, G. Zanotti and R. Rossi, J. Organomet. Chem., 142 (1977) C21.

30 Li Xing-Fu, Feng Xi-Zhang, Xu Ying-Ting, Wang Hai-Tung, Shi Jie, Liu Li and Sun Peng-Nian Inorg. Chim. Acta, 116 (1986) 85 and references therein.