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Synthesis and structural study of the ate-complex *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$ and the polymeric compound $\{rac\text{-}(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb[(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2]_2Li(THF)_2\}_\infty$

Alexei V. Khvostov [a], Vitalii K. Belsky [b], Alexandr I. Sizov [a], Boris M. Bulychev [a,*], Nataliya B. Ivchenko [a]

[a] *Department of Chemistry, M.V. Lomonosov Moscow State University, 119899 Moscow, Russia*

[b] *L. Ya. Karpov Physico-Chemical Institute, ul. Vorontsovo pole 10, 103064 Moscow, Russia*

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Abstract

The ate-complex *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$ (**1**) was obtained in ether from the dilithium salt of 2,2-bis(3-trimethylsilylcyclopentadienyl)propane $[(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Li_2]$ and ytterbium (III) chloride. The reaction between **1** and a 50% excess of $LiBH_4$ in THF afforded the borohydride *ansa*-ytterbocene complex $\{rac\text{-}(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb[(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2]_2Li(THF)_2\}_\infty$ (**2**). Crystals of complex **1** are monoclinic: $a = 11.680(2)$ Å, $b = 21.823(4)$ Å, $c = 13.843(3)$ Å, $\beta = 99.03(3)°$, $D_{calc} = 1.360$ g cm^{-3}, $P2_1/c$, $Z = 4$. Average Yb–Cl, Yb–Cp bond lengths and Cl–Yb–Cl, Cp–Yb–Cp angles are equal to 2.57 and 2.30 Å, 85.9 and 113.6°, respectively. Crystals of compound **2** are triclinic: $a = 7.0030(10)$ Å, $b = 11.370(2)$ Å, $c = 11.895(2)$ Å, $\alpha = 106.42(3)°$, $\beta = 95.24(3)°$, $\gamma = 98.91(3)°$, $D_{calc} = 1.250$ g cm^{-3}, $P\bar{1}$, $Z = 1$. Average Yb–B, Yb–Cp bond lengths and B–Yb–B, Cp–Yb–Cp angles are equal to 2.59 and 2.33 Å, 96.3 and 111.0°, respectively. The BH_4-groups in compound **2** were found to be tetradentate and linked with six-coordinate lithium atoms via (μ_2-H)-bridges which resulted in a polymeric chain structure. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ytterbium (III); *Ansa*-metallocenes; Borohydrides; Crystal structure

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1. Introduction

Currently complexes with *ansa*-bound cyclopentadienyl ligands are being widely used as catalysts for stereospecific polymerization of α-olefins and, therefore, are playing an important role in IVb group metallocene chemistry [1]. However, less attention has been given to similar compounds of lanthanide and group IIIb elements. Although complexes with polymethylene bridges such as $(CH_2)_3$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$, $(CH_2)_2N(CH_3)(CH_2)_2$ etc. were studied [2,3] and a few examples of complexes with ligands with short bridges, viz. Me_4C_2 and Me_2Si, and with bulky ring-substituents are known [4–6], no Me_2C-bridged lanthanidocenes were reported.

Since the metallocenes of the lanthanides and the group IIIb elements are isoelectronic to the group IVb metallocene cations they can polymerise without a cocatalyst [6]. This fact facilitates significantly the study of α-olefin polymerization mechanism and the influence of the metal ligand environment on the structure and properties of the resultant polymer.

In this paper we report on the synthesis and structures of the two complexes: lithium *rac*-(2,2-bis-(η^5-3-trimethylsilylcyclopentadienyl)propane)dichlorobis(di-

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[*] Corresponding author. Fax: +7 95 9328846, e-mail: bulychev@highp.chem.msu.su

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ethyl ether)ytterbate(III) and lithium *rac*-(2,2-bis-(η^5-3-trimethylsilylcyclopentadienyl)propane)bis(tetrahydroborato)bis(tetrahydrofuran) ytterbate(III).

2. Experimental

All operations related to the preparation of reagents, synthesis, and studies of products were performed under vacuum or argon by means of Schlenk technique. The solvents were refluxed with $LiAlH_4$ for 3 h followed by distillation. $LiBH_4$ was recrystallised in ether. $(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Li_2$ was synthesized using the method described in [7] for related compounds. Anhydrous $YbCl_3$ was prepared by desolvation of $YbCl_3 \cdot 6H_2O$ with NH_4Cl [8].

2.1. *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**1**)

A suspension of $(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Li_2$ (2.53 g, 7.70 mmol) in ether (100 ml) was added to a stirred suspension of $YbCl_3$ (2.15 g, 7.70 mmol) in the same solvent (100 ml). A green solution with a precipitate was obtained and vigorously stirred for 48 h. The precipitate was filtered and washed with ether until white. After this, the ether fractions were combined and diluted with benzene (30 ml). The solution obtained was concentrated in vacuum to isolate green crystals of compound **1** (2.02 g, yield 37%). Anal. Found, (%): C, 45.47; H, 7.11; Yb, 24.4; Li, 1.1; Cl, 9.82. Calculated for $C_{27}H_{50}Cl_2O_2Si_2LiYb$, (%): C, 45.43; H, 7.06; Yb, 24.24; Li, 0.97; Cl, 9.93.

Table 1
Crystal data and structure refinement for *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**1**) and *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(BH_4)_2Li(THF)_2$ (**2**)

Compound	**1**	**2**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.680(2)	7.0030(10)
b (Å)	21.823(4)	11.370(2)
c (Å)	13.843(3)	11.895(2)
α (°)		106.42(3)
β (°)	99.03(3)	95.24(3)
γ (°)		98.91(3)
V (Å^3)	3484.7(12)	888.4(3)
D_{calc} (mg m^{-3})	1.360	1.250
Wavelength (Å)	0.71073	0.71073
Temperature (K)	293(2)	293(2)
Z	4	1
Diffractometer	CAD-4	Syntex P-1
Collection method	$\theta/2\theta$	$\theta/2\theta$
Radiation type	Mo–K$_\alpha$	Mo–K$_\alpha$
Radiation monochromator	beta-filter	beta-filter
Absorption coefficient (mm^{-1})	2.925	2.718
Crystal size (mm)	$0.26 \times 0.24 \times 0.12$	$0.23 \times 0.20 \times 0.17$
Theta range for data collection (°)	1.76 to 22.38	2.19 to 25.05
Reflections collected	1302	2783
Independent reflections	1219	2783
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0920$	$R_1 = 0.0235$, $wR_2 = 0.0573$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**

Atom	x	y	z	U_{eq}
Yb	1120(1)	4171(1)	7156(1)	48(1)
Cl(1)	2389(5)	3202(3)	7243(5)	64(2)
Cl(2)	2228(6)	4525(3)	5792(5)	66(2)
Si(1)	3395(7)	5558(4)	8139(7)	80(3)
Si(2)	−655(7)	2742(4)	5692(6)	71(2)
C(1)	2226(23)	5018(12)	8353(17)	53(7)
C(2)	1081(31)	5134(11)	8199(18)	73(8)
C(3)	465(23)	4698(14)	8607(19)	59(8)
C(4)	1344(23)	4251(13)	9012(15)	62(7)
C(5)	2369(21)	4454(11)	8854(16)	51(7)
C(6)	−622(20)	3480(12)	6278(18)	57(7)
C(7)	−812(20)	3601(12)	7301(19)	60(7)
C(8)	−988(20)	4238(13)	7378(19)	65(7)
C(9)	−918(21)	4515(12)	6482(23)	70(8)
C(10)	−734(21)	4059(12)	5835(17)	64(7)
C(11)	−831(26)	4582(12)	8391(19)	67(8)
C(12)	−1535(24)	5163(13)	8287(22)	98(10)
C(13)	−1258(20)	4201(17)	9169(17)	95(10)
C(14)	3860(30)	5993(16)	9266(29)	161(18)
C(15)	4688(28)	5152(14)	7853(28)	135(14)
C(16)	2865(30)	6102(14)	7154(27)	129(13)
C(17)	200(28)	2794(14)	4681(21)	116(12)
C(18)	−116(27)	2143(13)	6530(20)	98(11)
C(19)	−2138(32)	2555(15)	5141(26)	138(14)
O(1)	3383(18)	3145(10)	4824(13)	96(7)
C(20)	2875(38)	3365(22)	3848(30)	154(20)
C(21)	3422(48)	3590(28)	3330(43)	260(33)
C(22)	3758(77)	2610(28)	4922(73)	346(54)
C(23)	3531(53)	2137(23)	5248(47)	212(32)
O(2)	5070(15)	3675(9)	6591(16)	89(6)
C(24)	5505(33)	3493(23)	7591(37)	151(16)
C(25)	5947(46)	2919(22)	7701(36)	191(22)
C(26)	5995(45)	3939(24)	6172(45)	183(22)
C(27)	5752(44)	4248(30)	5446(45)	242(35)
Li	3433(40)	3632(18)	6008(28)	65(13)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.2. *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(BH_4)_2Li(THF)_2$ (**2**)

A suspension of ytterbium (III) chloride (2.70 g, 9.66 mmol) in THF (100 ml) was slowly added to a stirred suspension of $(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Li_2$ (3.15 g, 9.59 mmol) in THF (150 ml). The resulting dark-cherry solution was concentrated in vacuum to 30 ml followed by dilution with ether (100 ml). A white precipitate of LiCl was filtered off. After this, a solution of $LiBH_4$ (0.31 g, 14.23 mmol) in ether (50 ml) was combined with the filtrate and stirred. After the isolation of lithium chloride hexane (ca. 40 ml) was added to the filtrate and the resulting solution was concentrated. Green crystals of compound **2** (1.98 g, yield 31%) were formed after keeping the solution for 1 month. Anal. Found, (%): Yb, 25.8; Li, 1.1. Calculated for $C_{27}H_{54}B_2O_2Si_2LiYb$, (%): Yb, 25.88; Li, 1.04.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

Atom	*x*	*y*	*z*	U_{eq}
Yb	5000	5000	5000	55(1)
Si(1)	3938(6)	2185(4)	1777(3)	94(1)
Si(2)	6294(6)	8263(4)	7811(4)	95(1)
C(1)	3514(12)	2788(8)	3339(8)	67(2)
C(2)	4449(12)	2558(8)	4350(8)	69(2)
C(3)	3414(14)	2940(8)	5312(8)	74(2)
C(4)	1883(12)	3453(8)	4910(9)	75(2)
C(5)	1914(12)	3331(8)	3702(9)	72(2)
C(6)	6249(13)	6574(9)	7207(7)	73(2)
C(7)	4786(14)	5582(9)	7266(7)	70(2)
C(8)	5444(13)	4440(9)	6944(7)	73(2)
C(9)	7324(14)	4720(11)	6662(8)	79(3)
C(10)	7855(13)	6009(10)	6823(8)	77(2)
C(11)	4165(17)	3138(10)	6585(8)	89(3)
C(12)	5360(26)	2160(12)	6733(11)	126(5)
C(13)	2478(22)	3087(13)	7317(11)	118(4)
C(14)	3130(37)	3169(22)	937(13)	189(9)
C(15)	6475(21)	2108(13)	1654(12)	117(4)
C(16)	2530(31)	582(19)	1162(15)	165(9)
C(17)	7813(29)	9166(13)	7041(19)	158(6)
C(18)	3855(24)	8641(15)	7715(14)	129(5)
C(19)	7318(32)	8751(14)	9392(14)	143(6)
B(1)	3164(16)	6685(10)	4600(11)	78(3)
B(2)	7685(18)	5299(13)	3696(12)	79(3)
Li	10309(22)	6754(15)	3259(15)	80(4)
O(1)	9545(12)	8366(7)	3487(8)	114(3)
C(20)	7584(24)	8374(14)	3007(17)	153(7)
C(21)	7212(28)	9539(17)	3558(27)	202(11)
C(22)	8907(28)	10331(14)	4154(20)	162(7)
C(23)	10406(21)	9559(14)	4155(17)	136(5)
O(2)	10493(13)	6271(9)	1563(7)	120(3)
C(24)	9048(35)	5516(30)	648(20)	192(9)
C(25)	9906(115)	5467(55)	−276(28)	418(39)
C(26)	11785(87)	6495(49)	94(38)	387(34)
C(27)	12032(45)	6805(23)	1129(22)	211(11)
H(1YB)	5204(136)	6368(90)	4953(84)	87(27)
H(1B1)	2408(158)	5649(98)	5159(105)	91(32)
H(2B1)	2442(157)	7447(106)	4476(97)	106(32)
H(3B1)	2657(212)	6106(144)	3935(136)	134(50)
H(1B2)	8197(135)	6049(99)	4090(91)	74(26)
H(2B2)	8763(179)	5138(111)	2845(111)	121(38)
H(3B2)	6077(229)	5040(130)	3285(129)	117(44)
H(4B2)	7725(189)	4509(126)	4009(122)	143(40)

U_{eq} is defined as one third of the *trace* of the orthogonalized U_{ij} tensor.

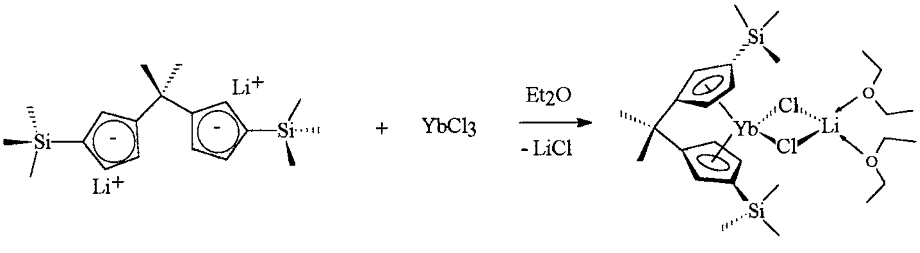
2.3. X-ray structure refinement for 1 and 2

The details of the unit cell determination, data collection and structure refinement are given in Table 1. Experimental data were processed using the PROFIT procedure [9]. An absorption correction was not applied. The structure was solved by the heavy atom technique and refined using full-matrix anisotropic least-squares. Hydrogen atoms positions were found from a difference synthesis. The coordinates and isotropic thermal parameters of the hydrogen atoms were also refined and other hydrogen atoms were included in the refinement with fixed positional and thermal parameters. The structure solution and refinement were performed using SHELXTL-81 [10] and SHELXL-93 [11] packages, respectively. Atomic coordinates for compounds **1** and **2** are presented in Tables 2 and 3, respectively.

3. Results and discussion

The 'ate' complex $(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2YbCl_2Li(OEt_2)_2$ (**1**) was synthesized using the typical reaction between a dilithio salt of an *ansa* ligand and ytterbium (III) chloride (Scheme 1). The use of ether as a solvent provides better *rac*-isomer crystallization conditions because of the higher solubility of the *meso*-isomer. Performing the reaction in THF results in the formation of a non-crystallising oil containing, probably, *rac*- and *meso*-forms mixture of **1**.

The crystal structure of **1** is comprised of *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ molecules (Fig. 1). The composition of that molecule is rather common for such substances. An average Yb–Cl bond distance (Table 4) of 2.57 Å falls in the range of the values found for ytterbium (III) chloride solvates and ytterbocenes $(YbCl_3(THF)_3$ 2.52 Å [12], $YbCl_3(C_6H_{10}O_2)(THF)_2$ 2.53 Å [13], $YbCl_3(HMPA)_3$ 2.59 Å [14], $(^tBuC_5H_4)_2YbCl\cdot THF$ 2.54 Å [15]) as well as for the following complexes: $[Me_4C_2(C_5H_4)_2YbCl_2]^-[Mg_2Cl_3\cdot 6THF]^+\cdot THF$ 2.53 and 2.56 Å [4], $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ 2.59 Å, $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ 2.59 and 2.60 Å [16]. The Cl–Yb–Cl angle is equal to 85.9° and comparable also with 86.0 and 87.1° values in complexes $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ [16], respectively. The lithium coordination sphere including Li–O (1.94 and 1.96 Å) and Li–Cl (2.40 and 2.44 Å) bonds is reasonably conventional, except for the short Li–C(22) distance of 2.75(7) Å. This is likely



(1)

Scheme 1.

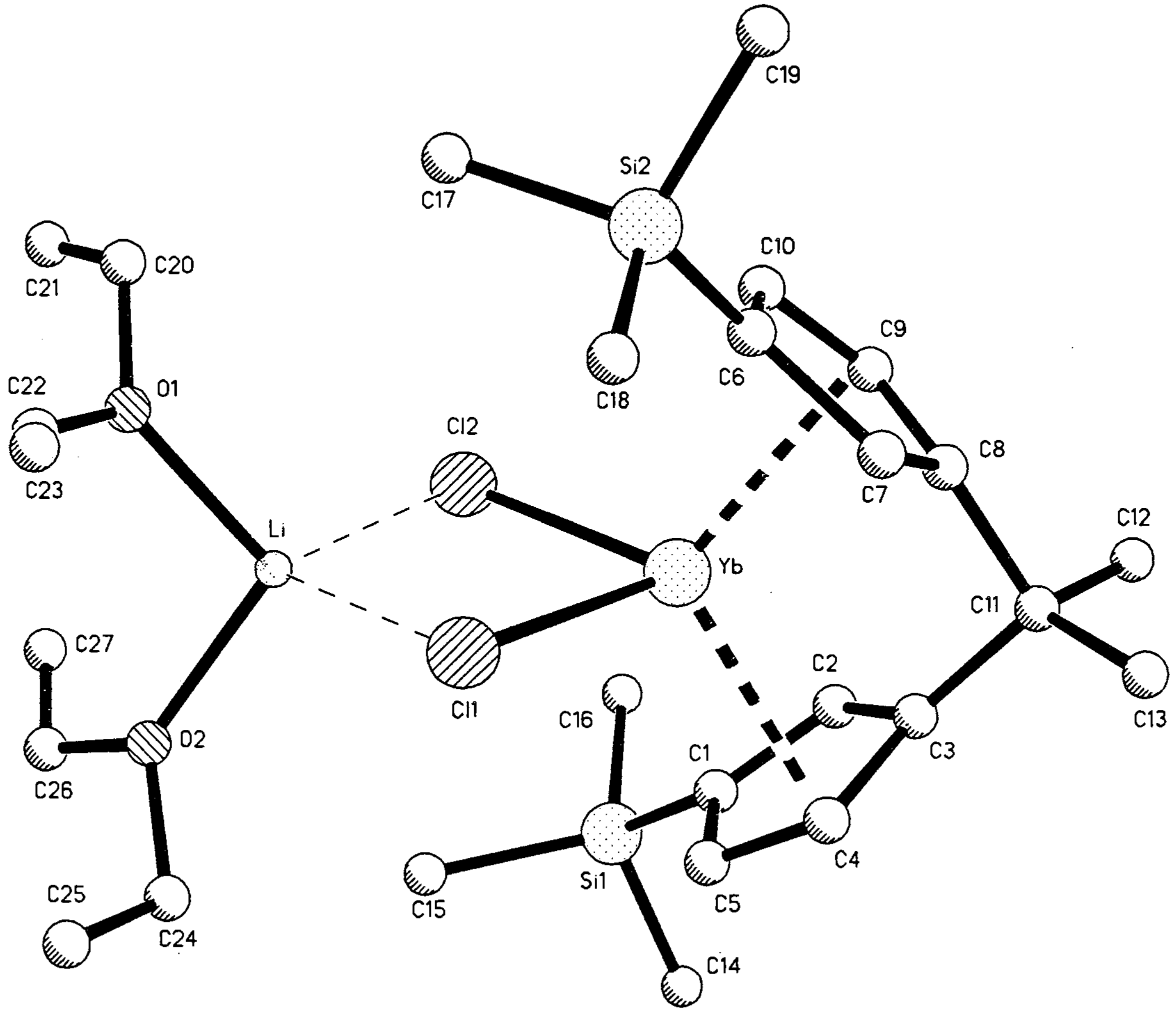


Fig. 1. Molecular structure of *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**1**).

the result of the unsaturated nature of the tetrahedral lithium coordination sphere.

On dissolving in benzene complex **1** decomposes with the elimination of LiCl and the formation of an *ansa*-ytterbocene chloride complex. It was expected that the reaction between **1** and $LiBH_4$ would afford the appropriate mono-borohydride. Unfortunately the IR spectrum of the crystals **2** obtained by reacting the THF-derivative of **1** and a $LiBH_4$ ether solution (Scheme 2), is not informative, because the broad band in the 2100–2450 cm^{-1} region with maxima at 2260, 2300 and 2415 cm^{-1} is observed. From the IR results it may be only stated that the compound **2** is not ionic tetrahydroborate complex. At the same time, the elemental analysis of the crystals **2** indicates that the ate-complex was formed again. Nevertheless, taking into consideration the larger radius of the BH_4-group in comparison with chloride and the value of the Cl–Yb–Cl angle in **1**, the appearance of a borohydride ate-complex was doubtful.

Table 4
Selected bond lengths (Å) and angles (°) for **1**

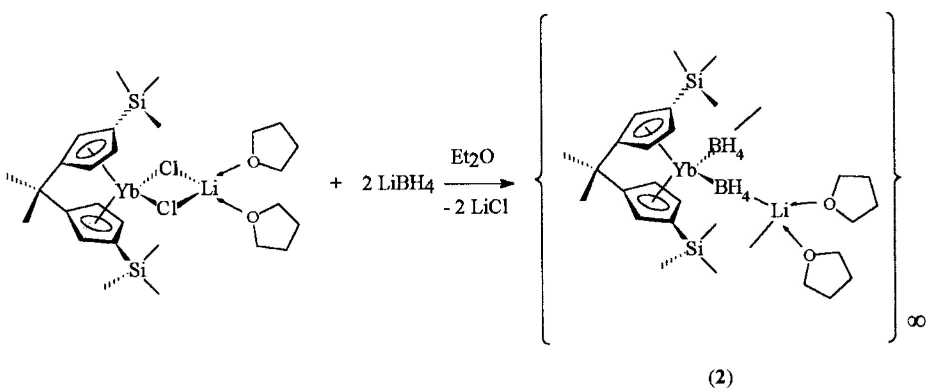
Bond	d (Å)	Angle	ω (°)
Yb–C(8)	2.53(2)	Cl(2)–Yb–Cl(1)	85.9(2)
Yb–C(3)	2.53(2)	Li–Cl(1)–Yb	89.9(9)
Yb–C(9)	2.53(2)	Li–Cl(2)–Yb	91.0(10)
Yb–C(4)	2.55(2)	O(1)–Li–O(2)	106(2)
Yb–C(2)	2.55(2)	Cl(2)–Li–Cl(1)	92.9(14)
Yb–Cl(2)	2.569(6)	Cl(2)–Li–Yb	46.4(7)
Yb–Cl(1)	2.574(6)	Cl(1)–Li–Yb	46.6(7)
Yb–C(7)	2.61(2)	C(3)–C(11)–C(8)	103(2)
Yb–C(10)	2.62(2)	$(C'–C''–C''')_{av}^{Cp}$	108
Yb–C(5)	2.64(2)	Cp(1)\Cp(2)	74.0
Yb–C(6)	2.67(2)	Cp(1)–Yb–Cp(2)	113.6
Yb–C(1)	2.68(2)		
Cl(1)–Li	2.44(4)		
Cl(2)–Li	2.40(4)		
O(1)–Li	1.94(4)		
O(2)–Li	1.96(5)		
$(C–C)_{av}^{Cp}$	1.40		
$(Yb–Cp)_{av}$	2.30		

Actually, in the crystal structure of compound **2** (Fig. 2) the lithium atom is a bridge for two ytterbocene borohydride fragments. The coordination polyhedron of lithium is a very distorted octahedron (Fig. 3, Table 6). As a result, the compound is a polymer composed of ytterbocene moieties connected into a $\{Li(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2Yb(\mu_2\text{-}H)_2B(\mu_2\text{-}H)_2\}_\infty$ chain by two tetradentate borohydride groups. In that chain, each Li atom is out of the B(1)YbB(2) plane by 1.10 Å, whereas the Li′ atom is out of the same plane by 1.67 Å but in opposite direction. The value of the B(1)–M–B(2) angle (96.3°) approaches the parameter known for the neutral bis-borohydride $(MeC_5H_4)_2Hf(BH_4)_2$ (101.4°) [17]. Thus, compound **2** is an *ansa*-ytterbocene borohydride complex with $LiBH_4$ rather than an ate-complex. The structures of related compounds are unknown, but the formation of unstable complexes in solution was presumed elsewhere [18]. Numerous lithium borohydride complexes with inorganic borohydrides of transition metals, lanthanides and actinides have been described [19].

In terms of ytterbium–boron and boron–lithium distances (Table 5) both borohydride groups are identical to each other but can be distinguished by the B–H bonds and angles in the BH_4 group. In spite of the low precision of the hydrogen atom positions, very short Yb–H (1.6 Å) and very large B–H (1.6 Å) bonds lengths are apparent. The rest of the Yb–H bond lengths are in the range from 2.1 to 2.6 Å. The B–H distance which of 1.6 Å (Table 6) exceeds B–H bond lengths in the borohydride structures $(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$ (1.05–1.19 Å) [20], $[C_5H_3(SiMe_3)_2]_2Sc(\mu_2\text{-}H)_2BH_2$ (1.19 Å) [21] and $\{(\eta^5\text{-}C_5H_3^tBu_2)_2Ce[\mu{:}\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ (0.94–1.40 Å) [22].

The parameters described above and the large value of the B(1)–Yb–B(2) angle indicate that there are steric difficulties in the location of two bulky BH_4-groups. The most distorted BH_4-group seems to have the BH_3 fragment ‘prepared’ for the elimination. Unfortunately, we can’t prove this supposition because when treated with triethylamine, **2** forms a non-crystallising oil. $LiBH_4$ could be isolated, however. Probably, a similar phenomenon occurs in the case of zirconocene bis-borohydride complexes which on treating with trialkylamines lose readily BH_3 with the generation of the hydride-borohydride derivative $Cp_2Zr(H)BH_4$ [23].

Evidently, the formation and stability of the ytterbocene borohydride complex with $LiBH_4$ is specified by the geometry and coordination type of the cyclopentadienyl ligand with a short Me_2C bridge. In that ligand, the silicon atom of the trimethylsilyl group is out of the plane of the cyclopentadienyl rings by 0.31–0.33 Å in the direction opposite to the ytterbium atom. An analogous phenomenon was also observed in the following structures: $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (0.23 and 0.41 Å) [16], $[1,3\text{-}(SiMe_3)_2C_5H_3]_2Yb\cdot THF$ (0.14 Å) [24]. C(11) bridge atoms in structures **1** and **2** are out of the cyclopentadienyl ring plane in the ytterbium direction by ca. 13°.



(2)

Scheme 2.

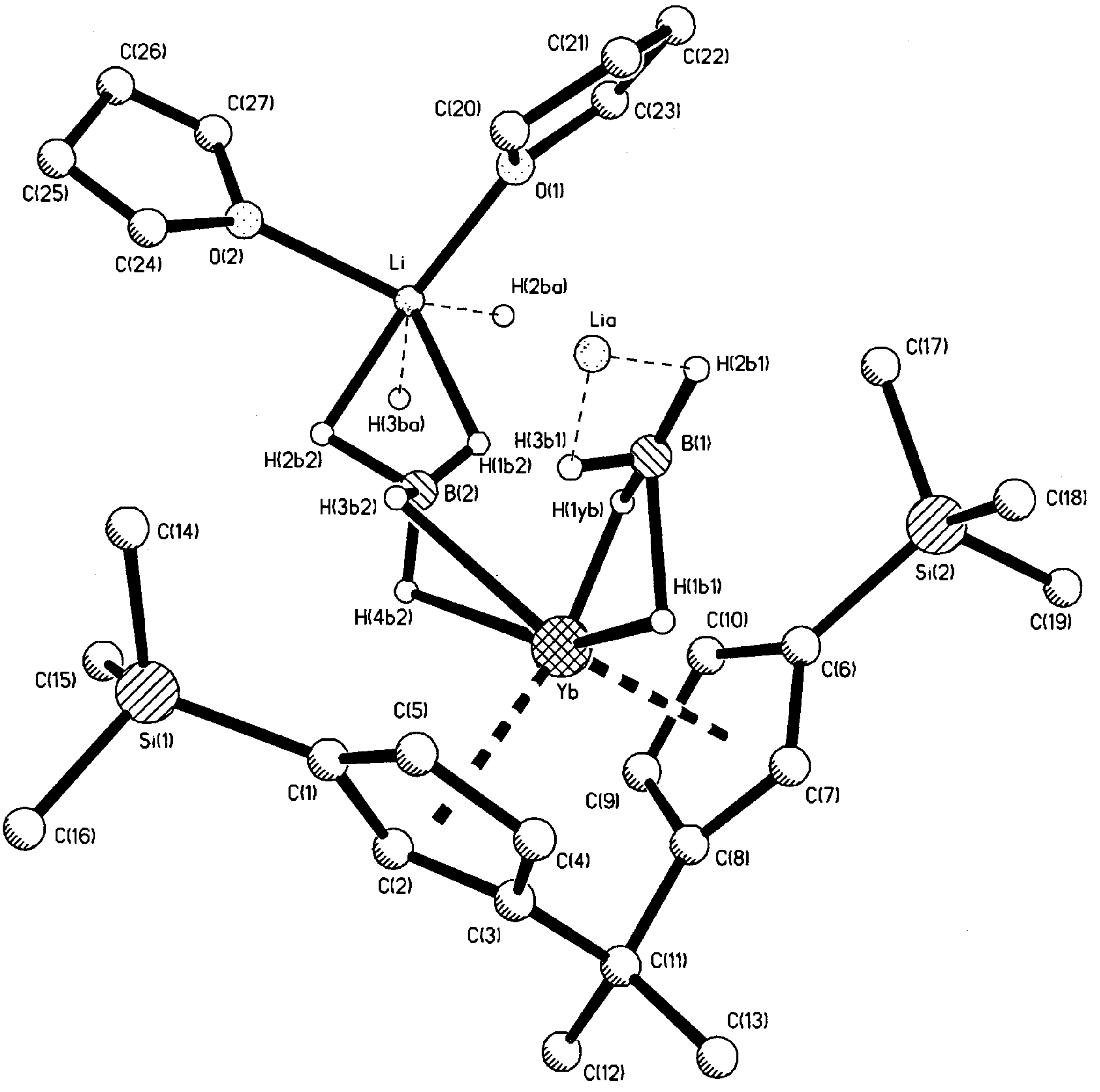


Fig. 2. Fragment of the structure of $\{rac\text{-}(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(BH_4)_2Li(THF)_2\}_\infty$ (**2**).

The average Yb–C^{Cp} distance (2.59 Å in **1** and 2.62 Å in **2**) is practically the same as in the related ytterbocenes $[Me_4C_2(C_5H_4)_2YbCl_2]^-[Mg_2Cl_3\cdot 6THF]^+\cdot THF$ (2.60 Å) [4], $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (2.61 Å), $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (2.63 Å) [16], $({}^tBuC_5H_4)_2YbCl\cdot THF$ (2.63 Å) [15] and $(C_5Me_5)_2YbCl\cdot THF$ (2.65 Å) [25]. The Yb–C bond lengths are slightly different for complexes **1** and **2** on the one hand (2.53–2.68 Å in **1** and 2.54–2.71 Å in **2**) and for the compounds $[Me_4C_2(C_5H_4)_2YbCl_2]^-[Mg_2Cl_3\cdot 6THF]^+\cdot THF$ [4], $({}^tBuC_5H_4)_2YbCl\cdot THF$ [15], $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ [16] on the other hand (2.56–2.71 Å).

In spite of a coincidence of the Yb–C bond distances there is a pronounced difference in the bond angle characteristics for *ansa*-bound species on one hand and the usual ytterbocenes fragments on the other. In particular, the dihedral angle between cyclopentadienyl planes in **1** (74.0°) and **2** (76.2°) exceeds considerably that in complexes $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2AlCl_2$, $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (42.7–49.6°) which contain non-associated rings [16]. Correspondingly, the Cp–Yb–Cp angles decrease to 113.6° in **1** and 111.0° in **2** as opposed to 120–150° values for regular complexes. This leads to the 'opening' of the wedge between cyclopentadienyl planes where two BH_4-groups can be located.

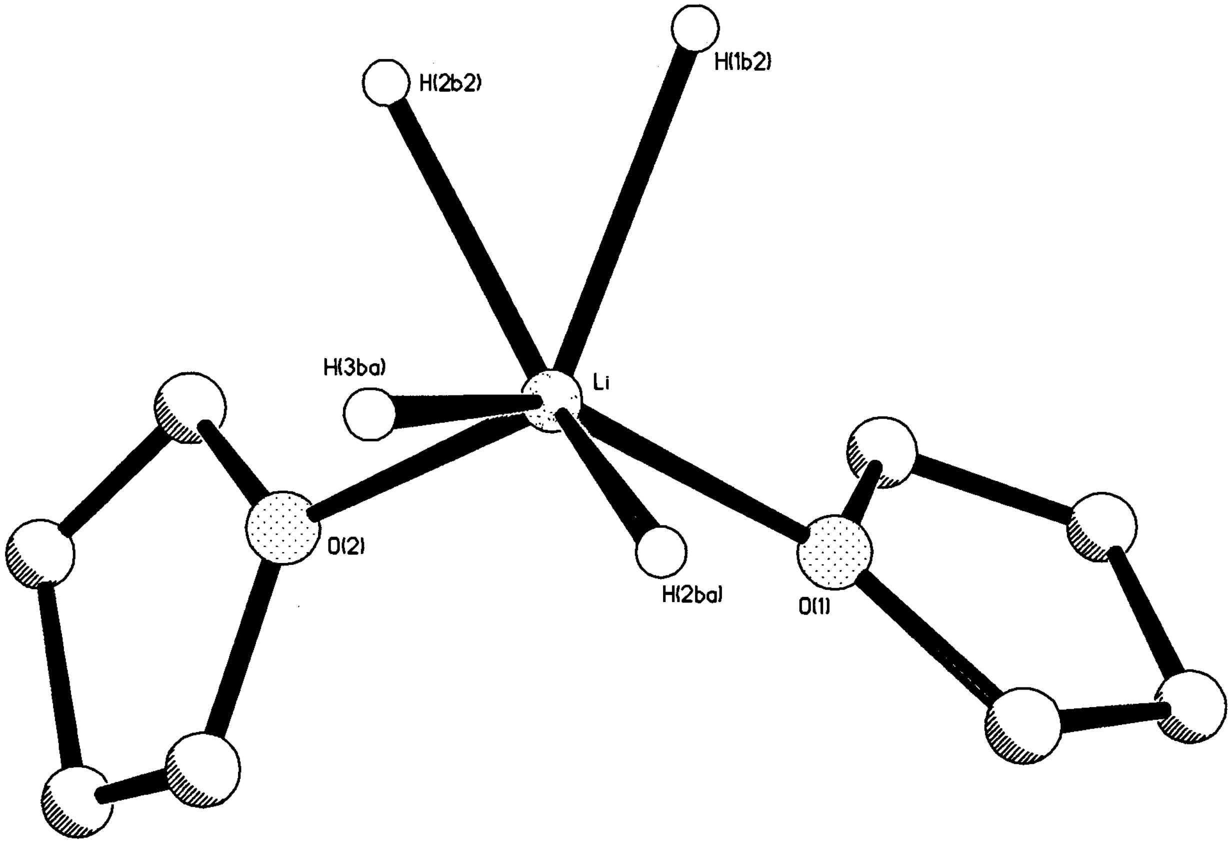


Fig. 3. Coordination sphere of lithium atom in the structure **2**.

Table 5
Selected bond lengths (Å) and angles (°) for **2**

Bond	*d* (Å)	Angle	*ω* (°)
Yb–B(2)	2.587(11)	B(2)–Yb–B(1)	96.3(4)
Yb–B(1)	2.592(10)	^{a}Li–B(1)–Yb	137.2(6)
Yb–C(4)	2.556(9)	Li–B(2)–Yb	147.2(7)
Yb–C(9)	2.567(8)	^{b}B(1)–Li–B(2)	102.3(7)
Yb–C(8)	2.571(7)	C(3)–C(11)–C(8)	102.5(7)
Yb–C(3)	2.573(8)	Cp(1)–Yb–Cp(2)	111.0
Yb–C(7)	2.612(8)	Cp(1)\Cp(2)	76.2
Yb–C(2)	2.619(8)	(C–C–C)$_{av}^{Cp}$	108.0
Yb–C(10)	2.666(8)		
Yb–C(5)	2.668(8)		
Yb–C(6)	2.702(8)		
Yb–C(1)	2.705(8)		
B(1)–Li^{a}	2.47(2)		
B(2)–Li	2.47(2)		
Li–O(1)	1.94(2)		
Li–O(2)	1.96(2)		
Li–B(1)^{b}	2.47(2)		
(Yb–Cp)$_{av}$	2.33		
(C–C)$_{av}^{Cp}$	1.41		

Symmetry transformations used to generate equivalent atoms: ^{a} $x-1$, y, z and ^{b} $x+1$, y, z.

Table 6
Selected hydrogen bond lengths (Å) and angles (°) for **2**

Bond	*d* (Å)	Angle	ω (°)
B(1)–H(1Yb)	1.6(1)	H(1Yb)–B(1)–H(1B1)	83(1)
B(1)–H(1B1)	1.5(1)	H(1Yb)–B(1)–H(2B1)	143(1)
B(1)–H(2B1)	1.1(1)	H(1Yb)–B(1)–H(3B1)	105(1)
B(1)–H(3B1)	0.9(1)	H(1B1)–B(1)–H(3B1)	83(1)
		H(2B1)–B(1)–H(1B1)	128(1)
		H(2B1)–B(1)–H(3B1)	99(1)
Yb–H(1Yb)	1.6(1)		
Yb–H(1B1)	2.1(1)		
Yb–H(3B1)	2.6(1)		
B(2)–H(1B2)	0.8(1)	H(1B2)–B(2)–H(2B2)	99(1)
B(2)–H(2B2)	1.3(1)	H(3B2)–B(2)–H(4B2)	97(1)
B(2)–H(3B2)	1.1(1)	H(1B2)–B(2)–H(3B2)	121(1)
B(2)–H(4B2)	1.1(1)	H(1B2)–B(2)–H(4B2)	125(1)
		H(2B2)–B(2)–H(3B2)	109(1)
		H(2B2)–B(2)–H(4B2)	104(1)
Yb–H(3B2)	2.2(1)		
Yb–H(4B2)	2.4(1)		
Li–H(2B2)	1.9(1)	H(2B2)–Li–H(1B2)	50(1)
Li–H(2B1)	1.9(1)	H(2B2)–Li–H(3B1)	90(1)
Li–H(1B2)	2.0(1)	H(1B2)–Li–H(3B1)	99(1)
Li–H(3B1)	2.1(1)	H(1B2)–Li–H(2B1)	103(1)
		H(2B2)–Li–H(2B1)	127(1)

4. Supplementary material

Listings of anisotropic temperature factors, hydrogen atom parameters, complete bond distances and angles of complexes **1** and **2** can be obtained from the authors on request.

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