Synthesis of a Uranium(IV) Hydride from the Corresponding Borohydride: Preparation of $\{(MeOCH_2CH_2OMe)U(BH_4)_3(\mu\text{-}H)\}_2$ and the Crystal Structure of its Toluene Solvate

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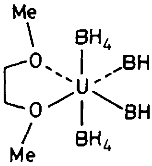
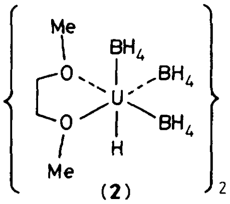
Elimination of BH_3 from $(MeOCH_2CH_2OMe)U(BH_4)_4$ affords the title compound, the structure of which has been determined.

Synthesis of d-transition metal hydrides from the corresponding borohydrides is classical;[1] this reaction is, in certain cases, impeded by the concomitant reduction of the metal ion. Hydride complexes of uranium, which are very rare, have been obtained from alkyl[2] or amide[3] uranium derivatives. It seemed to us that it would be interesting to prepare uranium hydrides from the stable $L_2U(BH_4)_4$ compounds. We have found that the dimethoxyethane adduct $(dme)U(BH_4)_4$ (**1**) (dme = $MeOCH_2CH_2OMe$) undergoes BH_3 elimination to give the hydride bridged dimer $\{(dme)U(BH_4)_3(\mu\text{-}H)\}_2$ (**2**). Here we describe the synthesis and the *X*-ray crystal structure of (**2**).

Addition of dme (0.4 ml) to a solution of $U(BH_4)_4$[4] (150 mg) in toluene (20 ml) gave immediately and quantitatively the adduct (**1**) which was recrystallized from toluene–pentane and



(**1**)



(**2**)

$\{(dme)U(BH_4)_3\}_n$

(**3**)

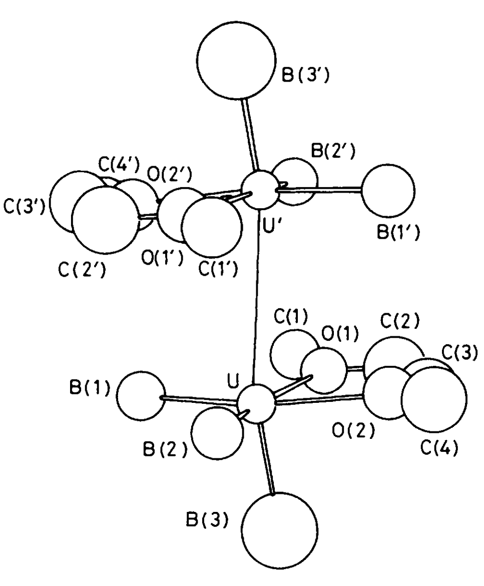


Figure 1. The X-ray crystal structure of (**2**). Some important distances (Å) and angles (°): U–O(1) 2.53(2), U–O(2) 2.47(2), U–B(1) = U–B(2) 2.64(4), U–B(3) 2.53(6); O(1)–U–O(2) 65.1(6), O(1)–U–B(1) 93.4(8), B(1)–U–B(2) 105(1), B(2)–U–O(2) 96(1), B(3)–U–B(2) 97(1), B(3)–U–O(1) 84(1), B(3)–U–B(1) 103(2), B(3)–U–O(2) 78(2); U'–U–B(3) 159; the U atom is 0.1 Å from the O(1)O(2)B(1)B(2) plane on the B(3) side. Primed atoms are related to unprimed atoms by the symmetry centre.

isolated as pale green crystals. The ^1H n.m.r. spectrum of (**1**)† shows two inequivalent pairs of borohydride ligands; the low field signal is assigned to the BH_4 groups which are mutually *trans* in an octahedral configuration.[5] Thermal decomposition (150 °C; 1 h) of (**1**) [prepared from 140 mg of $U(BH_4)_4$] in toluene (20 ml) gave a bright orange solution and dark red crystals (90 mg) the elemental analysis of which indicated the formula $\{(dme)U(BH_4)_3\}_n$ (**3**); the insolubility of (**3**) in usual organic solvents suggests a polymeric structure.

The reduction of the uranium(IV) tetraborohydrides into the corresponding $U(BH_4)_3$ derivatives[6] reflects the ready accessibility of the uranium(III) oxidation state.[7] However, the uranium(IV) hydride (**2**) could be synthesized by heating a solution of (**1**) in toluene at 110 °C during 1.5 h. The pale orange mixture thus obtained was dried *in vacuo* and the residue was extracted with toluene, leaving a small quantity of a tan insoluble product, presumably a uranium(III) species. Green crystals of (**2**) were obtained by crystallisation from toluene–pentane (*ca.* 50% yield). In a separate experiment in the presence of PPh_3, formation of the adduct PPh_3–BH_3 was observed (by n.m.r.).‡ That (**2**) is an intermediate in the reduction of (**1**) was confirmed by its thermal conversion into (**3**) (toluene; 150 °C). The ^1H n.m.r. spectrum† indicates that (**2**) is derived from (**1**) by replacing one of the two *trans* BH_4 groups by a hydride ligand; the latter, however, was not observed.[3]

Crystals of a toluene solvate of (**2**) suitable for X-ray diffraction were obtained from toluene; the dimeric structure§ is shown in Figure 1. The difference map around the symmetry centre of the dimer shows some electron density (*ca.* 4 e Å^{-3}) which impeded the localisation of the bridging hydrides. This spurious peak, the intensity of which is slightly dependent on the absorption correction, could not be satisfactorily explained. The U–B distances are characteristic of tridentate BH_4^- ligands.[1] The distance between the uranium atoms (4.12 Å) is similar to that found between the thorium atoms (4.00 Å) in $\{(C_5Me_5)_2ThH(\mu\text{-}H)\}_2$.[8] The U–U' vector is perpendicular to the plane defined by O(1), O(2), B(1), and B(2); this plane is the equatorial plane of the monomeric unit in a pseudo-octahedral configuration with the $B(3)H_4$ and the hydride ligands at the apices.

Received, 19th November 1986; Com. 1651

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† Complexes (**1**)—(**3**) gave satisfactory elemental analysis (C,H,B). I.r. ν (Nujol) (**1**): 2490, 2200, 2140, 1155, 1085, and 1025 cm^{-1}; (**2**): 2480, 2210, 2140, 1195, 1170, 1095, and 1035 cm^{-1}. N.m.r. δ (60 MHz; −60 °C; [$^2H_8$]toluene) (**1**): 597 (8H, br., $W_{\frac{1}{2}}$ 370 Hz, *trans* BH_4), −46.2 (4H, s, CH_2), −61.1 (6H, s, CH_3), −94.3 (8H, br., $W_{\frac{1}{2}}$ 175 Hz, *cis* BH_4); (**2**): 752.6 (4H, br., $W_{\frac{1}{2}}$ 530 Hz, B^3H_4), −31.6 and −52.3 (2H and 2H, s, CH_2), −62.8 (6H, s, CH_3), and −121.3 (8H, br., $W_{\frac{1}{2}}$ 140 Hz, B^1H_4 and B^2H_4). Numbering of B atoms is as in Figure 1.

‡ Identification by comparison with an authentical commercial sample.

§ *Crystal data* for (**2**): $(C_4H_{23}B_3O_2U)_2$, C_7H_8, triclinic, space group $P\bar{1}$, $a = 8.126(3)$, $b = 8.950(6)$, $c = 11.638(3)$ Å, $\alpha = 83.50(5)$, $\beta = 89.44(3)$, $\gamma = 69.76(5)°$, $U = 789$ Å^3, $Z = 1$, $D_c = 1.768$ g cm^{-3}, $\mu = 97.38$ cm^{-1}. Data were collected using an Enraf-Nonius CAD-4 diffractometer (Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.71073$ Å) in the range $2 < 2\theta < 40°$. 1202 reflections with $I > 3.5\,\sigma(I)$ were used after Lorentz, polarization, intensity decay (−28.4% after 19 h), and empirical absorption[9] corrections (min: 0.617, max.: 1.624). The structure was solved by using Patterson and Fourier syntheses and refined by full matrix least squares minimizing $w(F_o - F_c)^2$ with unit weights.[10] Analytical scattering factors for neutral atoms were corrected for f' and f''. Hydrogen atoms were not located; those of the dme ligand were introduced in idealized positions and constrained to ride their carbon atoms. The unit cell contains a molecule of toluene, disordered on a symmetry centre. The final R values were $R = 0.050$ and $R_w = 0.060$ ($w = 1$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.