## Title

PREPARATION OF TERTIARY PHOSPHINE COMPLEXES OF TETRAVALENT AND TRIVALENT URANIUM METHYLTRIHYDROBORATES; THE CRYSTAL STRUCTURES OF TETRAKIS(METHYLTRIIIYDROBORATO) URANIUM (IV) 1,2-DIMETHYLPHOSPHINOETHANE AND TRIS (METHYL-TRIHYDROBORATO)URANIUM (III) B...

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# PREPARATION OF TERTIARY PHOSPHINE COMPLEXES OF TETRAVALENT AND TRIVALENT URANIUM METHYLTRIHYDROBORATES; THE CRYSTAL STRUCTURES OF TETRAKIS(METHYLTRIHYDROBORATO)URANIUM(IV) 1,2-DIMETHYLPHOSPHINOETHANE AND TRIS(METHYLTRIHYDROBORATO)URANIUM(III) BIS(1,2-DIMETHYLPHOSPHINOETHANE)

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and N. Edelstein

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# Preparation of Tertiary Phosphine Complexes of Tetravalent and Trivalent Uranium Methyltrihydroborates; the Crystal Structures of Tetrakis(methyltrihydroborato)uranium(IV) 1,2-dimethylphosphinoethane and tris(methyltrihydroborato) uranium(III)bis(1,2-dimethylphosphinoethane)

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## Abstract

$(CH_3BH_3)_4U[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ 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, $P2_1/c$, $\underline{a} = 9.439(3)$Å, $\underline{b} = 14.023(4)$Å, $\underline{c} = 16.596(2)$Å, $\beta = 97.48(4)$Å, $Z = 4$, $d_x = 1.536$ 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, $P4_32_12$, $a = 11.297(4)$, $c = 23.03(2)$, $Z = 4$, $d_x = 1.412$ 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 distance for the U(IV) and U(III) complexes average 2.57 ± 0.01Å and 2.63 ± 0.02Å,

respectively; the U-P distances for the U(IV) and U(III) complexes average 3.02 ± 0.01Å and 3.13 ± 0.06Å, respectively.

## Introduction

Four Lewis base etherate adducts of $U(BH_4)_4$ have been structurally characterized and 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-dimethylphosphinoethane) and $U(BH_4)_3(Ph_2Ppy)_2$ ($Ph_2Ppy$ = 2-(diphenylphosphino)pyridine) from the reactions of $U(BH_4)_3THF_x$ (THF = tetrahydrofuran) with the appropriate ligands.[4] An 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, and 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-dimethylphosphinoethane 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 dry box 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 dry box 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 pmr 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 0.24g (0.68 mmole) $U(BH_3CH_3)_4$ dissolved in 20 ml pentane, 0.11 ml (0.66 mmoles) of DMPE was added with stirring, giving a green ppt. The solution was stirred for 5 minutes and then pumped to dryness. The green residue was dissolved in 10 ml toluene, filtered, concentrated to 3 ml, and the solution was cooled at -20°C. After 3 hours green crystals had formed. The supernate was removed and the green crystals washed with 2 ml ether and pumped to dryness. A yield of 0.16 g (48 percent yield) $U(BH_3CH_3)_4$DMPE was recovered. Mp = 131-2°C (dec). Calculated 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 mmole) $U(BH_3CH_3)_4$DMPE dissolved in 10 ml. toluene, 0.40 ml (2.4 mmoles) of DMPE was added with stirring. The solution was heated to ~80°C for several hours, during which it turned deep brown. After cooling to room temperature, the toluene was pumped off and a solution of the dark brown residue in 15 ml. 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 percent yield) of $U(BH_3CH_3)_3(DMPE)_2$ was recovered. M.p. = 130-2°C. Calculated for $C_{15}H_{50}B_3P_4U$: C, 28.83; H, 8.07. Found: C, 29.01; H, 8.25.

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-two 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 3-dimensional Patterson maps, and subsequent least-squares 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 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 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 are given in Tables V and VI. Tables of thermal parameters, hydrogen positions, least-squares plane, and observed structure factors are given as supplementary material.

## Discussion

In $U(BH_3CH_3)_4$DMPE the uranium (IV) atom is at the center of a distorted octahedron of B and P atoms, see fig. 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. 2.5Å 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 phosphorous atoms for a total of 14 atoms. The average U-B distance, 2.57(1)Å, is longer than the average of 2.48Å 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 distances of 3.10Å and 3.02Å found in $U(OC_6H_5)_4(DMPE)_2$[6a] and $U(CH_2Ph)_3Me(DMPE)$,[6b] respectively.

In $U(BH_3CH_3)_3(DMPE)_2$, the U(III) atom is at the center of a distorted pentagonal bipyramid of B and P atoms, see fig. 2. In the equatorial plane, consisting of 2P(1), 2P(2), B(1), and U, no atom is more than 0.003Å from the least-squares plane, and the B(2) atoms are 2.58Å 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 9 hydrogen and 4 phosphorous 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 $U(BH_3CH_3)_3(DMPE)_2$ is comparable to the average value of 2.68(4)Å for the axial tridentate U-B bond distance in $U(BH_4)_3(DMPE)_2$; however in the latter compound the equatorial U-B distance is 2.84(3)Å and 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 $BH_3R$ ($R=H,CH_3$) ligands. In $U(BH_3CH_3)_3(DMPE)_2$ 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 $U(BH_3CH_3)_3(DMPE)_2$, the U-P(2) distance of 3.085(3)Å is 0.09Å shorter than the U-P(1) distance of 3.174(3)Å, and can be explained as a steric effect by comparing inter-ligand contact distances. At the P(2) site, methyl carbons C(7) and C(8) are more than 4Å away from B(1), B(2), and C(1); at the P(1) site, the inter-ligand C(3)-C(4') distance is 3.80Å. Given a van der Waals radius for the methyl group of 2.0Å,[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 $U(BH_3CH_3)_3(DMPE)_2$ are each 0.03Å longer than the comparable bond lengths in $U(BH_4)_3(DMPE)_2$[4a].

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

Considering $U(BH_3CH_3)_4DMPE$ and $U(BH_3CH_3)_3(DMPE)_2$ 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 I shows the observed chemical shifts for the $BH_3CH_3$ groups. At low temperatures two resonances can be observed due to the $BH_3CH_3$ 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 $BH_3CH_3$ groups exchange rapidly, leading to an observed coalescence at +10 C. The chemical shift difference between the cis and trans $BH_3$ 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 phosphine ligands down to -95 C. The U(IV) $BH_3CH_3$ exchange mechanism will be discussed in detail in a subsequent paper.

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

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# Table I

## Infrared Spectroscopic Data ($cm^{-1}$)

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

### Table II

### Proton Magnetic Resonances Data[a,b]

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

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[a] All samples 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.

## 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<br>0k0, k=2n | 00l, l=4n<br>h00, h=2n |
| space group | $P2_1/c$ | $P4_32_12$ |
| data crystal dimens., mm | 0.15X0.17X0.29 | 0.12X0.14X0.66 |
| abs coeff, $cm^{-1}$ | 71.9 | 54.5 |
| abs correction range | 1.46-4.88 | 1.81-2.11 |
| crystal decay corr | 1.00-1.02 | 1.00-1.08 |
| 2θ range, deg. | 4-50 | 4-45 |
| hkl range | $0<h<11$<br>$0<k<16$<br>$-19<l<19$ | $-12<h<12$<br>$0<k<12$<br>$0<l<24$ |
| 2θ scan width (deg) | 1.10+.693 tanθ | 1.50+.693 tanθ |
| no. of standards | 3 | 3 |
| no. reflections between stds | 100 | 250 |
| no. scan data | 8091 | 4296 |
| no. unique reflections | 3976 | 1960 |
| no. non-zero weighted data | 2220 ($F^2>3\sigma$) | 1395 ($F^2>3\sigma$) |

Table III continued

| | $U(BH_3CH_3)_4DMPE^{(a)}$ | $U(BH_3CH_3)_3(DMPE)_2{}^{(a)}$ |
|---|---|---|
| $p^b$ | 0.030 | 0.035 |
| extinction $k^c$ | $1.08X10^{-7}$ | $1.32X10^{-7}$ |
| R (non-zero wtd data)[d] | 0.024 | 0.024 |
| $Rw^e$ | 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 MoKα components of 47 reflections (20<2θ<35) and 31 reflections (20<2θ<30), respectively.

[b] In the least-squares, the assigned weights to the data are $w[\sigma(F)]^{-2}$ were derived from $\sigma(F^2) = [S^2+pF^2]^{1/2}$, 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 $(F_o)_{corr}=(1+KI)F_o$, 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] $Rw = \Sigma[w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

[f] $\sigma_1$ = 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.

## Table IV.
## Positional Parameters

### $U(BH_3CH_3)_4DMPE$

| ATOM | X | Y | Z |
|---|---|---|---|
| U | .23288(3) | .12147(2) | .23278(2) |
| P(1) | .33030(21) | -.04850(14) | .33826(13) |
| P(2) | .145898(21) | -.06610(14) | .15196(13) |
| B(1) | .1279(9) | .2399(6) | .1220(5) |
| B(2) | .3571(10) | .2125(7) | .3560(6) |
| B(3) | .4504(9) | .0885(6) | .1593(5) |
| B(4) | -.0082(8) | .0925(6) | .2861(6) |
| C(1) | .0678(9) | .3103(6) | .0499(5) |
| C(2) | .4330(10) | .2663(6) | .4356(5) |
| C(3) | .5883(8) | .0650(7) | .1156(5) |
| C(4) | -.1511(8) | .0664(6) | .3237(5) |
| C(5) | .2904(9) | -.0438(7) | .4435(5) |
| C(6) | .5195(8) | -.0790(6) | .3495(5) |
| C(7) | .2426(9) | -.1585(5) | .2968(5) |
| C(8) | .2430(9) | -.1647(5) | .2068(5) |
| C(9) | .1819(9) | -.0842(6) | .0482(5) |
| C(10) | -.0399(8) | -.1036(6) | .1477(5) |

### $U(BH_3CH_3)_3(DMPE)_2$

| ATOM | X | Y | Z |
|---|---|---|---|
| U | .05158(3) | .0516 | 0.0 |
| P(1) | -.22217(25) | .00515(26) | .02115(15) |
| P(2) | -.09975(26) | .26816(25) | .03391(13) |
| B(1) | .2180(7) | .2180 | 0.0 |
| B(2) | -.0217(9) | .0720(9) | -.1073(3) |
| C(1) | .3205(7) | .3205 | 0.0 |
| C(2) | -.0772(9) | .0803(11) | -.1728(3) |
| C(3) | -.2717(12) | -.0611(13) | .0876(5) |
| C(4) | -.3085(9) | -.0717(13) | -.0313(5) |
| C(5) | -.3062(10) | .1428(13) | .0218(7) |
| C(6) | -.2539(13) | .2382(12) | .0536(6) |
| C(7) | -.0539(13) | .3608(10) | .0930(5) |
| C(8) | .1193(12) | .3717(9) | -.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) |
| -B(2) | 2.56(1) | U-2B(2) | 2.62(1) |
| -B(3) | 2.56(1) | | |
| -B(4) | 2.58(1) | | |
| U-P(1) | 3.029(2) | U-2P(1) | 3.174(3) |
| -P(2) | 3.017(2) | -2P(2) | 3.085(3) |
| P(1)-C(5) | 1.84(1) | P(1)-C(3) | 1.79(1) |
| -C(6) | 1.82(1) | -C(4) | 1.78(1) |
| -C(7) | 1.84(1) | -C(5) | 1.82(2) |
| P(2)-C(8) | 1.83(1) | P(2)-C(6) | 1.83(2) |
| -C(9) | 1.82(1) | -C(7) | 1.79(1) |
| -C(10) | 1.82(1) | -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) |

### Table VI.
### Selected Angles

| $U(BH_3CH_3)_4DMPE$ | | $U(BH_3CH_3)_3(DMPE)_2$ | |
|---|---|---|---|
| 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] Atoms at y,x,-z.

## Figure Captions

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

Figure 2. ORTEP drawing of $U(BH_3CH_3)_3(DMPE)_2$

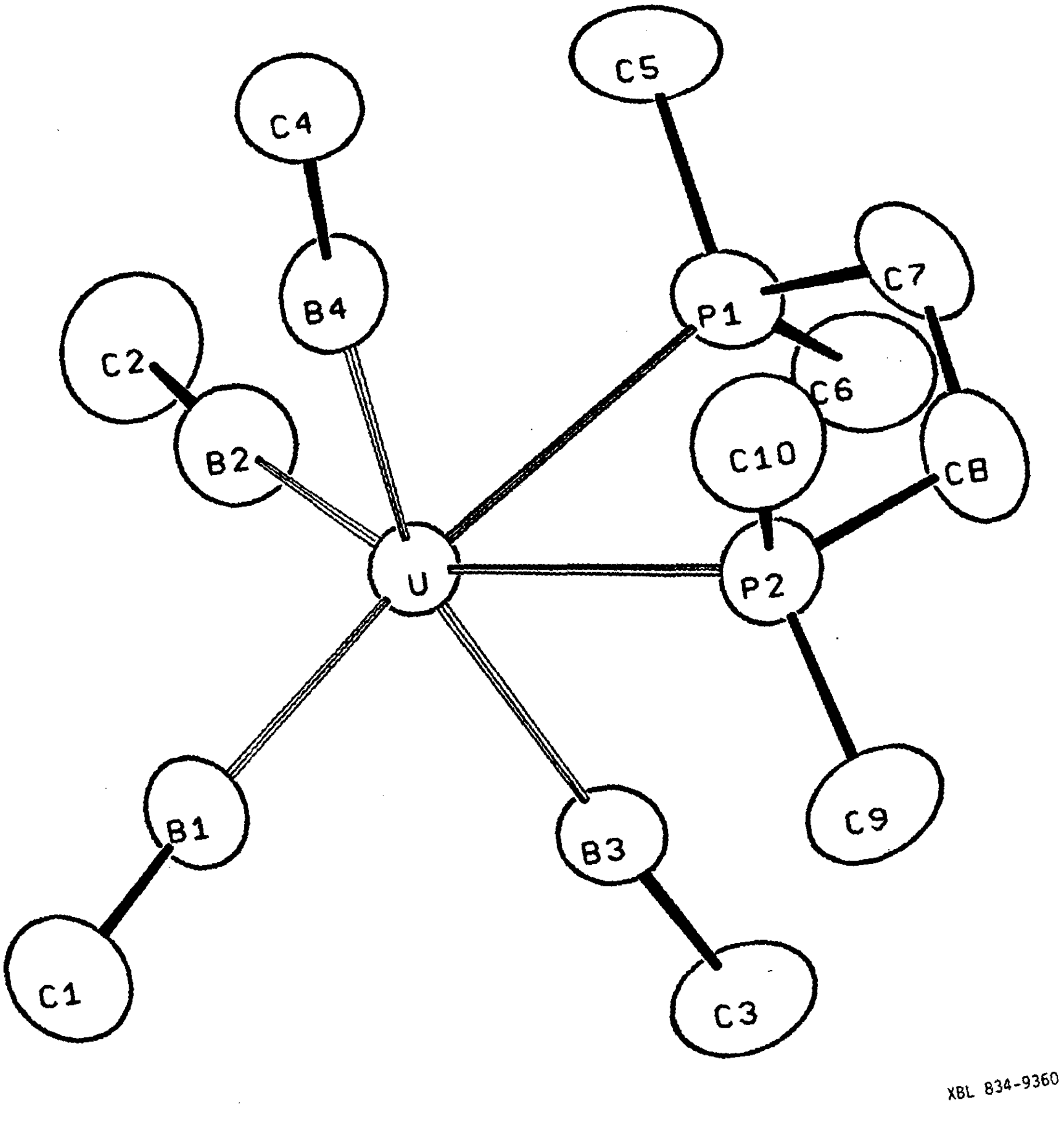
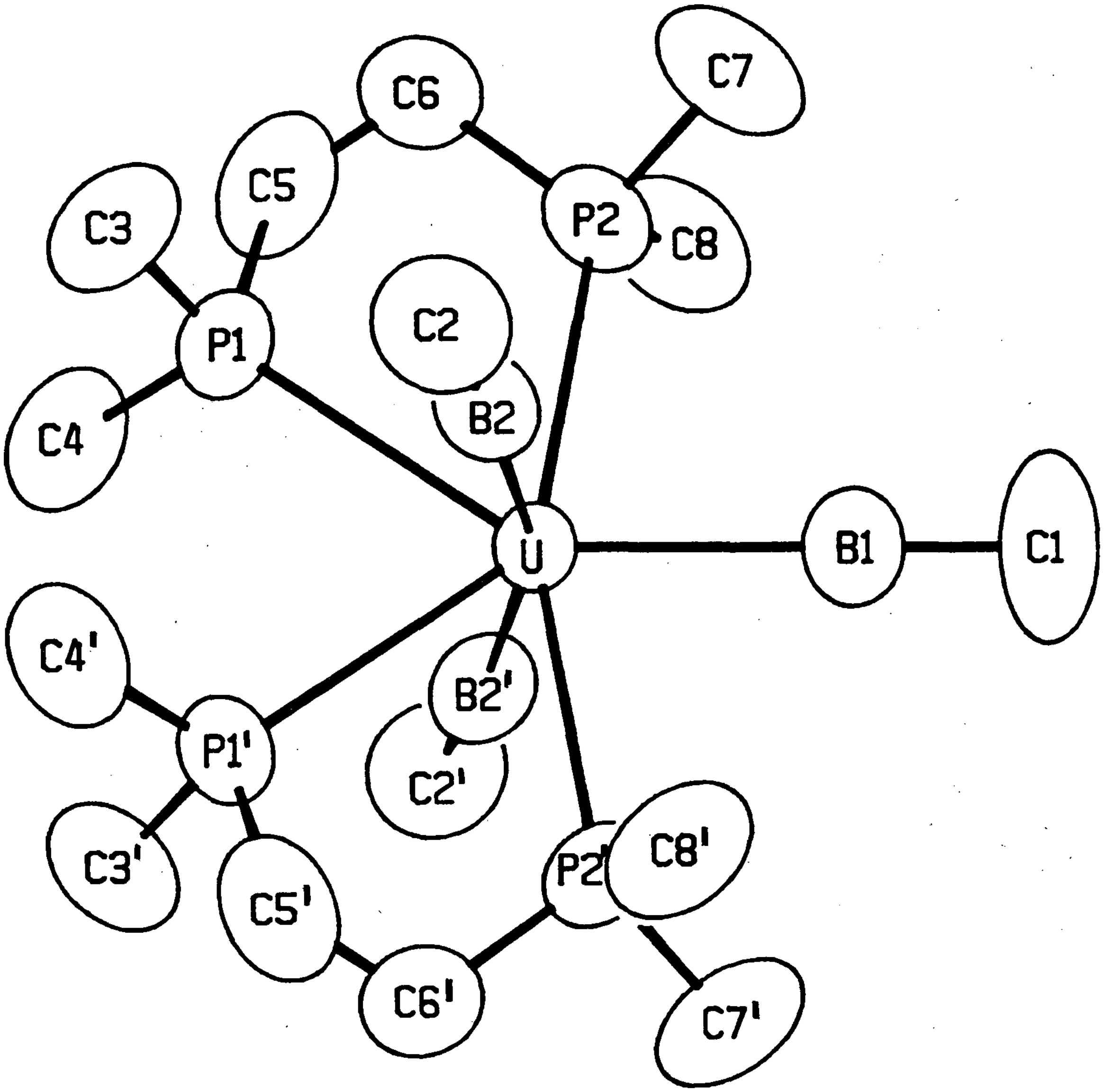


Figure 1



XBL 841-8

Figure 2

## Supplementary Material

# Preparation of Tertiary Phosphine Complexes of Tetravalent and Trivalent Uranium Methyltrihydroborates; the Crystal Structures of Tetrakis(methyltrihydroborato)uranium(IV) 1,2-dimethylphosphinoethane and tris(methyltrihydroborato) uranium(III)bis(1,2-dimethylphosphinoethane)

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# Table of Hydrogen Positions [a]

## $U(BH_3CH_3)_4$ DMPE

| | | | |
|---|---|---|---|
| H(1) | .110(4) | .1617(7) | .1043(15) |
| H(2) | .074(4) | .2515(25) | .1787(11) |
| H(3) | .2472(16) | .2491(25) | .1410(21) |
| H(4) | .113(5) | .300(3) | .0003(14) |
| H(5) | .084(6) | .3782(7) | .0650(18) |
| H(6) | -.0363(17) | .303(3) | .0338(27) |
| H(7) | .317(4) | .2643(15) | .3056(12) |
| H(8) | .262(3) | .1687(27) | .3700(14) |
| H(9) | .4341(26) | .1616(26) | .3306(19) |
| H(10) | .478(6) | .2207(14) | .4769(17) |
| H(11) | .3647(25) | .304(4) | .4623(23) |
| H(12) | .509(5) | .310(4) | .4230(14) |
| H(13) | .437(3) | .0351(22) | .2094(20) |
| H(14) | .457(3) | .1621(16) | .1882(25) |
| H(15) | .3478(13) | .096(3) | .1149(13) |
| H(16) | .6780(12) | .084(4) | .1499(18) |
| H(17) | .597(4) | .039(3) | .0636(18) |
| H(18) | .596(4) | -.0037(11) | .104(3) |
| H(19) | .034(3) | .1661(15) | .3053(24) |
| H(20) | -.0240(25) | .031(3) | .2170(7) |
| H(21) | .0816(19) | .0397(21) | .3068(23) |
| H(22) | -.2322(21) | .108(3) | .303(3) |
| H(23) | -.182(4) | -.0002(17) | .311(3) |
| H(24) | -.1386(29) | .072(4) | .3836(8) |
| H(25) | .342(4) | .0099(23) | .4664(12) |
| H(26) | .323(5) | -.1034(18) | .4652(12) |
| H(27) | .1891(14) | -.036(4) | .4382(9) |
| H(28) | .5283(18) | -.1339(23) | .3838(27) |
| H(29) | .5572(13) | -.0241(18) | .3739(29) |
| H(30) | .5400(19) | -.031(4) | .2957(10) |
| H(31) | .1480(15) | -.1535(14) | .3133(10) |
| H(32) | .2967(24) | -.2381(7) | .3273(8) |
| H(33) | .3378(14) | -.1601(15) | .1900(9) |
| H(34) | .1948(24) | -.2208(6) | .1823(9) |
| H(35) | .152(5) | -.1478(15) | .0347(13) |
| H(36) | .2825(16) | -.075(4) | .0496(11) |
| H(37) | .126(4) | -.0368(25) | .0168(8) |
| H(38) | -.0539(21) | -.115(4) | .2026(9) |
| H(39) | -.0472(21) | -.1598(22) | .1147(27) |
| H(40) | -.0945(12) | -.0514(18) | .1231(29) |

## Table of Hydrogen Positions (continued)

### $U(BH_3CH_3)_3$ $DMPE_2$

| | | | |
|---|---|---|---|
| H(1) | .129(5) | .259(8) | .014(15) |
| H(2) | .244(15) | .144(15) | .032(13) |
| H(3) | .209(23) | .178(24) | -.0460(27) |
| H(4) | -.075(4) | .005(4) | -.0801(10) |
| H(5) | .0755(19) | .042(6) | -.1097(9) |
| H(6) | -.026(5) | .1633(18) | -.0852(12) |
| H(7) | .381(17) | .300(17) | .029(13) |
| H(8) | .284(8) | .397(7) | .010(16) |
| H(9) | .356(24) | .325(24) | -.039(4) |
| H(10) | -.118(4) | .1561(24) | -.1769(11) |
| H(11) | -.133(4) | .015(3) | -.1783(11) |
| H(12) | -.0129(16) | .075(5) | -.2010(5) |
| H(13) | -.241(5) | -.1418(23) | .0893(15) |
| H(14) | -.3581(13) | -.052(5) | .0876(14) |
| H(15) | -.241(5) | -.014(4) | .1199(4) |
| H(16) | -.280(4) | -.052(5) | -.0702(4) |
| H(17) | -.3914(14) | -.048(5) | -.0272(22) |
| H(18) | -.301(5) | -.1568(12) | -.0246(20) |
| H(19) | -.3886(13) | .1202(17) | .014(4) |
| H(20) | -.276(5) | .190(4) | -.0109(26) |
| H(21) | -.2898(23) | .3161(14) | .060(3) |
| H(22) | -.2496(16) | .195(6) | .0906(19) |
| H(23) | .016(4) | .435(5) | .0809(13) |
| H(24) | -.036(6) | .3102(17) | .1263(11) |
| H(25) | -.1183(26) | .415(4) | .1022(21) |
| H(26) | -.0417(16) | .403(4) | -.0348(19) |
| H(27) | -.171(4) | .436(3) | -.0106(12) |
| H(28) | -.155(5) | .3305(20) | -.0569(11) |

[a] These positions are the result of distance-restrained least-squares refinements, and the quoted estimated standard deviations in parentheses are not significant.

## Tables of Anisotropic Thermal Parameters [a]

### $U(BH_3CH_3)_4$ DMPE

| ATOM | B11 | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|
| U | 3.145(11) | 3.009(10) | 3.953(12) | -.195(14) | .984(8) | -.037(14) |
| P(1) | 3.83(9) | 4.57(10) | 4.30(11) | -.05(8) | .66(8) | .75(8) |
| P(2) | 4.33(9) | 3.99(9) | 4.45(11) | -.30(8) | .92(9) | -.48(8) |
| B(1) | 4.3(4) | 4.0(4) | 5.4(6) | .5(4) | 1.1(4) | .0(4) |
| B(2) | 5.4(5) | 4.6(5) | 6.1(6) | -1.4(4) | 1.2(5) | -1.1(4) |
| B(3) | 4.7(4) | 4.5(4) | 5.0(5) | .0(4) | 1.4(4) | .8(4) |
| B(4) | 4.4(4) | 4.2(4) | 6.2(6) | .1(3) | 1.3(4) | -.4(4) |
| C(1) | 7.4(5) | 5.9(5) | 6.1(5) | 1.2(4) | 1.1(4) | 1.0(4) |
| C(2) | 8.2(5) | 7.7(6) | 6.3(6) | -2.0(5) | .1(5) | -1.6(5) |
| C(3) | 4.6(4) | 8.7(6) | 6.5(6) | .9(4) | 2.1(4) | .2(5) |
| C(4) | 4.8(4) | 6.0(5) | 8.0(6) | .0(4) | 2.9(4) | .9(4) |
| C(5) | 6.1(5) | 8.3(6) | 4.9(5) | -.7(4) | 1.0(4) | 1.3(4) |
| C(6) | 4.7(4) | 7.6(5) | 6.3(6) | .7(4) | 1.2(4) | 2.1(4) |
| C(7) | 6.3(5) | 4.8(4) | 5.3(5) | .2(4) | .3(4) | 2.2(3) |
| C(8) | 7.2(5) | 3.5(3) | 5.3(5) | -.6(4) | -.7(5) | -.8(3) |
| C(9) | 6.8(5) | 7.0(5) | 6.3(6) | .0(4) | 1.7(4) | -1.1(4) |
| C(10) | 5.6(4) | 5.7(5) | 6.9(5) | -1.5(4) | .7(4) | -.9(4) |

### $U(BH_3CH_3)_3$ $DMPE_2$

| ATOM | B11 | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|
| U | 4.304(13) | 4.3042 | 3.486(16) | -.495(22) | -.085(16) | .085 |
| P(1) | 5.07(13) | 7.16(15) | 10.54(25) | -1.03(12) | 1.71(14) | -1.65(14) |
| P(2) | 7.51(17) | 5.09(14) | 6.99(15) | .42(11) | -.2((13) | -.81(13) |
| B(1) | 8.6(7) | 8.5644 | 5.6(8) | -2.8(9) | .7(8) | -.7399 |
| B(2) | 6.1(5) | 7.7(7) | 4.7(4) | -.4(5) | .0(4) | .6(5) |
| C(1) | 13.9(10) | 13.9274 | 9.8(10) | -5.4(12) | -2.9(11) | 2.8824 |
| C(2) | 9.3(5) | 12.9(11) | 5.6(4) | -.1(6) | -1.8(5) | .5(6) |
| C(3) | 10.2(9) | 11.2(9) | 15.6(12) | -1.3(8) | 6.3(9) | -.5(10) |
| C(4) | 5.2(6) | 17.5(14) | 15.8(12) | -3.2(8) | .5(7) | -4.9(11) |
| C(5) | 4.7(6) | 9.9(9) | 22.0(19) | .6(6) | 2.0(8) | -1.3(11) |
| C(6) | 8.0(9) | 6.7(8) | 16.3(11) | 1.2(5) | 3.0(8) | -3.0(8) |
| C(7) | 14.1(9) | 7.3(6) | 9.2(7) | 1.6(8) | -2.0(8) | -2.3(6) |
| C(8) | 14.8(11) | 5.4(6) | 10.2(9) | 2.1(7) | -.8(8) | .5(6) |

[a] Anisotropic temperature factor has the form $\exp[-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)]$.

## Tables of Isotropic Thermal Parameters[a]

### $U(BH_3CH_3)_4$ DMPE

| | | | |
|---|---|---|---|
| H(1) | 6.5(5) | H(21) | 6.5162 |
| H(2) | 6.5162 | H(22) | 9.9572 |
| H(3) | 6.5162 | H(23) | 9.9572 |
| H(4) | 10.0(8) | H(24) | 9.9572 |
| H(5) | 9.9572 | H(25) | 7.6(7) |
| H(6) | 9.9572 | H(26) | 7.5887 |
| H(7) | 6.5162 | H(27) | 7.5887 |
| H(8) | 6.5162 | H(28) | 7.5887 |
| H(9) | 6.5162 | H(29) | 7.5887 |
| H(10) | 9.9572 | H(30) | 7.5887 |
| H(11) | 9.9572 | H(31) | 6.7(11) |
| H(12) | 9.9572 | H(32) | 6.6782 |
| H(13) | 6.5162 | H(33) | 6.6782 |
| H(14) | 6.5162 | H(34) | 6.6782 |
| H(15) | 6.5162 | H(35) | 7.5887 |
| H(16) | 9.9572 | H(36) | 7.5887 |
| H(17) | 9.9572 | H(37) | 7.5887 |
| H(18) | 9.9572 | H(38) | 7.5887 |
| H(19) | 6.5162 | H(39) | 7.5887 |
| H(20) | 6.5162 | H(40) | 7.5887 |

### $U(BH_3CH_3)_3$ $DMPE_2$

| | | | |
|---|---|---|---|
| H(1) | 10.000 | H(15) | 10.000 |
| H(2) | 10.000 | H(16) | 10.000 |
| H(3) | 10.000 | H(17) | 10.000 |
| H(4) | 10.000 | H(18) | 10.000 |
| H(5) | 10.000 | H(19) | 10.000 |
| H(6) | 10.000 | H(20) | 10.000 |
| H(7) | 10.000 | H(21) | 10.000 |
| H(8) | 10.000 | H(22) | 10.000 |
| H(9) | 10.000 | H(23) | 10.000 |
| H(10) | 10.000 | H(24) | 10.000 |
| H(11) | 10.000 | H(25) | 10.000 |
| H(12) | 10.000 | H(26) | 10.000 |
| H(13) | 10.000 | H(27) | 10.000 |
| H(14) | 10.000 | H(28) | 10.000 |

---

[a] The form of the isotropic temperature factor is $\exp(-B\sin^2\theta/\lambda^2)$.

## Distance Restraints

| $U(BH_3CH_3)_4$ DMPE | |
|---|---|
| B - $H_B$ | 1.14(1) |
| C - $H_C$ | 0.98(1) |
| $H_B$ - $H_B$ | 1.83(1) |
| $H_C$ - $H_C$ | 1.59(1) |
| $H_C$ - B | 2.18(1) |
| $H_B$ - C | 2.28(1) |
| $H_C$ - P | 2.26(1) |

| $U(BH_3CH_3)$ $DMPE_2$ | |
|---|---|
| B - $H_B$ | 1.150(5) |
| C - $H_C$ | 0.980(5) |
| $H_B$ - $H_B$ | 1.88(1) |
| $H_C$ - $H_C$ | 1.60(1) |
| $H_C$ - B | 2.16(1) |
| $H_B$ - C | 2.30(1) |
| $H_C$ - P | 2.29(1) |
| $H_B$ - $H_C$ | 2.35(1) |

U - H Distances (Å)

$U(BH_3CH_3)_4$ DMPE

| | |
|---|---|
| U - H(1) | 2.36 |
| U - H(2) | 2.46 |
| U - H(3) | 2.37 |
| U - H(7) | 2.42 |
| U - H(8) | 2.35 |
| U - H(9) | 2.40 |
| U - H(13) | 2.35 |
| U - H(14) | 2.40 |
| U - H(15) | 2.41 |
| U - H(19) | 2,44 |
| U - H(20) | 2.44 |
| U - H(21) | 2.31 |

Average = 2.39 ± 0.04

$U(BH_3CH_3\ DMPE_2$

| | |
|---|---|
| U - 2 H(1) | 2.52 |
| U - 2 H(2) | 2.52 |
| U - 2 H(3) | 2.52 |
| U - 2 H(4) | 2.39 |
| U - 2 H(5) | 2.54 |
| U - 2 H(6) | 2.49 |

Average = 2.50 ± 0.05

## Least Squares Plane in $U(BH_3CH_3)$ $DMPE_2$

### Equation of Plane

$$2.056\,a - 2.056\,b + 22.254\,c = 0$$

### Distances to the Plane (Å)

| | |
|---|---|
| Atoms in the plane | |
| U | 0.000 |
| P(1) | 0.003 |
| P(1)' | -0.003 |
| P(2) | -0.002 |
| P(2)' | 0.002 |
| B(1) | 0.000 |
| Atoms not in the plane | |
| B(2) | -2.580 |
| C(1) | 0.000 |

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