Synthesis and characterization of phosphine adducts of thorium borohydride, $Th(BH_4)_4$
Crystal structures of $Th(BH_4)_4(PEt_3)_2$ and $Th(BH_4)_4(Me_2PCH_2CH_2PMe_2)_2$

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ABSTRACT

Addition of tertiary phosphines to $Th(BH_4)_4(Et_2O)_2$ yields the new Lewis base adducts, $Th(BH_4)_4(PMe_3)_2$, $Th(BH_4)_4(PEt_3)_2$, and $Th(BH_4)_4(dmpe)_2$, where dmpe = 1,2-bis(dimethylphosphino)ethane. If one considers the BH_4^- groups to occupy one coordination site, then $Th(BH_4)_4(PEt_3)_2$ adopts a trans-octahedral geometry, and $Th(BH_4)_4(dmpe)_2$ adopts a trigonal dodecahedral geometry with the dmpe ligands bridging between the "inner" sites. In the PMe_3 and PEt_3 complexes, all four BH_4^- groups are κ^3, whereas in the dmpe complex two of the BH_4^- groups are κ^2 and two are κ^3. In the dmpe complex, the $Th \cdots B$ distances to the κ^2 and κ^3 BH_4^- groups are 2.91 and 2.69 Å, respectively. All of the Lewis base adducts of $Th(BH_4)_4$ are volatile and may be sublimed in vacuum. They have been characterized by infrared and ^1H, ^{11}B, and ^{31}P NMR spectroscopy. The results show that thorium complexes of unidentate phosphines can be made and are stable enough to isolate and characterize. ^{31}P NMR coordination chemical shifts of thorium phosphine complexes are on the order of 30–45 ppm. The compound $Th(BH_4)_4(dmpe)_2$ is the first thorium complex to contain κ^2 BH_4^- groups.

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1. Introduction

The thorium(IV) ion was classically regarded a class A or hard Lewis acid that binds strongly to hard Lewis bases such as nitrogen and oxygen donors, but poorly to soft Lewis bases such as phosphorus or sulfur donors [1,2]. This view was supported by unsuccessful efforts to make tertiary phosphine complexes of thorium in the 1960s [3,4]. In fact, thorium can form phosphine complexes as shown in the 1980s by Andersen, who prepared a series of ThX_4 (dmpe)$_2$ complexes where dmpe is 1,2-bis(dimethylphosphino) ethane and X is halide, alkyl, or alkoxide [5,6]. Since then, however, only a few other thorium phosphine complexes have been described: $Cp_2ThX_2(dmpe)$, where X is halide, alkyl, or alkoxide [7,8]; the mixed phosphinophosphide $Th[P(CH_2CH_2PMe_2)_2]_4$ and its CO insertion product [9]; and phosphinoamide complexes of stoichiometry $ThCl_x[N(CH_2CH_2PR_2)_2]_{4-x}$, where $x = 1-3$ [9]. Although competitive binding studies show that trivalent actinides bind phosphines in preference to amines [10], there have been no comparable studies of tetravalent actinides. In all known thorium phosphine complexes, the phosphine is chelating, which suggests that perhaps thorium(IV) binds phosphines weakly compared with trivalent actinides. The preparation of a thorium(IV) complex of a unidentate phosphine would be of interest in this context.

Here we report the synthesis of three trialkylphosphine adducts of $Th(BH_4)_4$, including the first complexes of thorium bearing a unidentate phosphine ligand. Crystal structures of two of them are described.

2. Results and discussion

2.1. Synthesis of phosphine adducts of $Th(BH_4)_4$

An obvious starting material for the preparation of Lewis base adducts of the form $Th(BH_4)_4L_x$ is the known binary compound $Th(BH_4)_4$, which was originally made by the reaction of ThF_4 with explosive $Al(BH_4)_3$ [11]. A more convenient starting material is the etherate $Th(BH_4)_4(Et_2O)_2$, which can be prepared by the reaction of $ThCl_4$ with $LiBH_4$ in diethyl ether [12]. We find that addition of trialkylphosphines to $Th(BH_4)_4(Et_2O)_2$ in diethyl ether yields the

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new phosphine complexes $Th(BH_4)_4(PMe_3)_2$ (**1**), $Th(BH_4)_4(PEt_3)_2$ (**2**), and $Th(BH_4)_4(dmpe)_2$ (**3**), where dmpe = $Me_2PCH_2CH_2PMe_2$.

$$Th(BH_4)_4(Et_2O)_2 + 2PR_3 \longrightarrow Th(BH_4)_4(PR_3)_2 + 2Et_2O$$

1, $PR_3 = PMe_3$
2, $PR_3 = PEt_3$
3, $PR_3 = dmpe$
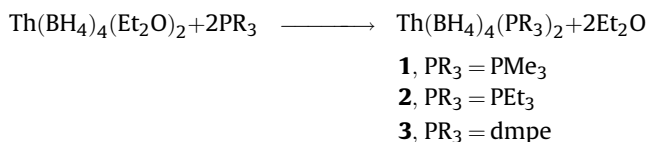
These complexes form colorless crystals; the triethylphosphine adduct **2** is a low-melting colorless solid. All three can be sublimed in vacuum without decomposition.

All three compounds show B–H stretching features in the IR spectrum: they occur at 2496, 2333, 2214, and 2137 cm^{-1} for the PMe_3 complex **1**, at 2465, 2335, 2205, and 2110 cm^{-1} for the PEt_3 adduct **2**, and at 2445, 2390, and 2002 cm^{-1} for the dmpe compound **3**. In the infrared spectra of **1** and **2**, the single strong band at high frequency (near 2470 cm^{-1}), the medium intensity band of intermediate frequency (2335 cm^{-1}), and the strong doublet at low frequency (centered at 2170 cm^{-1}) are characteristic of κ^3–BH_4^- ligands [13,14]. In contrast, the pattern of B–H stretching bands in the IR spectrum of **3** most closely resemble those expected for κ^2–BH_4^- ligands: a doublet at high frequency (centered at 2420 cm^{-1}) and a single band at low frequency (2002 cm^{-1}) [14,15]. These conclusions have been corroborated by single crystal X-ray diffraction studies (see below), although they reveal that **3** contains a mixture of κ^2 and κ^3–BH_4^- ligands.

The ^1H NMR spectrum of the trimethylphosphine complex **1** shows a broad 1:1:1:1 quartet (J_{BH} = 87 Hz) at δ 3.75 for the BH_4^- groups, and a doublet (J_{PH} = 6 Hz) at δ 0.89 for the PMe_3 ligands (Fig. 1). The ^{11}B NMR spectrum is a quintet (J_{BH} = 87 Hz) at δ –4.6, and the $^{31}P\{^1H\}$ NMR chemical shift of **1** at –80 °C is δ –22.2, which corresponds to a coordination chemical shift (i.e., relative to the shift of the free phosphine) of +41 ppm. The NMR spectra of the triethylphosphine complex **2** are very similar except for the resonances due to the phosphine ligands; the ^{31}P NMR coordination chemical shift of **2** of +32 ppm shows that the Th-P bonding is significant. For comparison, Zr^{IV} and Hf^{IV} complexes of dmpe show coordination chemical shifts of +38 ppm [16].

The ^1H NMR spectrum of the dmpe complex **3** at 20 °C shows a 1:1:1:1 quartet (J_{BH} = 86 Hz) at δ 2.83 for the BH_4^- groups, and the ^{11}B NMR spectrum exhibits a quintet (J_{BH} = 86) at δ –18.9. The $^{31}P\{^1H\}$ NMR chemical shift is δ –14.9, and the coordination chemical shift is +34 ppm. Variable temperature $^{31}P\{^1H\}$ NMR spectra show that the resonance of **3** coalesces with that due to free dmpe (added in excess) at temperatures above 30 °C; evidently, there is rapid phosphine exchange on the NMR time scale at these temperatures. Cooling the sample after it had been heated above the coalescence point restores the original $^{31}P\{^1H\}$ NMR resonances due to **3** and free dmpe.

2.2. Crystal structures of thorium complexes

Crystal data for the two structurally characterized complexes are listed in Table 1, and selected bond distances and angles are given in
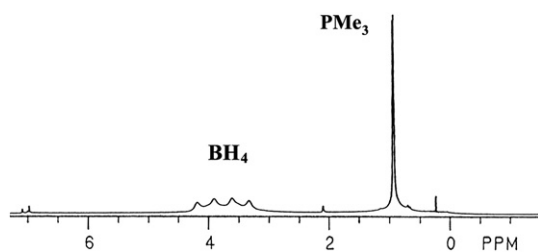

Fig. 1. ^1H NMR spectrum of $Th(BH_4)_4(PMe_3)_2$, **1**, at 40 °C in C_7D_8.

Table 1
Crystallographic data for $Th(BH_4)_4(PEt_3)_2$, **2**, and $Th(BH_4)_4(dmpe)_2$, **3**, at 193 K.

	2	**3**
Formula	$C_{12}H_{46}B_4P_2Th$	$C_{12}H_{48}B_4P_4Th$
FW (g mol^{-1})	527.71	591.66
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$
a (Å)	39.188(2)	14.1270(5)
b (Å)	7.9065(4)	40.0668(15)
c (Å)	15.7708(8)	14.3018(5)
V ($Å^3$)	4886.5(4)	8095.2(5)
Z	8	12
ρ_{calc} (g cm^{-3})	1.435	1.456
μ (mm^{-1})	6.223	5.757
R(int)	0.2568	0.0969
Abs. corr. method	Integration	Integration
Max., min. transm. factors	0.482, 0.182	0.618, 0.284
Data/restraints/parameters	10823/726/437	17900/1261/685
GOF on F^2	0.993	0.970
R_1 [$I > 2\sigma(I)$][a]	0.0599	0.0371
wR_2 (all data)[b]	0.1468	0.0787
Max, min $\Delta\rho_{electron}$ (e $Å^{-3}$)	1.58/−2.00	3.36/−2.23

[a] $R_1 = \sum |F_o| - |F_c| / |\sum |F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$ for all reflections.

Tables 2 and 3. The triethylphosphine complex **2** crystallizes in the $Pca2_1$ space group with two independent molecules in the asymmetric unit. If we regard the BH_4^- groups as occupying one coordination site, then the overall coordination geometry is trans-octahedral (Fig. 2). The P–Th–P angles of 178.6(1)° in molecule 1 and 178.0(1)° in molecule 2 are essentially linear. The Th–P distances range from 3.096(3) to 3.135(4) Å, and are similar to Th–P distances seen in other thorium phosphine complexes (see below).

The four BH_4 groups form an equatorial girdle that shows a slight S_4 ruffle, in which each boron atom lies ∼0.53 Å out of the mean plane. The Th···B distances all lie within a small range, from 2.60(1) to 2.66(1) Å and are characteristic of κ^3 BH_4^- groups (see below). The hydrogen atoms surfaced in the difference maps, and their locations could be refined subject to light constraints. The hydrogen locations confirm that all four BH_4^- groups are κ^3. The average Th–H distance is 2.48 Å. One B–H bond in two mutually trans BH_4^- groups eclipses the Th–P1 bond, one B–H bond in the

Table 2
Selected bond distances and angles for $Th(BH_4)_4(PEt_3)_2$, **2**.

Bond distances (Å)			
Th(1)−B(1)	2.612(13)	Th(2)−B(7)	2.617(14)
Th(1)−B(2)	2.620(15)	Th(2)−B(8)	2.635(15)
Th(1)−B(3)	2.617(15)	Th(2)−B(6)	2.639(15)
Th(1)−B(4)	2.596(14)	Th(2)−B(5)	2.663(15)
Th(1)−P(1)	3.100(3)	Th(2)−P(3)	3.105(4)
Th(1)−P(2)	3.096(3)	Th(2)−P(4)	3.135(4)

Bond angles (°)			
B(1)−Th(1)−B(2)	90.9(5)	B(5)−Th(2)−B(6)	92.7(6)
B(1)−Th(1)−B(3)	156.8(5)	B(5)−Th(2)−B(7)	156.0(6)
B(1)−Th(1)−B(4)	93.5(6)	B(5)−Th(2)−B(8)	91.5(6)
B(2)−Th(1)−B(3)	93.6(6)	B(6)−Th(2)−B(7)	93.3(6)
B(2)−Th(1)−B(4)	156.8(5)	B(6)−Th(2)−B(8)	156.7(6)
B(3)−Th(1)−B(4)	91.2(6)	B(7)−Th(2)−B(8)	92.2(6)
B(1)−Th(1)−P(1)	100.8(4)	B(5)−Th(2)−P(3)	103.9(4)
B(1)−Th(1)−P(2)	78.9(4)	B(5)−Th(2)−P(4)	78.2(4)
B(2)−Th(1)−P(1)	78.2(4)	B(6)−Th(2)−P(3)	78.1(4)
B(2)−Th(1)−P(2)	101.6(4)	B(6)−Th(2)−P(4)	101.9(4)
B(3)−Th(1)−P(1)	102.5(4)	B(7)−Th(2)−P(3)	100.1(4)
B(3)−Th(1)−P(2)	77.9(4)	B(7)−Th(2)−P(4)	77.9(4)
B(4)−Th(1)−P(1)	78.6(4)	B(8)−Th(2)−P(3)	78.6(4)
B(4)−Th(1)−P(2)	101.6(4)	B(8)−Th(2)−P(4)	101.3(4)
P(2)−Th(1)−P(1)	179.58(10)	P(3)−Th(2)−P(4)	177.98(11)

Table 3
Selected bond distances and angles for $Th(BH_4)_4(dmpe)_2$, **3**.

Bond distances (Å)			
Th(1)–B(1)	2.694(8)	Th(1)–P(1)	3.121(2)
Th(1)–B(2)	2.950(8)	Th(1)–P(2)	3.133(2)
Th(1)–B(3)	2.686(9)	Th(1)–P(3)	3.112(2)
Th(1)–B(4)	2.879(9)	Th(1)–P(4)	3.117(2)
Bond angles (°)			
B(1)–Th(1)–B(2)	149.5(3)	B(3)–Th(1)–P(1)	85.2(2)
B(1)–Th(1)–B(3)	93.0(3)	B(3)–Th(1)–P(2)	73.8(2)
B(1)–Th(1)–B(4)	99.7(3)	B(3)–Th(1)–P(3)	76.1(2)
B(1)–Th(1)–P(1)	74.4(2)	B(3)–Th(1)–P(4)	139.9(2)
B(1)–Th(1)–P(2)	136.7(2)	B(4)–Th(1)–P(1)	70.41(17)
B(1)–Th(1)–P(3)	85.7(2)	B(4)–Th(1)–P(2)	76.9(2)
B(1)–Th(1)–P(4)	75.0(2)	B(4)–Th(1)–P(3)	133.66(18)
B(2)–Th(1)–B(3)	99.3(3)	B(4)–Th(1)–P(4)	72.00(19)
B(2)–Th(1)–B(4)	83.9(3)	P(1)–Th(1)–P(2)	63.65(6)
B(2)–Th(1)–P(1)	133.8(2)	P(1)–Th(1)–P(3)	151.97(6)
B(2)–Th(1)–P(2)	73.7(2)	P(1)–Th(1)–P(4)	125.80(7)
B(2)–Th(1)–P(3)	70.9(2)	P(2)–Th(1)–P(3)	128.06(7)
B(2)–Th(1)–P(4)	77.5(2)	P(2)–Th(1)–P(4)	139.36(6)
B(3)–Th(1)–B(4)	148.1(3)	P(3)–Th(1)–P(4)	65.06(7)

other two BH_4^- groups eclipses the Th–P2 bond. This eclipsing (and non-bonded H⋯P repulsion) is probably responsible for the displacement of the BH_4^- groups out of the mean equatorial plane. This arrangement also results in the BH_4^- groups being 'geared' so that the eclipsing B–H bond points alternately up and down as one circumnavigates the periphery of the equatorial plane. The total coordination number of the thorium atom in **2** is 14 (2 phosphorus plus 12 hydrogen atoms).

The dmpe complex **3** also crystallizes in the $Pca2_1$ space group, but with three independent molecules in the asymmetric unit. The structures of all three independent molecules are roughly similar,
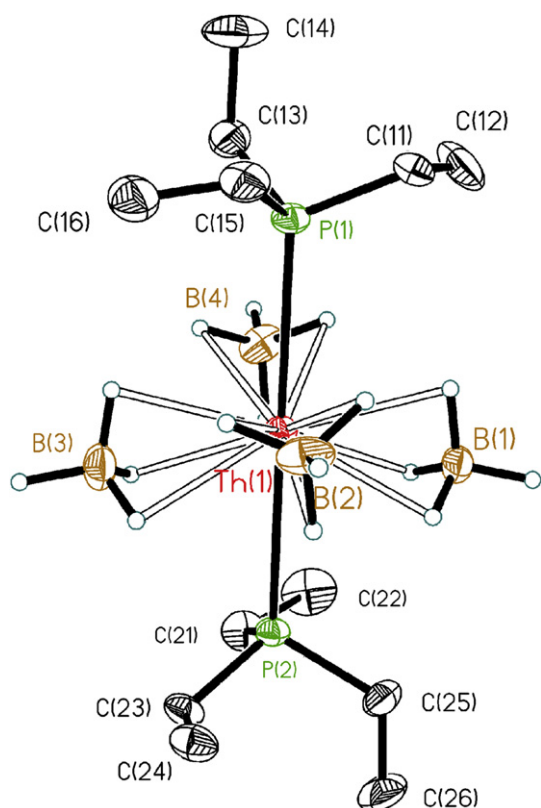

Fig. 2. Molecular structure of $Th(BH_4)_4(PEt_3)_2$, **2**. Ellipsoids are drawn at 30% probability level. Hydrogen atoms attached to carbon have been deleted for clarity.

and we will confine our discussion to molecule 1. Overall, if the BH_4^- groups are considered to occupy one coordination site, then **3** adopts a trigonal dodecahedral structure in which the dmpe groups occupy the 'inner' sites of the two interpenetrating trapezoids (Fig. 3), as observed for other $ThX_4(dmpe)_2$ molecules [5,6]. The Th–P distances are all rather similar, and range from 3.112(2) to 3.133(2) Å. These distances are also similar to previously published thorium–phosphine bond distances: 3.16(1) Å in $Th(CH_2Ph)_4$ (dmpe) [6], 3.142(2) and 3.237(2) Å in $Cp_2Th(CH_2Ph)_2(dmpe)$ [7], 3.146(2) Å in $Cp_2ThMe_2(dmpe)$ [8], 3.122(2) Å in $Cp_2ThCl_2(dmpe)$ [8], 3.062(5)–3.105(2) Å in $Th[P(CH_2CH_2PMe_2)_2]_4$ [16–18], and 3.116(4) and 3.207(5) Å in $ThCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2$ [9].

In **3**, the four Th⋯B distances fall into two quite distinct sets: two are relatively short, 2.694(8) and 2.686(9) Å, and two are relatively long, 2.950(8) and 2.879(9) Å. The former are due to BH_4^- groups bound in a κ^3 fashion, whereas the latter are κ^2. The κ^3 Th⋯B distances in **3** are similar to those reported in other complexes: 2.61 (3) Å in $Th(BH_4)[N(SiMe_3)_2]_3$ [19], 2.48(2)–2.60(2) Å in $Th_2(BH_3Me)_8(Et_2O)$ [20], 2.61(8)–2.632(9) Å in $Th_2(BH_3Me)_8(thf)$ [20], and 2.49(6)–2.71(7) Å in $Th(BH_3CH_3)_4$ [21]. Compound **3** is the first thorium complex to contain κ^2 BH_4^- groups; the κ^2 Th⋯B distances are similar to those of 2.882(3)–2.949(3) Å in the 15 coordinate aminodiboranate complex $Th(H_3BNMe_2BH_3)_4$ [22]. The total coordination number of the thorium atom in **3** is 14 (4 phosphorus plus 10 hydrogen atoms).

2.3. Attempts to prepare thorium hydrides

The reactions of trialkylphosphines with $Zr(BH_4)_4$ and $Hf(BH_4)_4$ are well known to afford zirconium(IV) and hafnium(IV) hydrides such as $M_2H_3(BH_4)_5(PMe_3)_2$, $M_3H_6(BH_4)_6(PMe_3)_4$, $MH(BH_4)_3(dmpe)$, and $M_2H_4(BH_4)_4(dmpe)_2$ [23]. All of these reactions are accompanied by loss of BH_3 as the borane–phosphine $BH_3 \cdot PR_3$. Somewhat similarly, addition of phosphines to $U(BH_4)_4$ yields phosphine complexes of uranium(III) such as $U(BH_4)_3(PEt_3)_2$ and $U(BH_4)_3(PEt_2Ph_2)_2$, which are proposed to form by means of uranium(IV) hydride intermediates that subsequently eliminate H_2 [24,25].

In contrast, an NMR study showed that the only product formed from the reaction of $Th(BH_4)_4(Et_2O)_2$ with excess dmpe in C_7D_8 is
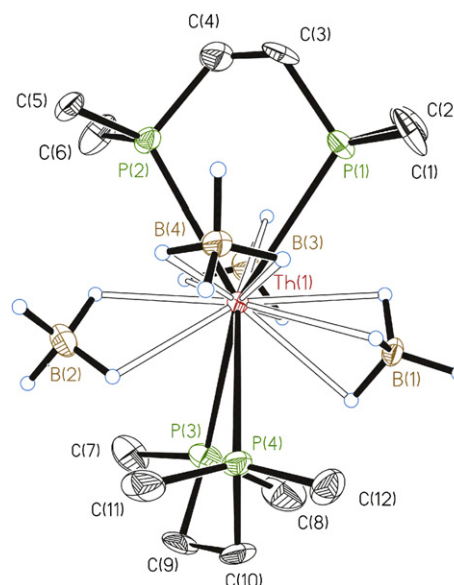

Fig. 3. Molecular structure of $Th(BH_4)_4(dmpe)_2$, **3**. Ellipsoids are drawn at 30% probability level. Hydrogen atoms attached to carbon have been deleted for clarity.

Th(BH$_4$)$_4$(dmpe)$_2$, **3**, even at temperatures as high as 100 °C. Under no circumstances were we able to detect or generate thorium hydrides by addition of trialkylphosphines to Th(BH$_4$)$_4$(Et$_2$O)$_2$, despite the fact that hydrides of thorium are known with other ancillary ligands [26–28].

One interesting question is why U(BH$_4$)$_4$ reacts with phosphines to give hydride intermediates but Th(BH$_4$)$_4$ does not. One possibility is that uranium (like zirconium and hafnium) interacts sufficiently strongly with the BH$_4$ ligands to weaken the B–H bonds and promote the loss of BH$_3$, which is then trapped by phosphine. Evidently, thorium does not interact with the BH$_4^-$ groups sufficiently strongly to make loss of BH$_3$ kinetically competent.

2.4. Conclusions

The results show that thorium complexes of unidentate phosphines can be made and are stable enough to isolate and characterize. ^{31}P NMR coordination chemical shifts of the thorium phosphine complexes are on the order of 30–45 ppm and suggest that the Th-P bonding is not weak. The compound Th(BH$_4$)$_4$(dmpe)$_2$ is the first thorium complex to contain κ^2 BH$_4^-$ groups.

3. Experimental section

All operations were carried out in vacuum or under argon using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium benzophenone (pentane and diethyl ether) or from sodium (toluene) immediately before use. The compounds Th(BH$_4$)$_4$(Et$_2$O)$_2$ [12], trimethylphosphine [29], triethylphosphine [30], and 1,2-bis(dimethylphosphino)ethane [31] were prepared by literature routes.

Elemental analyses were carried out by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B infrared spectrometer as Nujol mulls. The ^{1}H NMR data were obtained on a General Electric QE-300 spectrometer at 300 MHz or a General Electric GN-500 spectrometer at 500 MHz. The ^{11}B and ^{31}P NMR data were recorded on a GN-300 NB spectrometer at 96.25 and 121.44 MHz, respectively, or on the GN-500 spectrometer at 160.44 and 202.44 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to SiMe$_4$ (^{1}H), BF$_3$·Et$_2$O (^{11}B), or 85% H$_3$PO$_4$ (^{31}P). Melting points were recorded on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

3.1. Tetrakis(tetrahydroborato)bis(trimethylphosphine)thorium(IV), 1

To Th(BH$_4$)$_4$(Et$_2$O)$_2$ (0.52 g, 1.18 mmol) in diethyl ether (150 mL) was added PMe$_3$ (0.60 mL, 5.91 mmol). The clear, colorless mixture was stirred for 24 h at 25 °C, and then the solvent was removed under vacuum. The residue was sublimed at 100 °C (10^{-4} Torr) to give white microcrystals. Yield: 0.36 g (69%). Mp: 140 °C (dec). Anal. Calcd for C$_6$H$_{34}$B$_4$P$_2$Th: C, 16.3; H, 7.73. Found: C, 16.2; H, 8.13. ^{1}H NMR (C$_7$D$_8$, 20 °C): δ 3.75 (broad quartet, J_{BH} = 87 Hz, BH$_4$), 0.89 (d, J_{PH} = 6 Hz, PMe$_3$). ^{1}H NMR (C$_7$D$_8$, −80 °C): δ 3.95 (broad s, BH$_4$), 0.68 (s, PMe$_3$). ^{11}B NMR (C$_7$D$_8$, 20 °C): δ −4.6 (quintet, J_{BH} = 87). ^{31}P{^{1}H} NMR (C$_7$D$_8$, 20 °C): δ −22.2 (s). ^{31}P{^{1}H} NMR (C$_7$D$_8$, −80 °C): δ −18.2 (s). IR (cm^{-1}): 2496 s, 2333 m, 2214 s, 2137 s, 1431 s, 1423 s, 1337 w, 1310 m, 1287 m, 1206 m, 1165 s, 955 s, 867 w, 733 m, 706 w, 669 w.

3.2. Tetrakis(tetrahydroborato)bis(triethylphosphine)thorium(IV), 2

To Th(BH$_4$)$_4$(Et$_2$O)$_2$ (0.50 g, 1.13 mmol) in diethyl ether (150 mL) was added triethylphosphine (1.5 mL, 10.2 mmol). A white precipitate formed immediately and the solution was stirred for 24 h at 25 °C. The solution was filtered and the residue was extracted with diethyl ether (100 mL). The extracts were filtered and combined with the filtered reaction solution. The combined filtrates were concentrated to ca. 10 mL and cooled to −20 °C to give white microcrystals. Yield: 0.16 g (27 %). Anal. Calcd for C$_{12}$H$_{46}$B$_4$P$_2$Th: C, 27.3; H, 8.79. Found: C, 27.3; H, 8.92. The product is a low-melting solid. ^{1}H NMR (C$_7$D$_8$, 20 °C): δ 3.85 (br q, J_{BH} = 83 Hz, BH$_4$), 1.38 (q, J_{HH} = 7 Hz, PCH$_2$), 0.80 (t, J_{HH} = 7 Hz, Me). ^{1}H NMR (C$_7$D$_8$, −80 °C): δ 4.00 (br s, BH$_4$), 1.35 (br q, J_{HH} = 7 Hz, PCH$_2$), 0.72 (br t, J_{HH} = 7 Hz, Me). ^{11}B NMR (C$_7$D$_8$, 20 °C): δ −3.1 (quintet, J_{BH} = 83 Hz). ^{31}P{^{1}H} NMR (C$_7$D$_8$, 20 °C): δ 10.8 (s). ^{31}P{^{1}H} NMR (C$_7$D$_8$, −80 °C): δ 11.8 (s). IR (cm^{-1}): 2465 s, 2335 m, 2205 s, 2110 s, 1415 m, 1255 m, 1165 s, 1090 s, 1032 s, 1000 sh, 860 w, 780 s, 750 s, 725 m, 710 m, 690 w, 680 w, 655 w, 360 s.

3.3. Tetrakis(tetrahydroborato)bis(1,2-bis(dimethylphosphino) ethane)thorium(IV), 3

To Th(BH$_4$)$_4$(Et$_2$O)$_2$ (0.50 g, 1.13 mmol) in toluene (50 mL) was added 1,2-bis(dimethylphosphino)ethane (0.75 mL, 4.52 mmol). The solution was heated to 60 °C for 3 h to bring the Th (BH$_4$)$_4$(Et$_2$O)$_2$ into solution. The clear colorless mixture was stirred for 24 h at 25 °C and then the solvent was removed under reduced pressure. The product was washed with cold (0 °C) pentane (2 × 40 mL) and extracted with toluene (30 mL). The filtered extract was concentrated to ca. 4 mL and cooled to −20 °C to give white microcrystals. Yield: 0.37 g (53%). Mp. 176 °C (dec). Anal. Calcd for C$_{12}$H$_{48}$B$_4$P$_4$Th: C, 24.4; H, 8.18. Found: C, 24.4; H, 8.23. ^{1}H NMR (C$_7$D$_8$, 20 °C): δ 2.83 (br q, J_{BH} = 86 Hz, BH$_4$), 1.36 (d, J_{PH} = 13 Hz), 1.16 (s, PMe$_2$ + PCH$_2$). ^{1}H NMR (C$_7$D$_8$, −60 °C): δ 2.93 (br s, BH$_4$), 1.28 (s, PMe$_2$ + PCH$_2$). ^{31}P{^{1}H} NMR (C$_7$D$_8$, 20 °C): δ −14.9 (s). ^{31}P{^{1}H} NMR (C$_7$D$_8$, −60 °C): δ −12.1 (s). ^{11}B{^{1}H} NMR (C$_7$D$_8$, 20 °C): δ −18.9 (s). IR (cm^{-1}): 2445 m, 2390 s, 2002 s, 1418 m, 1299 w, 1282 m, 1135 m, 1104 m, 948 m, 930 m, 892 w, 867 vw, 832 vw, 732 w, 702 w, 643 vw.

3.4. Crystallographic studies [32]

Single crystals of **2** and **3**, obtained from pentane, were mounted on glass fibers with Paratone oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures, followed by least-square refinement yielded the cell dimensions given in Table 1. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, a face-indexed absorption correction was applied. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. Except were noted, all unique data were used in the least-squares refinement. The structure was solved using direct methods (SHELXTL). The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. Correct atomic positions were deduced from an E-map (SHELX); least-squares refinement and difference Fourier calculations were used to locate atoms not found in the initial solution. Except where noted, the hydrogen atoms attached to carbon were placed in idealized positions. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms, unless otherwise noted. The displacement parameters for methylene and boranyl hydrogens were set equal to 1.2 times U_{eq} for the attached atom, and methyl hydrogens were set equal to 1.5 times U_{eq}. A final analysis of variance between observed and calculated structure factors showed no

apparent errors. Aspects of the refinement unique to each structure are reported below.

3.4.1. Th(BH$_4$)$_4$(PEt$_3$)$_2$, 2

The orthorhombic lattice and systematic absences 0kl ($l \neq 2n$) and h0l ($h \neq 2n$) were consistent with the space groups Pca2$_1$ and Pbcm. Three of the ethyl groups in molecule 2 showed evidence of disorder; one of them was best modeled as single atoms (but with large displacement parameters) but the other two ethyl groups were best modeled as disordered over two sites. The site occupancy factors (SOFs) for the two disordered components were constrained to add to 1; the SOF for the major component refined to 0.65(2). The disordered carbon atoms were refined isotropically. The C–C distances within the disordered ethyl groups were constrained to be 1.52 ± 0.02 Å. Hydrogen atoms were apparent in the difference maps, but their locations were reasonable only by imposing constraints. The BH$_4$ groups were constrained to have near-ideal tetrahedral geometries with B–H = 1.15 ± 0.02 Å, and the Th–H distances were constrained to be similar within 0.02 Å. No correction for isotropic extinction was necessary, but analysis of the diffraction intensities suggested inversion twinning; therefore, the intensities were calculated from the equation $I = xI_a + (1-x)I_b$, where x is a scale factor that relates the volumes of the inversion-related twin components. The scale factor refined to a value of 0.53 (1). Successful convergence was indicated by the maximum shift/error of 0.002 for the last cycle. The largest peak in the final Fourier difference map (1.58 e Å^{-3}) was located at 0.89 Å from Th2.

3.4.2. Th(BH$_4$)$_4$(dmpe)$_2$, 3

The orthorhombic lattice and systematic absences 0kl ($l \neq 2n$) and h0l ($h \neq 2n$) were consistent with the space groups Pca2$_1$ and Pbcm. The average values of the normalized structure factors suggested the non-centrosymmetric space group Pca2$_1$, and this choice was confirmed by successful refinement of the proposed model. One reflection (020) was obscured by the beamstop and was deleted. Carbon atoms C15 and C27 were each disordered over two sites sufficiently far apart to justify splitting them into two components. The occupancy factors at each site were constrained to add to 1, and the site occupancy factor for the major site refined to 0.54(1) and 0.71(1) for C15 and C27, respectively. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.034P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The disordered atoms C15A,B and C27A,B were refined isotropically with a common displacement parameter. Many of the hydrogens on the boron atoms in molecules 1 and 2 were apparent in the difference maps, and their positions were refined subject to the constraints B–H distances were 1.15 ± 0.01 Å, the BH$_4$ groups were roughly tetrahedral, and chemically equivalent Th–H distances were equal within an esd of 0.02 Å. Many small electron density peaks surrounded the boron atoms in molecule 3, but no clear choice could be made among them, and so these hydrogen atoms were omitted from the final model. No correction for isotropic extinction was necessary. Analysis of the diffraction intensities suggested that the data crystal was an inversion twin; therefore, the intensities were calculated from the equation $I = xI_a + (1-x)I_b$, where x is a scale factor that relates the volumes of the inversion-related twin components. The scale factor refined to a value of 0.477(6). Successful convergence was indicated by the maximum shift/error of 0.002 for the last cycle. The largest peak in the final Fourier difference map (3.36 e Å^{-3}) was located at 1.01 Å from Th3.

Appendix A. Supporting information

X-ray crystallographic data for compounds 1 and 2, CCDC nos. 796117 and 796118. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

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