a vertex bridges an edge of a closed polyhedral structure. It shows the value of including the bridging cobalt atom as an integral part of the heteropolyboron structure. If this cobalt atom were described as a ligand bridge, the bridging ligands between the dodecahedron and the cobalt atom could not be specifically described under present rules.

Compound C in Figure 10 illustrates a *conjuncto*-polyboron hydride analogue that could be named as a "monocommo" system between two edge-capped polyhedral fragments as shown. To us, this name is easier to visualize than one based on a $(7v)[D_{3h}\text{-}(33v^4 3)\text{-}\Delta^{14}\text{-}closo(-2v)^{8,9}]$ polyhedral fragment.

The recently reported compound shown as D in Figure 10 demonstrates that the capping technique we proposed could be extended to partial capping. Without such an extension, this structure would have to be treated as a cyclo–edge capped–dicommo system or a seco–tricommo system, both of which result in much more complex names.

Coordination Nomenclature for *conjuncto*-Metallopolyboron Hydrides

As for closed and nonclosed metallopolyboron hydrides,[1b] principles of coordination nomenclature may be applied for naming certain *conjuncto*-polyboron hydrides by using the methods developed in this and earlier papers[1] to specify the structure of the polyboron hydride fragments as ligands. Coordination names for such compounds in this paper (D in Figure 2; A, B, C, and D in Figure 3; Figure 4; A and D in Figure 10) and compounds II in Figure A and II in Figure D of the supplementary material are listed in Table A in the supplementary material; ligand numberings, where needed, are shown in Figure H in the supplementary material.

Summary

Nomenclature for *conjuncto*-polyboron hydrides, i.e., polyboron hydride structures consisting of two or more polyhedra or polyhedral fragments and their hetero analogues and derivatives, has been proposed on the basis of the descriptor system developed earlier for closed, capped closed, and nonclosed polyboron hydrides. Limitations of methods given in current rules are discussed. The descriptor method for capped closed polyhedra developed earlier is extended to include bridging vertices (edge capping) and internal bridging atoms.

Supplementary Material Available: Table A, giving coordination names for some *conjuncto*-polyboron hydrides, Figures A–G, showing additional structures and names of *conjuncto*-polyboron hydrides, and Figure H, giving ligand numberings for the coordination names in Table A (12 pages). Ordering information is given on any current masthead page.

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Preparation of Tertiary Phosphine Complexes of Tetravalent and Trivalent Uranium Methyltrihydroborates. Crystal Structures of Tetrakis(methyltrihydroborato)(1,2-bis(dimethylphosphino)ethane)uranium(IV) and Tris(methyltrihydroborato)bis(1,2-bis(dimethylphosphino)ethane)uranium(III)

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$(CH_3BH_3)_4U[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ and $(CH_3BH_3)_3U[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ have been synthesized and their molecular structures determined by single-crystal X-ray diffraction. The space groups, unit cell parameters, and *R* factors are as follows: $(CH_3BH_3)_4U[(CH_3)_2PCH_2CH_2P(CH_3)_2]$, monoclinic, $P2_1/c$, $a = 9.439$ (3) Å, $b = 14.023$ (4) Å, $c = 16.596$ (2) Å, $\beta = 97.48$ (4)°, $Z = 4$, $d_x = 1.536$ g/cm^3, $R = 0.024$ ($F^2 > 3\sigma(F^2)$); $(CH_3BH_3)_3U[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$, tetragonal, $P4_32_12$, $a = 11.297$ (4) Å, $c = 23.03$ (2) Å, $Z = 4$, $d_x = 1.412$ g/cm^3, $R = 0.024$ ($F^2 > 3\sigma(F^2)$). Both complexes are unimolecular in the crystalline state. The uranium(IV) atom is coordinated to four BH_3CH_3 groups through tridentate hydrogen bridges and to two P atoms of the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ligand. The uranium(III) complex is coordinated to three BH_3CH_3 groups through tridentate hydrogen bridges and to four P atoms from the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ligands. The U–B distances for the U(IV) and U(III) complexes average 2.57 ± 0.01 and 2.63 ± 0.02 Å, respectively; the U–P distances for the U(IV) and U(III) complexes average 3.02 ± 0.01 and 3.13 ± 0.06 Å, respectively.

Introduction

Four Lewis base etherate adducts of $U(BH_4)_4$ have been structurally characterized and shown to display a variety of structural types.[1] $U(BH_4)_4$ also forms adducts with other Lewis bases, but these compounds have not been isolated.[2] A number of U(III) tetrahydroborate complexes have recently been reported. Marquet-Ellis et al. have thermally decomposed $U(BH_4)_4$ in toluene solution and reacted the $U(BH_4)_3$ formed by this process with crown ethers to form soluble compounds.[3] Wasserman et al. have isolated and structurally characterized $U(BH_4)_3(DMPE)_2$ (DMPE = 1,2-bis(dimethylphosphino)ethane) and $U(BH_4)_3(Ph_2Ppy)_2$ (Ph_2Ppy = 2-(diphenylphosphino)pyridine) from the reactions of $U(BH_4)_3(THF)_x$ (THF = tetrahydrofuran) with the appropriate ligands.[4] An

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Table I. Infrared Spectroscopic Data (cm^{-1})

	$U(BH_3CH_3)_4DMPE$		
2950 m	2100 s	1415 w	1300 m
1285 m	1220 s	1075 s	940 s
925 s	890 m	865 m	830 m
795 m	735 m	705 m	645 m
	$U(BH_3CH_3)_3(DMPE)_2$		
2950 m	2310 w	2165 m	1420 w
1290 m	1260 w	1215 m (br)	1140 w
1075 w	940 m	930 m	890 m
825 w	730 m	720 m	700 m
690 m	640 m		

unusual feature of the $U(BH_4)_3(DMPE)_2$ complex is that two of the BH_4^- ligands are bonded to the U atom by tridentate hydrogen bridges while the third BH_4^- group is linked to the U atom by a bidentate hydrogen bridge.

We recently reported the syntheses and crystal structures of $M(BH_3CH_3)_4$ (M = Zr, Th, U, Np).[5] Following the first structural characterization of an actinide phosphine compound by Andersen,[6] we have been exploring the coordination chemistry of the $M(BH_3CH_3)_4$ compounds (M = Th, U) with phosphine ligands. We report in this paper the synthesis and structure of $U(BH_3CH_3)_4DMPE$ and its thermal decomposition product (in toluene with excess DMPE), $U(BH_3CH_3)_3(DMPE)_2$.

Experimental Section

All preparations were carried out under an argon atmosphere. Hexane was dried over CaH_2 and distilled under argon. Pentane was distilled from sodium benzophenone ketyl. Toluene was dried over Na and distilled under argon before use; 1,2-bis(dimethylphosphino)ethane was prepared as reported.[7] $U(BH_3CH_3)_4$ was prepared as described previously.[5]

Infrared spectra were recorded on a Perkin-Elmer IR-283 spectrophotometer and calibrated with polystyrene film. Nujol and Fluorolube mulls were prepared in an argon-filled drybox with dry, degassed Nujol and Fluorolube. Nuclear magnetic spectra were recorded on a JEOL FX 90Q 90-MHz FT spectrometer and referenced to tetramethylsilane. Samples were prepared in toluene-d_8 in an argon-filled drybox and sealed under vacuum or capped with serum stoppers. Melting points were determined in sealed, argon-filled capillaries. IR data are given in Table I and ^1H NMR data in Table II. Elemental analyses were conducted by the analytical laboratories of the University of California, Berkeley.

Preparation of $U(BH_3CH_3)_4DMPE$. To 0.24 g (0.68 mmol) of $U(BH_3CH_3)_4$ dissolved in 20 mL of pentane was added 0.11 mL (0.66 mmol) of DMPE with stirring, giving a green precipitate. The solution was stirred for 5 min and then pumped to dryness. The green residue was dissolved in 10 mL of toluene, the mixture filtered, and the resulting solution concentrated to 3 mL and cooled at −20 °C. After 3 h, green crystals had formed. The supernate was removed, and the green crystals were washed with 2 mL of ether and pumped to dryness. A yield of 0.16 g (48%) of $U(BH_3CH_3)_4DMPE$ was recovered; mp 131–132 °C dec. Anal. Calcd for $C_{10}H_{40}B_4P_2U$: C, 23.85; H, 8.01. Found: C, 23.42; H, 8.25.

Preparation of $U(BH_3CH_3)_3(DMPE)_2$. To 0.12 g (0.24 mmol) of $U(BH_3CH_3)_4DMPE$ dissolved in 10 mL of toluene was added 0.40 mL (2.4 mmol) of DMPE with stirring. The solution was heated to ~80 °C for several hours, during which it turned deep brown. After the solution was cooled to room temperature, the toluene was pumped off and a solution of the dark brown residue in 15 mL of hexane was filtered and cooled slowly to −20 °C overnight. Fine brown-black needles were isolated and washed twice with cold (−78 °C) hexane. A yield of 0.06 g (10%) of $U(BH_3CH_3)_3(DMPE)_2$ was recovered; mp 130–132 °C. Anal. Calcd for $C_{15}H_{50}B_3P_4U$: C, 28.83; H, 8.07. Found: C, 29.01; H, 8.25.

Table II. Proton Magnetic Resonance Data[a,b]

T, °C	BH_3	CH_3	DMPE
	$U(BH_3CH_3)_4DMPE$		
−66	−32.97 (6 H, s) +450.14 (6 H, s)	−16.20 (6 H, s) +60.27 (6 H, s)	−15.64 (4 H, s) −8.14 (12 H, s)
−20	−25.16 (6 H, s) +373.80 (6 H, s)	−13.29 (6 H, s) +49.85 (6 H, s)	−12.59 (4 H, s) −6.71 (12 H, s)
+25[c]			−10.30 (4 H, s) −5.56 (12 H, s)
+74[d]		+13.67 (12 H, s)	−8.67 (4 H, s) −4.69 (12 H, s)
	$U(BH_3CH_3)_3(DMPE)_2$		
−68	+144.61 (9 H, s)	+12.44 (9 H, s)	−0.57 (24 H, s) −5.31 (8 H, s)
−22	+125.95 (9 H, s)	+10.23 (9 H, s)	−0.08 (24 H, s) −2.94 (8 H, s)
+25	+115.24 (9 H, s)	+8.92 (9 H, s)	−0.07 (24 H, s) −1.09 (8 H, s)
+70	+112.99 (9 H, s)	+8.39 (9 H, s)	+0.13 (24 H, s) −0.24 (8 H, s)

[a] All samples were prepared in toluene-d_8. [b] Shifts in ppm from Me_4Si. Positive sign indicates a downfield shift. [c] Methyltrihydroborate protons broadened into the baseline due to rapid exchange of BH_3CH_3 sites. [d] Single averaged methyl peak found. No averaged BH_3 peak found.

X-ray Crystallography. Because of their extreme sensitivity to air, the crystals were sealed inside 0.3-mm quartz capillaries and then mounted on a modified Picker automatic FACS-I diffractometer equipped with a Mo X-ray tube ($\lambda(K\alpha_1) = 0.70930$ Å) and a graphite monochromator. The $\theta-2\theta$ scan data were collected and corrected for crystal decay, absorption (analytical method),[8] and Lorentz and polarization effects. Details of the data collection and results are shown in Table III.

The U atoms were located with the use of three-dimensional Patterson maps, and subsequent least-squares refinement and electron density maps revealed the locations of all of the non-hydrogen atoms. The structures were refined by full-matrix least squares using anisotropic thermal parameters on all of the non-hydrogen atoms. The positions of the hydrogen atoms on the DMPE ligand were estimated from its known geometry. Some of the hydrogen atom positions of the methyltrihydroborate groups were located in the difference electron density maps, and with these positions the remaining hydrogen atom positions could be estimated. All of the hydrogen atoms were included in the least-squares refinements with isotropic thermal parameters. Because the hydrogen atoms are not well resolved in the electron density maps, their positional parameters do not refine well in the least-squares procedure; therefore, restraints on the distances involving the hydrogen atoms were introduced into the least-squares refinements by using a procedure suggested by Waser[9] and described elsewhere.[10] A sufficient number of distances to the hydrogen atoms were included to enforce tetrahedral geometry about the boron and carbon atoms. Neutral-atom scattering factors for U, P, B, C,[11] and H[12] were used in these calculations with the corrections for anomalous scattering applied.

In the tetragonal $U(BH_3CH_3)_3(DMPE)_2$ structure, the Friedel pairs were not averaged but were treated as individual reflections. At an earlier stage of the least-squares refinement with all atoms anisotropic, and no hydrogen atoms included, the structure refined to an R factor of 0.050 in space group $P4_12_12$, and 0.034 in space group $P4_32_12$. This result established the absolute configuration of the data crystal in the latter space group.

Results of the least-squares refinements are given in Table III. Positional parameters are given in Table IV, and distances and angles

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Table III. Crystallographic Summary and Data Processing

	$U(BH_3CH_3)_4DMPE^a$	$U(BH_3CH_3)_3(DMPE)_2{}^a$
a, Å	9.439 (3)	11.297 (4)
b, Å	14.023 (4)	11.297 (4)
c, Å	16.596 (2)	23.030 (20)
β, deg	97.48 (4)	
V, $Å^3$	2178.0	2939.1
d(calcd), g/cm^{-3}	1.536	1.412
Z	4	4
mol formula	$C_{10}H_{40}B_4P_2U$	$C_{15}H_{50}B_3P_4U$
fw	503.65	624.92
cryst syst	monoclinic	tetragonal
systematic absences	$h0l$, $l = 2n$	$00l$, $l = 4n$
	$0k0$, $k = 2n$	$h00$, $h = 2n$
space group	$P2_1/c$	$P4_32_12$
data cryst dimens, mm	0.15 × 0.17 × 0.29	0.12 × 0.14 × 0.66
abs coeff, cm^{-1}	71.9	54.5
abs cor range	1.46–4.88	1.81–2.11
cryst decay cor	1.00–1.02	1.00–1.08
2θ range, deg	4–50	4–45
hkl range	$0 < h < 11$	$-12 < h < 12$
	$0 < k < 16$	$0 < k < 12$
	$-19 < l < 19$	$0 < l < 24$
2θ scan width, deg	$1.10 + 0.693 \tan \theta$	$1.50 + 0.693 \tan \theta$
no. of stds	3	3
no. of reflcns between stds	100	250
no. of scan data	8091	4296
no. of unique reflcns	3976	1960
no. of nonzero weighted data ($F^2 > 3\sigma$)	2220	1395
p^b	0.030	0.035
extinction k^c	1.08×10^{-7}	1.32×10^{-7}
R (nonzero wtd data)^d	0.024	0.024
$R_w{}^e$	0.025	0.026
$\sigma_1{}^f$	1.03	1.00

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 47 reflections ($20 < 2\theta < 35$) and 31 reflections ($20 < 2\theta < 30$), respectively. [b] In the least squares, the assigned weights to the data are $w[\sigma(F)]^{-2}$ were derived from $\sigma(F^2) = [S^2 + (pF^2)^2]^{1/2}$, where S^2 is the variance due to counting statistics and *p* is assigned a value that adjusts the weights of the stronger reflections to be more in line with the rest of the data. [c] Simple extinction correction has the form $(F_o)_{cor} = (1 + kI)F_o$, where *I* is the uncorrected intensity and F_o is the observed scattering amplitude. [d] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [e] $R_w = \Sigma [w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. [f] σ_1 = error in observation of unit weight = $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variables.

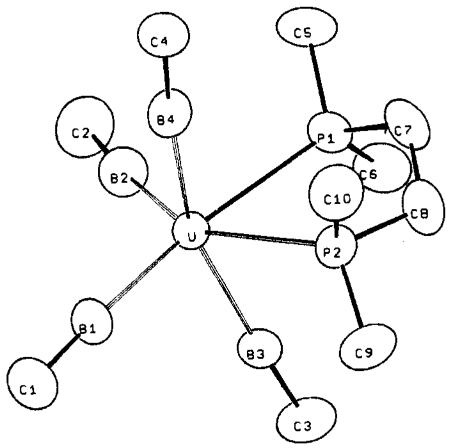

Figure 1. ORTEP drawing of $U(BH_3CH_3)_4DMPE$.

are given in Tables V and VI. Tables of thermal parameters, hydrogen positions, a least-squares plane, and observed structure factors are given as supplementary material.

Table IV. Positional Parameters

atom	*x*	*y*	*z*
	$U(BH_3CH_3)_4DMPE$		
U	0.23288 (3)	0.12147 (2)	0.23278 (2)
P(1)	0.33030 (21)	−0.04850 (14)	0.33826 (13)
P(2)	0.145898 (21)	−0.06610 (14)	0.15196 (13)
B(1)	0.1279 (9)	0.2399 (6)	0.1220 (5)
B(2)	0.3571 (10)	0.2125 (7)	0.3560 (6)
B(3)	0.4504 (9)	0.0885 (6)	0.1593 (5)
B(4)	−0.0082 (8)	0.0925 (6)	0.2861 (6)
C(1)	0.0678 (9)	0.3103 (6)	0.0499 (5)
C(2)	0.4330 (10)	0.2663 (6)	0.4356 (5)
C(3)	0.5883 (8)	0.0650 (7)	0.1156 (5)
C(4)	−0.1511 (8)	0.0664 (6)	0.3237 (5)
C(5)	0.2904 (9)	−0.0438 (7)	0.4435 (5)
C(6)	0.5195 (8)	−0.0790 (6)	0.3495 (5)
C(7)	0.2426 (9)	−0.1585 (5)	0.2968 (5)
C(8)	0.2430 (9)	−0.1647 (5)	0.2068 (5)
C(9)	0.1819 (9)	−0.0842 (6)	0.0482 (5)
C(10)	−0.0399 (8)	−0.1036 (6)	0.1477 (5)
	$U(BH_3CH_3)_3(DMPE)_2$		
U	0.05158 (3)	0.0516	0.0
P(1)	−0.22217 (25)	0.00515 (26)	0.02115 (15)
P(2)	−0.09975 (26)	0.26816 (25)	0.03391 (13)
B(1)	0.2180 (7)	0.2180	0.0
B(2)	−0.0217 (9)	0.0720 (9)	−0.1073 (3)
C(1)	0.3205 (7)	0.3205	0.0
C(2)	−0.0772 (9)	0.0803 (11)	−0.1728 (3)
C(3)	−0.2717 (12)	−0.0611 (13)	0.0876 (5)
C(4)	−0.3085 (9)	−0.0717 (13)	−0.0313 (5)
C(5)	−0.3062 (10)	0.1428 (13)	0.0218 (7)
C(6)	−0.2539 (13)	0.2382 (12)	0.0536 (6)
C(7)	−0.0539 (13)	0.3608 (10)	0.0930 (5)
C(8)	0.1193 (12)	0.3717 (9)	−0.0241 (4)

Table V. Distances (Å)

$U(BH_3CH_3)_4DMPE$		$U(BH_3CH_3)_3(DMPE)_2$	
U–B(1)	2.58 (1)	U–B(1)	2.66 (1)
U–B(2)	2.56 (1)	U–2B(2)	2.62 (1)
U–B(3)	2.56 (1)		
U–B(4)	2.58 (1)		
U–P(1)	3.029 (2)	U–2P(1)	3.174 (3)
U–P(2)	3.017 (2)	U–2P(2)	3.085 (3)
P(1)–C(5)	1.84 (1)	P(1)–C(3)	1.79 (1)
P(1)–C(6)	1.82 (1)	P(1)–C(4)	1.78 (1)
P(1)–C(7)	1.84 (1)	P(1)–C(5)	1.82 (2)
P(2)–C(8)	1.83 (1)	P(2)–C(6)	1.83 (2)
P(2)–C(9)	1.82 (1)	P(2)–C(7)	1.79 (1)
P(2)–C(10)	1.82 (1)	P(2)–C(8)	1.79 (1)
B(1)–C(1)	1.60 (1)	B(1)–C(1)	1.64 (1)
B(2)–C(2)	1.61 (1)	B(2)–C(2)	1.64 (1)
B(3)–C(3)	1.60 (1)		
B(4)–C(4)	1.60 (1)		
C(7)–C(8)	1.50 (1)	C(5)–C(6)	1.43 (2)

Discussion

In $U(BH_3CH_3)_4DMPE$, the uranium(IV) atom is at the center of a distorted octahedron of B and P atoms (see Figure 1); P(1), P(2), B(1), and B(2) are on the equatorial plane and B(3) and B(4) are above and below the plane. The methyltrihydroborate groups coordinate to uranium through tridentate hydrogen bridges. This type of tridentate bridging is found in the $M(CH_3CH_3)_4$ complexes[5] (M = Zr, Th, U, Np) and is characterized by M–B–C angles close to 180° and short M–B distances, ca. 2.5 Å for U(IV). Additional evidence for this kind of bridging is the absence of terminal B–H stretching in the IR spectrum. The uranium atom is coordinated to 12 hydrogen and 2 phosphorus atoms for a total of 14 atoms. The average U–B distance, 2.57 (1) Å, is longer than the average of 2.48 Å found in the 12-coordinate (four tridentate methyltrihydroborates) $U(BH_3CH_3)_4$;[5] the larger U–B distance is attributed to the larger coordination number. The U–P distance average of 3.02 (1) Å is comparable to the U–P

Table VI. Selected Angles (deg)

$\mathrm{U(BH_3CH_3)_4DMPE}$		$\mathrm{U(BH_3CH_3)_3(DMPE)_2}$	
P(1)-U-P(2)	67.4 (1)	P(1)-U-P(1)'[a]	72.6 (2)
P(1)-U-B(1)	168.2 (2)	P(1)-U-P(2)	63.4 (1)
P(1)-U-B(2)	81.8 (2)	P(1)-U-B(2)	81.5 (3)
P(1)-U-B(3)	86.1 (2)	P(1)-U-B(2)'	83.6 (3)
P(1)-U-B(4)	83.9 (2)	P(2)-U-P(2)'	160.6 (1)
P(2)-U-B(1)	100.8 (2)	P(2)-U-B(1)	80.3 (1)
P(2)-U-B(2)	149.2 (2)	P(2)-U-B(2)	89.7 (3)
P(2)-U-B(3)	79.6 (2)	P(2)-U-B(2)'	93.5 (3)
P(2)-U-B(4)	79.3 (2)	B(1)-U-B(2)	99.3 (2)
B(1)-U-B(2)	110.0 (3)	B(2)-U-B(2)'	161.4 (5)
B(1)-U-B(3)	92.0 (3)	U-B(1)-C(1)	180.0
B(1)-U-B(4)	94.1 (3)	U-B(2)-C(2)	175.5 (7)
B(2)-U-B(3)	99.1 (3)		
B(2)-U-B(4)	97.9 (3)		
B(3)-U-B(4)	158.8 (3)		
U-B(1)-C(1)	176.8 (6)		
U-B(2)-C(2)	177.7 (7)		
U-B(3)-C(3)	178.0 (6)		
U-B(4)-C(4)	174.8 (6)		

[a] Primed atoms at *y*, *x*, −*z*.

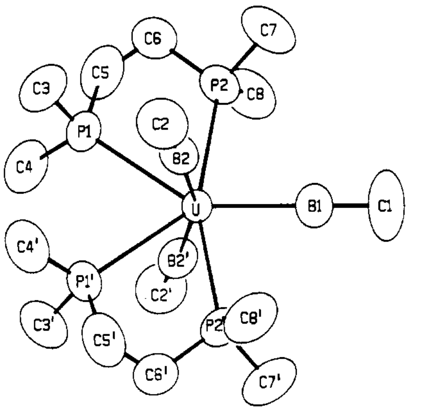

Figure 2. ORTEP drawing of $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$.

distances of 3.10 and 3.02 Å found in $\mathrm{U(OC_6H_5)_4(DMPE)_2}$[6a] and $\mathrm{U(CH_2Ph)_3Me(DMPE)}$,[6b] respectively.

In $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$, the U(III) atom is at the center of a distorted pentagonal bipyramid of B and P atoms (see Figure 2). In the equatorial plane, consisting of 2P(1), 2P(2), B(1), and U, no atom is more than 0.003 Å from the least-squares plane, and the B(2) atoms are 2.58 Å above and below the pentagonal plane. The borons are connected to the uranium atoms through tridentate hydrogen bridges (with U-B-C angles of ~180°); the coordination about the U(III) atom is nine hydrogen and four phosphorus atoms for a total of 13.

The M-B bond length can be correlated with the bonding mode of the hydrogen bridges, i.e., to distinguish between bidentate and tridentate hydrogen bridges.[13] The average U-B distance of 2.64 (2) Å in $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$ is comparable to the average value of 2.68 (4) Å for the axial tridentate U-B bond distance in $\mathrm{U(BH_4)_3(DMPE)_2}$; however, in the latter compound the equatorial U-B distance is 2.84 (3) Å, and it has been assigned to a bidentate hydrogen bridge bond.[4a] It is rather surprising that these two similar compounds exhibit different bonding modes for one of the $\mathrm{BH_3R}$ ($\mathrm{R = H, CH_3}$) ligands. In $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$, the axial U-B(1) distance (2.66 (1) Å) is marginally longer than the equatorial U-B(2) distance (2.62 (1) Å).

In $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$, the U-P(2) distance of 3.085 (3) Å is 0.09 Å shorter than the U-P(1) distance of 3.174 (3) Å and can be explained as a steric effect by comparing interligand contact distances. At the P(2) site, methyl carbons C(7) and C(8) are more than 4 Å away from B(1), B(2) and C(1); at the P(1) site, the interligand C(3)-C(4′) distance is 3.80 Å. Given a van der Waals radius for the methyl group of 2.0 Å,[14] it seems reasonable that methyl-methyl repulsive forces are the reason for the longer U-P(1) bond. The individual U-P bond lengths in $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$ are each 0.03 Å longer than the comparable bond lengths in $\mathrm{U(BH_4)_3(DMPE)_2}$.[4a]

The U-B distance is greater by ~0.07 Å for $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$ than for $\mathrm{U(BH_3CH_3)_4DMPE}$, due to the larger ionic radius of U(III). The average U-H distances in $\mathrm{U(BH_3CH_3)_4DMPE}$ and $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$ are 2.39 ± 0.1 and 2.50 ± 0.1 Å, respectively, and the average U-P distances are 3.02 ± 0.01 and 3.13 ± 0.06 Å, respectively.

Considering $\mathrm{U(BH_3CH_3)_4DMPE}$ and $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$ to be pseudo-six- and -seven-coordinate, respectively, their solution behavior then parallels that of the d-block metals. Octahedral d-transition-metal complexes are usually rigid on the NMR time scale, while seven-coordinate complexes are usually fluxional.[15] The same type of behavior is observed with these uranium complexes. Table II shows the observed chemical shifts for the $\mathrm{BH_3CH_3}$ groups. At low temperatures, two resonances can be observed due to the $\mathrm{BH_3CH_3}$ groups cis and trans to the P atoms of DMPE for the U(IV) compound. As the temperature of the sample is raised, the inequivalent $\mathrm{BH_3CH_3}$ groups exchange rapidly, leading to an observed coalescence at +10 °C. The chemical shift difference between the cis and trans $\mathrm{BH_3}$ protons is ~400 ppm at −20 °C. By comparison, the seven-coordinate U(III) compound is fluxional on the NMR time scale, and no inequivalent sites could be observed for either the methyltrihydroborate or the phosphine ligands down to −95 °C. The U(IV)-$\mathrm{BH_3CH_3}$ exchange mechanism will be discussed in detail in a subsequent paper.

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Registry No. $\mathrm{U(BH_3CH_3)_4DMPE}$, 92958-52-6; $\mathrm{U(BH_3CH_3)_3(DMPE)_2}$, 92958-53-7; $\mathrm{U(BH_3CH_3)_4}$, 86217-20-1.

Supplementary Material Available: Listings of hydrogen positions, thermal parameters, distance restraints, uranium-hydrogen distances, a least-squares plane, and observed structure factors (30 pages). Ordering information is given on any current masthead page.

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