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Structure of Bis[(1,2,3,3a,7a- η)-indenyl]bis(tetrahydroborato)uranium(IV)

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Abstract. $[\text{U}(\text{BH}_4)_2(\text{C}_9\text{H}_7)_2]$, $M_r = 498.03$, monoclinic, $P2_1/c$, $a = 8.636$ (6), $b = 26.35$ (1), $c = 7.765$ (6) Å, $\beta = 102.690$ (1)°, $V = 1724$ (4) Å³, $Z = 4$, $D_x = 1.919$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 89.191$ cm⁻¹, $F(000) = 928$, room temperature, $R = 0.062$ for 1148 observed reflections. The coordination geometry about the U atom is that of a tetrahedron formed by the two B atoms and the centroids of the five-membered rings of the indenyl ligands. The short U—B distances are characteristic of tridentate ligation by the borohydride ligands. U—C distances suggest a pentahapto covalent bonding to the indenyl ligands.

Introduction. The interest in organometallic tetrahydroborate complexes is mainly due to the bonding mode of the BH_4 group which may act as a monodentate, bidentate or tridentate ligand. Only a few structural investigations on actinide complexes are reported in the literature. They are principally concerned with cyclopentadienyl complexes of uranium: $[\text{U}(\text{C}_5\text{H}_5)_2(\text{BH}_4)_2]$ (Zanella, de Paoli, Bombieri, Zanotti & Rossi, 1977), $[\text{U}(\text{C}_5\text{H}_5)(\text{BH}_4)_3]$ (Baudry, Charpin, Ephritikhine, Folcher, Lambard, Lance,

Nierlich & Vigner, 1985). We report here the structure of an indenyl derivative in order to determine whether the mode of bonding of the BH_4^- anion is influenced by the nature of the other ligands coordinated to the metal.

Experimental. Bis(indenyl)bis(tetrahydroborato)uranium was prepared by reaction of indenyl (sodium) with uranium tetrahydroborate. Dark-brown prismatic single crystals obtained by crystallization in pentane. The specimen (0.2 × 0.2 × 0.3 mm) selected for X-ray analysis was sealed in a thin-walled glass capillary. Intensity data recorded on an Enraf-Nonius CAD-4 X-ray diffractometer, graphite-monochromated $\text{Mo } K\alpha$ radiation. Cell parameters refined by least squares from angle data of 25 reflections ($10 \leq 2\theta \leq 23^\circ$). Space group determined from systematic absences. 2153 unique reflections measured by ω - 2θ method in range $4 \leq 2\theta \leq 45^\circ$; 1836 with $I \geq 1\sigma(I)(\pm h, k, l)$. Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz-polarization effects; empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983), transmission coefficients: min. 0.53 and max. 1.52. Structure solved by

* Chercheur qualifié FNRS.

Table 1. Atomic positional parameters and isotropic temperature factors (\AA^2)

	x	y	z	B(\AA^2)
U	0.0970 (1)	0.13051 (4)	0.9006 (1)	3.50 (2*)
B(1)	0.062 (3)	0.189 (1)	0.639 (3)	2.6 (5)
B(2)	0.153 (4)	0.046 (2)	0.768 (4)	4.8 (8)
C(1)	-0.162 (5)	0.081 (2)	0.972 (5)	8 (1)
C(2)	-0.103 (4)	0.117 (1)	1.106 (3)	5.1 (7)
C(3)	-0.128 (5)	0.165 (2)	1.079 (4)	6.8 (9)
C(4)	-0.266 (5)	0.213 (2)	0.812 (5)	8 (1)
C(5)	-0.346 (5)	0.203 (2)	0.642 (4)	6.8 (9)
C(6)	-0.371 (6)	0.161 (2)	0.565 (5)	9 (1)
C(7)	-0.325 (6)	0.123 (2)	0.651 (5)	9 (1)
C(8)	-0.226 (4)	0.123 (1)	0.821 (4)	5.5 (7)
C(9)	-0.202 (4)	0.171 (1)	0.909 (3)	4.4 (7)
C(10)	0.403 (3)	0.155 (1)	1.003 (4)	4.3 (7)
C(11)	0.321 (3)	0.199 (1)	1.068 (3)	3.2 (5)
C(12)	0.243 (3)	0.178 (1)	1.202 (3)	4.2 (7)
C(13)	0.265 (3)	0.090 (1)	1.348 (3)	3.9 (6)
C(14)	0.338 (4)	0.045 (2)	1.351 (4)	5.3 (7)
C(15)	0.439 (4)	0.030 (1)	1.240 (4)	5.0 (7)
C(16)	0.466 (4)	0.065 (1)	1.127 (4)	4.9 (7)
C(17)	0.400 (3)	0.117 (1)	1.104 (3)	4.6 (6)
C(18)	0.299 (3)	0.126 (1)	1.226 (3)	4.1 (6)

* Atom refined anisotropically. $B_{\text{eq}} = \frac{1}{3}$ trace B.

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

E.s.d.'s are given in parentheses.			
U—B(1)	2.51 (2)	U—C(10)	2.66 (2)
U—B(2)	2.53 (3)	U—C(11)	2.75 (2)
U—C(1)	2.75 (3)	U—C(12)	2.71 (2)
U—C(2)	2.62 (2)	U—C(17)	2.77 (2)
U—C(3)	2.77 (3)	U—C(18)	2.74 (2)
U—C(8)	2.73 (3)	U—ind. (I)	2.46 (3)*
U—C(9)	2.82 (2)	U—ind. (II)	2.44 (3)*
B(1)—U—B(2)	101.9 (8)	B(2)—U—ind. (I)	112 (1)
B(1)—U—ind. (I)	103.7 (8)	B(2)—U—ind. (II)	108.2 (9)
B(1)—U—ind. (II)	109.9 (7)	Ind. (I)—U—ind. (II)	119.8 (8)

* Distance to the five-membered-ring centroid.

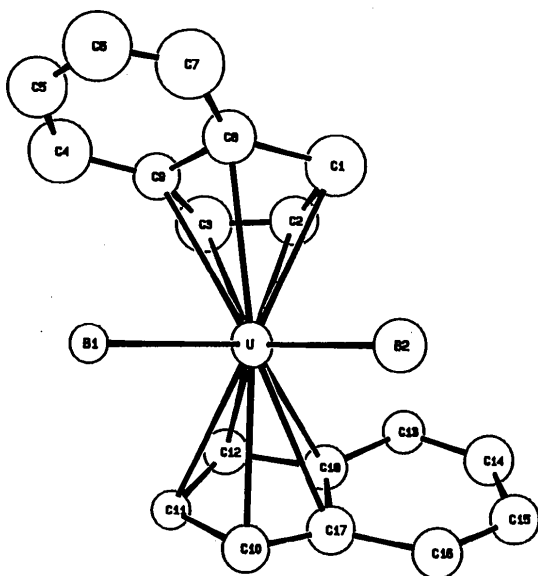


Fig. 1. The molecule of $[\text{U}(\text{C}_9\text{H}_7)_2(\text{BH}_4)_2]$. Thermal ellipsoids are at the 50% probability level (Johnson, 1976).

direct methods and Fourier techniques. Full-matrix least-squares refinement on F ; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (A/I)^2]^{1/2}/L_p$ where A , the ignorance factor, is 0.08; 1148 reflections with $F^2 \geq 3\sigma(F^2)$ ($h - 8/8$, $k 0/28$, $l 0/9$). U atom only refined anisotropically; indenyl H atoms were not refined but only introduced in the final structure-factor calculations, in idealized positions, with isotropic parameters equal to those of their C atom. H atoms of the BH_4 groups could not be located in the final difference Fourier synthesis, where the highest peaks were located near the U atom ($\Delta\rho$ within 1.73 and -1.74 e \AA^{-3}). A secondary-extinction coefficient refined to a value of $g = 7.94 (3.02) \times 10^{-8} \{F_c = F_o/[1 + g(F_o)^2 L_p]\}$. $R = 0.062$, $wR = 0.090$, $S = 1.983$, $(\Delta/\sigma)_{\text{max}} = 0.03$. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1986) *SDP-Plus*.

Discussion. Positional and isotropic thermal parameters are given in Table 1.* Important bond distances and angles are listed in Table 2. The structure consists of discrete molecules of $[\text{U}(\text{C}_9\text{H}_7)_2(\text{BH}_4)_2]$ (Fig. 1). The centers of the five-membered-ring portions of the indenyl ligands and the B atoms form a distorted tetrahedron around the U atom as shown by the angles reported in Table 2. The short U—B distances are characteristic of tridentate ligation by the BH_4 groups. Indeed in the absence of neutron diffraction data, the mode of ligation of the borohydride anions can only be identified by the observed U—B distances (Edelstein, 1981). In the case of $\text{U}(\text{BH}_4)_4$ (Charpin, Nierlich, Vigner, Lance & Baudry, 1987; Bernstein, Hamilton, Keiderling, La Placa, Lippard & Mayerle, 1972), where the BH_4 units are both bidentate and tridentate, the observed U—B distances are 2.84 (1) and 2.51 (1) \AA respectively. In $[\text{U}(\text{C}_5\text{H}_5)_2(\text{BH}_4)_2]$ (Zanella *et al.*, 1977) as in $[\text{U}(\text{C}_5\text{H}_5)(\text{BH}_4)_3]$ (Baudry *et al.*, 1985), U—B distances of 2.58, 2.61, 2.63 \AA and 2.46 (4), 2.57 (5) \AA , respectively, also correspond to triple hydrogen-bridge bonds.

From the small range of U—C distances reported in Table 2, it appears that the U atom is η^5 covalently bonded to the two indenyl rings.

* Lists of structure amplitudes, indenyl H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51937 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Bis(μ - η^3 -allyl)- μ_4 -sulfido-tetrakis(triphenylphosphine)-tetrapalladium(2 Pd-Pd) Tetrahydrofuran Solvate

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Abstract. $[\text{Pd}_4\text{S}(\text{C}_3\text{H}_5)_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]\cdot\text{C}_4\text{H}_8\text{O}$, $M_r = 1659.7$, triclinic, $P\bar{1}$, $a = 15.145$ (2), $b = 20.966$ (4), $c = 14.117$ (2) Å, $\alpha = 100.68$ (1), $\beta = 116.38$ (1), $\gamma = 69.94$ (1)°, $V = 3769.2$ Å³, $Z = 2$, $D_x = 1.46$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 10.76$ cm⁻¹, $F(000) = 1676$, $T = 291$ K. Final $R = 0.058$ ($wR = 0.077$) for 4733 unique observed reflections. The title compound contains a sulfido group bridging two μ -allyl-bis(triphenylphosphine)dipalladium groups. Each Pd atom is coplanar with its four neighbouring atoms, all deviations from the planes being less than 0.1 Å. One of the bridging allyl groups shows statistical disorder.

Introduction. In the course of an investigation of sulfur-containing polynuclear metal compounds of nickel, palladium and platinum, the characterization of complexes of the type $[(\eta^3\text{-C}_3\text{H}_5)\text{MSM}'(\eta^3\text{-C}_3\text{H}_5)]_x$, where x is unknown, proved to be difficult because of their generally low solubility (Benn, Bogdanović, Götsch & Rubach, 1983). In order to obtain more structural information we synthesized a phosphine adduct of the palladium complex with the composition, but as yet still unknown structure, $[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}_2\text{S}]_x$, by reacting it with an equimolar amount of triphenylphosphine. We were able to isolate crystals of the title compound, the structure of which indicates that a degradation and subsequent rearrangement of the starting material had occurred.

Experimental. The title compound (1) was prepared in a two-step reaction from bis(allyl)palladium (Rubach, 1981). (i) Preparation of $[(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}_2\text{S}]_x$

(2) (Bogdanović, Goddard, Götsch, Krüger, Schlichte & Tsay, 1983): a toluene solution of bis(allyl)palladium was added to a toluene solution of sulfur. A red-violet precipitate of (2) was formed after 12 h. The compound was isolated, washed and dried. (ii) Preparation of (1): triphenylphosphine was added to a suspension of (2) in tetrahydrofuran and allowed to react at room temperature. Yellow crystals of the title compound formed on the side of the glass reaction vessel after several days. The crystal chosen for data collection was $0.15 \times 0.16 \times 0.26$ mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 74 automatically centred reflections ($3.44 < \theta < 18.4^\circ$). Intensity data were measured within the range $1.04 < \theta < 21.44^\circ$ on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo } K\alpha$ X-radiation by a θ - 2θ -scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its e.s.d. were calculated from $I = \text{INT} - 2(\text{BGL} + \text{BGR})$ and $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{0.5}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the ω -scan range varied as $(3.2 + 1.25 \tan \theta)$ mm and $(0.8 + 0.35 \tan \theta)^\circ$. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{0.5}/2F$, where $k = 0.02$. Of a total of 9038 ($h - 15 \rightarrow 13$, $k - 21 \rightarrow 21$, $l 0 \rightarrow 14$) measured intensities, 4733 satisfied the criterion $I > 2.0\sigma(I)$, and only these were