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Tris(methyltrihydroborato)(tetrahydrofuran)ytterbium(III) complex: structure and volatility

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CONTENTS

1. Experimental. All preparations were carried out under an argon atmosphere in a glove box. Materials. Trimethylboroxine ($B_3O_3(CH_3)_3$) (50 wt. % in THF) was purchased from Aviabor Stock Company (Dzerzhinsk, Russia).
Diethyl ether was condensed onto a sodium mirror and then distilled. Pentane was dried by refluxing over sodium metal. Anhydrous $YbCl_3$ was prepared according to the standard procedure [S1] by heating the oxide with ammonium chloride.

2. Synthetic procedures
Synthesis of [$MeBH_3$]Li. Dry diethyl ether (90-100 ml) was condensed in *vacuo* into a 250-ml two-necked flask containing lithium aluminum hydride (3.34 g, 0.088 mol). The mixture was boiled with reflux for 3 h under argon and allowed to stand overnight. The resulting solution of LiAlH4 was decanted *via cannula* into a dropping funnel with a pressure compensator. A 250-ml three-necked flask was charged under Ar with dry pentane (100 ml) and trimethylboroxine (6 ml of 50 wt. % in THF), and the dropping funnel containing the lithium aluminum hydride solution was attached. The contents of the flask were cooled 0 – -5 °C using the isopropanol/liquid nitrogen bath, and the lithium aluminum hydride solution was slowly added in about half hour at that temperature. The reaction mixture was allowed to stand at room temperature for 2 h. The resulting solid (most likely, aluminum oxohydride Al(O)H) was separated by centrifugation and washed with dry pentane (20 ml). The washings were combined with the solution obtained after centrifugation. The resulting Li[CH_3BH_3] solution containing THF was then used to prepare the ytterbium complex.
Synthesis of Yb($MeBH_3$)$_3$*THF (1). To anhydrous ytterbium(III) chloride (3.3 g, 0.012 mol) the lithium methylborohydride (3.14 g, 0.088 mol) solution in ether/pentane (about 120 ml) containing THF (0.04 mol) as a neutral ligand, obtained as described above, was added. The reaction mixture was stirred for 2 d at room temperature under argon. The solvent was removed

under reduced pressure and the residue was sublimed at 70-80 °C in *vacuo* onto a water-cold finger. The resulting product was obtained as colorless prismatic crystals with a yield of about 1.6 g (41 %).

3. Elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O analyzer. The content of Yb in the samples was determined by ICP-OES on a Varian 725-OES instrument.

4. Infrared spectra were recorded on a FTIR 8700 instrument (Shimadzu) in the range 500-4000 cm^{-1} in Nujol or dichloromethane. Experimental IR spectra of (**1**) are presented in Figs. S1 and S2.

5. ^{1}H, $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra were recorded at the Center for Magnetic Resonance of the St.Petersburg State University on Bruker Avance III 400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, and 128.38 MHz for ^{11}B). Spectra were recorded at room temperature using CD_2Cl_2 (*abcr GmbH*) as a solvent and referenced through the solvent lock (2H) signal according to IUPAC recommended secondary referencing method. ^{1}H, $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra of (**1**) are shown in Figs S3, S4 and S5. As the substance is paramagnetic, the signals are possibly shifted in the spectrum, quite broad and partially overlapping, so that integrated intensities should be taken only as a rough estimate. The assignment of the CH_3–BH_3 fragment is supported by the results of the additional ^{1}H,^{13}C-HMQC and ^{11}B, ^{1}H -HETCOR experiments (not shown).

6. Single crystal X-ray diffraction. Data were collected at the X-ray Diffraction Centre of St. Petersburg State University on a Bruker SMART diffractometer equipped with an APEX II CCD planar detector operated with monochromatic MoKα radiation at 50 kV and 40 mA.

Prismatic crystal of **1** was mounted on thin glass fiber for X-ray diffraction analysis. More than a hemisphere of X-ray diffraction data (θ_{max} = 27.50°) were collected at 100 K for the crystal with frame widths of 0.5° in ω, and exposition of 5 s spent per each frame. Data were integrated and corrected for background, Lorentz, and polarization effects using the CrysAlisPro [S2] program complex. Empirical absorption correction for **1** was applied in CrysAlisPro [S2] using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The unit cell parameters of **1** (orthorhombic, a = 13.1239(5), b = 14.7655(5), c = 14.7931(4) Å, V = 2866.63(16) $Å^3$, Z = 8, space group *Pbca*) were determined and refined by the least-squares techniques on the basis of 29492 reflections with 2θ in the range of 4.98–55.00°. The structure was solved by direct methods and refined to R_1 = 0.033 (wR_2 = 0.059) for 2644 reflections with $|F_o| \geq 4\sigma_F$ using the *SHELXL*-97 program [S3] incorporated in the *OLEX2* program package [S4]. The C6-C7 fragment within the tetrahydrofuran cycle is crystallographically disordered over the two approximately half-occupied non-equivalent positions with the total site occupancy factor (s.o.f.) equal to 1.0 for each atom. The final model included coordinates and anisotropic displacement parameters for all non-hydrogen atoms. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, with U_{iso}(H) set to 1.5U_{eq}(C) and C–H 0.96 Å for the CH_3 groups and U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å for the tertiary CH_2 groups. Positions of boron-bound H atoms were localized from difference Fourier maps and refined with individual isotropic displacement parameters without any restraints. Supplementary crystallographic data for this paper have been deposited at

Cambridge Crystallographic Data Centre (CCDC 1538682) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for **1**.

Compound	**1**
Formula	$Yb(BH_3CH_3)_3(C_4H_8O)$
Crystal System	Orthorhombic
a (Å)	13.1239(5)
b (Å)	14.7655(5)
c (Å)	14.7931(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2866.63(16)
Molecular weight	331.75
Space group	*Pbca*
μ (mm^{-1})	6.488
Temperature (K)	100(2)
Z	8
D_{calc} (g/cm^3)	1.537
Crystal size (mm^3)	0.18×0.12×0.07
Radiation	Mo$K\alpha$
Total reflections	29492
Unique reflections	3283
Angle range 2θ (°)	4.98–55.00
Reflections with $\|F_o\| \geq 4\sigma_F$	2644
R_{int}	0.0484
R_σ	0.0199
R_1 ($\|F_o\| \geq 4\sigma_F$)	0.0333
wR_2 ($\|F_o\| \geq 4\sigma_F$)	0.0590
R_1 (all data)	0.0483
wR_2 (all data)	0.0627
S	1.196
ρ_{min}, ρ_{max}, e/Å^3	–1.022, 1.141

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S2. Bond angles and bond lengths for **1**.

Bond	
Yb1-H1A	2.12(6)
Yb1-H1B	2.13(4)
Yb1-H1C	2.03(7)
Yb1-H2A	2.06(6)
Yb1-H2B	2.23(6)
Yb1-H2C	2.10(6)
Yb1-H3A	2.20(4)
Yb1-H3B	2.24(5)
Yb1-H3C	2.20(6)
Yb1-O1	2.251(3)
B1-H1A	1.14(5)
B1-H1B	1.17(4)
B1-H1C	1.04(7)
B1-C1	1.586(7)
B2-H2A	1.11(5)
B2-H2B	1.12(6)
B2-H2C	1.20(6)
B2-C2	1.603(7)
B3-H3A	1.22(4)
B3-H3B	1.18(5)
B3-H3C	1.18(6)
B3-C3	1.591(7)
O1-C4	1.462(5)
O1-C7A	1.48(3)
O1-C7B	1.49(2)
C4-C5	1.486(8)
C5-C6B	1.34(3)
C5-C6A	1.63(3)
C6B-C7B	1.56(3)
C7A-C6A	1.48(3)

Angle	
H1A-Yb1-H1B	49.6(19)
H1A-Yb1-H1C	47(2)
H1A-Yb1-H2A	121(2)
H1A-Yb1-H2B	75(2)
H1A-Yb1-H2C	88(2)
H1A-Yb1-H3A	126.8(19)

H1A-Yb1-H3B	120(2)
H1A-Yb1-H3C	168(2)
H1B-Yb1-H1C	45(2)
H1B-Yb1-H2A	170.4(19)
H1B-Yb1-H2B	122.7(19)
H1B-Yb1-H2C	128(2)
H1B-Yb1-H3A	99.6(17)
H1B-Yb1-H3B	70.7(18)
H1B-Yb1-H3C	118.8(19)
H1C-Yb1-H2A	133(2)
H1C-Yb1-H2B	109(2)
H1C-Yb1-H2C	86(2)
H1C-Yb1-H3A	81(2)
H1C-Yb1-H3B	88(2)
H1C-Yb1-H3C	128(2)
H2A-Yb1-H2B	48(2)
H2A-Yb1-H2C	47(2)
H2A-Yb1-H3A	88(2)
H2A-Yb1-H3B	119(2)
H2A-Yb1-H3C	70(2)
H2B-Yb1-H2C	50(2)
H2B-Yb1-H3A	128.9(19)
H2B-Yb1-H3B	162.5(19)
H2B-Yb1-H3C	115(2)
H2C-Yb1-H3A	82(2)
H2C-Yb1-H3B	133(2)
H2C-Yb1-H3C	102(2)
H3A-Yb1-H3B	50.9(17)
H3A-Yb1-H3C	51.2(18)
H3B-Yb1-H3C	48.7(19)
H1A-B1-H1B	101(4)
H1A-B1-H1C	97(5)
H1B-B1-H1C	91(4)
C1-B1-H1A	120(3)
C1-B1-H1B	120(2)
C1-B1-H1C	122(4)
H2A-B2-H2B	101(4)
H2A-B2-H2C	91(4)
H2B-B2-H2C	105(4)
C2-B2-H2A	125(3)
C2-B2-H2B	113(3)
C2-B2-H2C	118(3)
H3A-B3-H3B	105(3)
H3A-B3-H3C	104(4)

H3B-B3-H3C	102(4)
C3-B3-H3A	116(2)
C3-B3-H3B	113(3)
C3-B3-H3C	115(3)
C4-O1-C7A	112.4(9)
C7B-O1-C4	104.7(9)
O1-C4-H4A	110.8
O1-C4-H4B	110.8
O1-C4-C5	104.7(5)
C4-C5-C6A	103.9(13)
C6B-C5-C4	103.7(16)
C5-C6B-C7B	101.4(18)
O1-C7A-C6A	106.9(17)
C7A-C6A-C5	104.9(16)
O1-C7B-C6B	100(3)

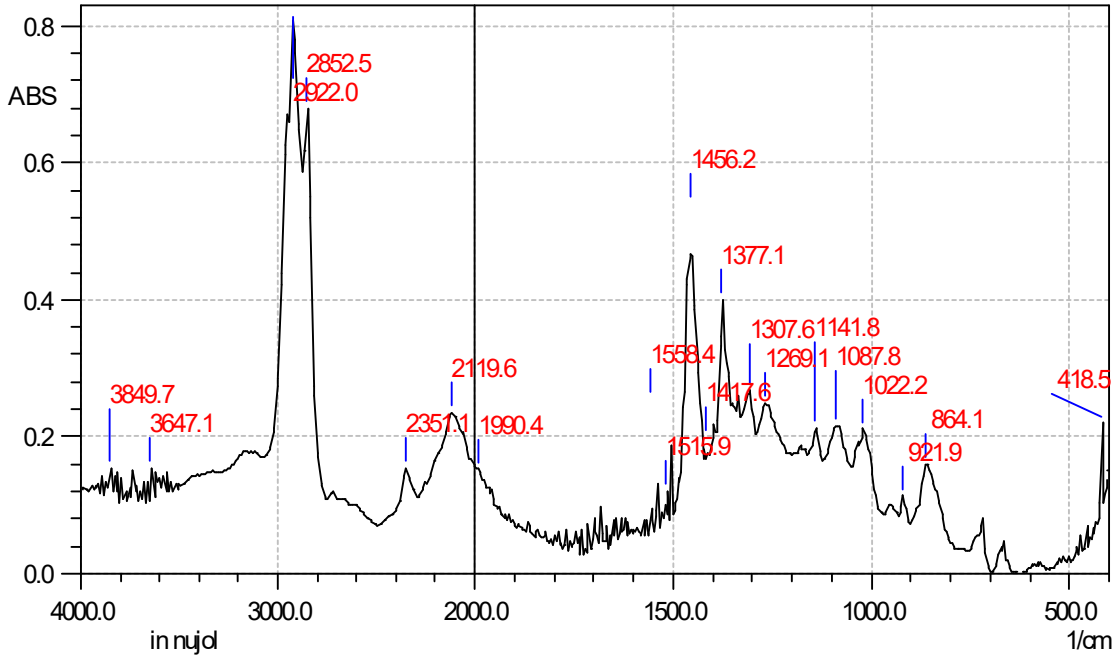

Figure S1. IR spectrum of (**1**) in Nujol.

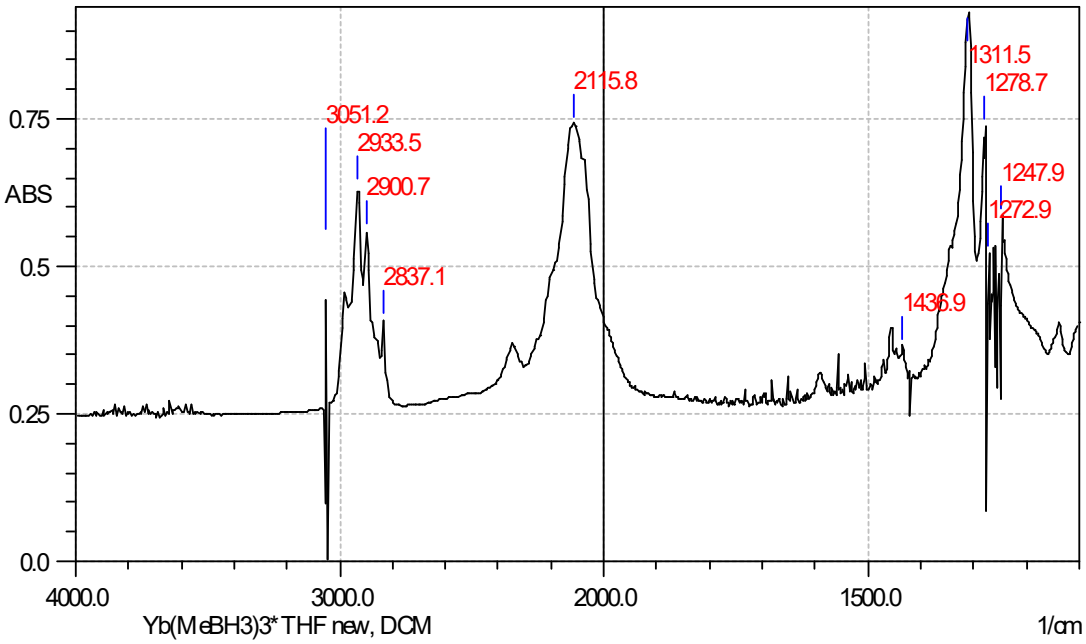

Figure S2. IR spectrum of (**1**) in dichloromethane.

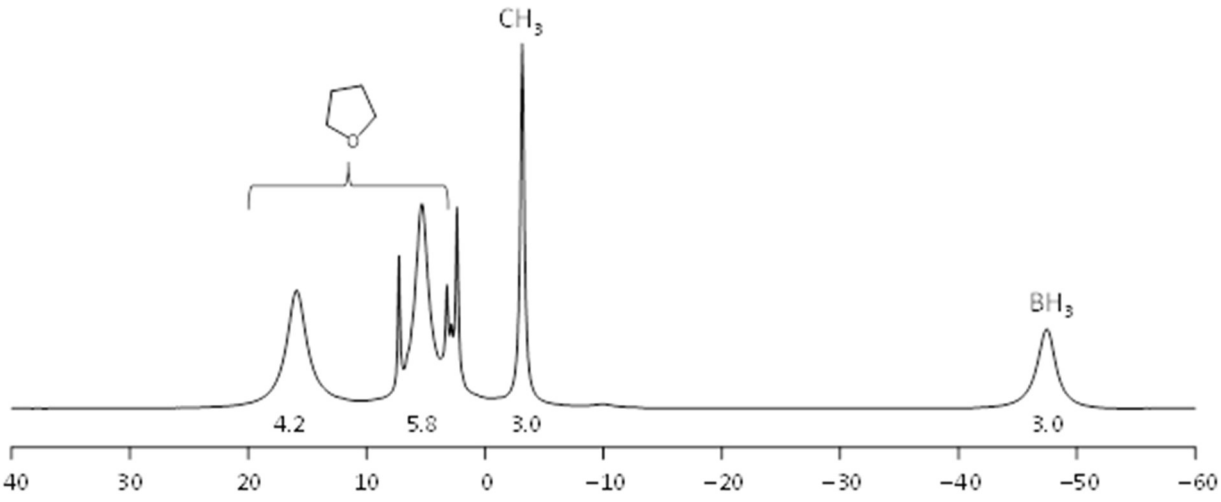

Figure S3. ^{1}H NMR spectrum of (**1**) in CD_2Cl_2.

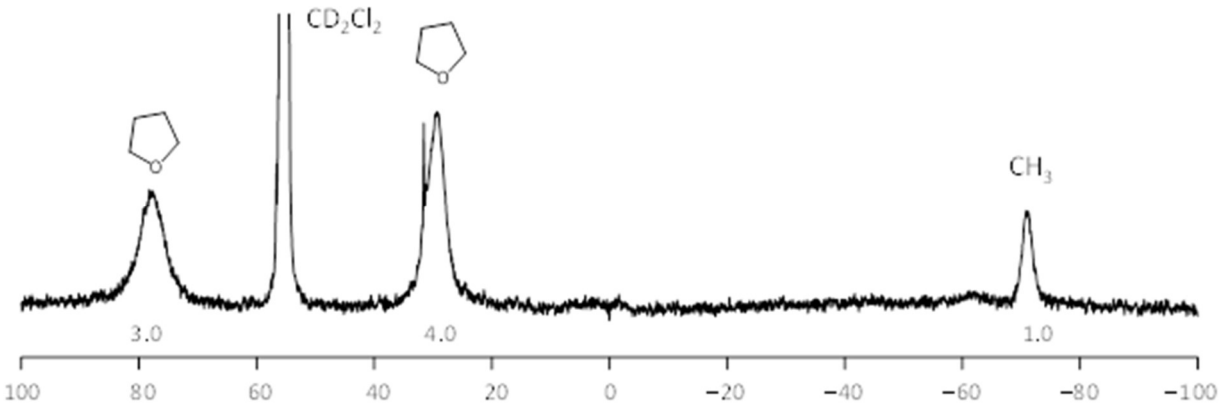

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **(1)** dissolved in CD_2Cl_2.

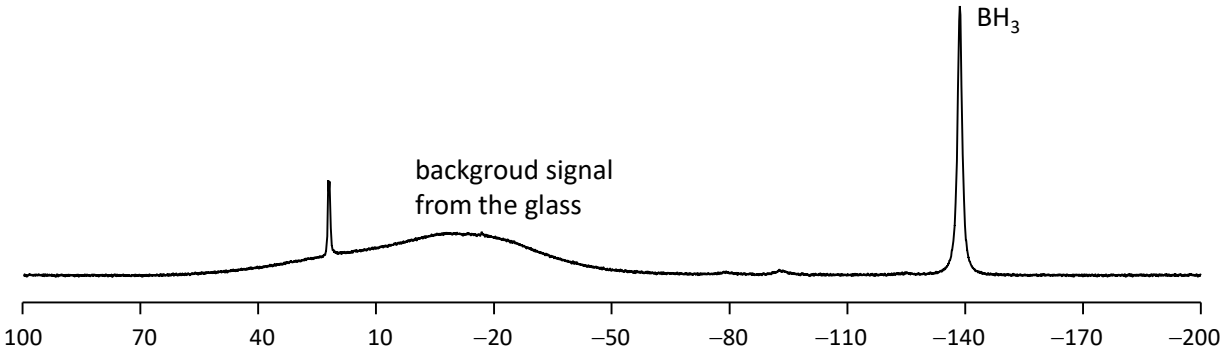

Figure S5. $^{11}B\{^{1}H\}$ NMR spectrum of **(1)** dissolved in in CD_2Cl_2.

7. SATURATED VAPOR PRESSURE MEASUREMENTS

The source cell was charged with 20-30 mg of the complex in a glove box under argon and then arranged at a bottom of the argon-filled flask. The flask was evacuated at room temperature to about 10^{-3} Torr. Then the flask was arranged into an air thermostat preliminarily heated to a desired temperature and held for 4 h. The temperature of the thermostat was maintained within ± 1 °C. The flask was removed from the thermostat and cooled in air to room temperature. A solid condensed on the walls of the flask was washed out with three portions (1-2 ml) of 3 M HNO_3 . Then the flask was washed with 10 ml of distilled water. The washings were combined, the volume was reduced to 10 ml and the resulting solution was analyzed for Yb by ICP OES. Based on the results the saturated vapor pressure of **1** was calculated from Clapeyron-Mendeleev equation:

$P = nRT/V$,

where n is number of moles of the complex deposited on the flask walls, R is the gas constant, T is temperature (K), and V is the flask volume (0.611 l).

The pressure measurement system was preliminarily calibrated with naphthalene and tris(hexafluoroacetylacetonato)iron(III) for which tabulated data are available.

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