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ansa-Ytterbocene(III) chloride and borohydride with a short bridge and bulky substituents: synthesis and crystal structures of $[meso\text{-}(CH_3)_2Si[3\text{-}(CH_3)_3SiC_5H_3]_2Yb(\mu_2\text{-}Cl)]_2$ and $meso\text{-}(CH_3)_2Si[3\text{-}(CH_3)_3SiC_5H_3]_2Yb[(\mu_2\text{-}H)_3BH](THF)$

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Abstract

The *ansa*-ytterbocene(III) *meso*-$(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2YbCl(THF)$ (**1**) undergoes desolvation during recrystallisation from toluene to give the dimeric complex $[meso\text{-}(CH_3)_2Si[3\text{-}(CH_3)_3SiC_5H_3]_2Yb(\mu_2\text{-}Cl)]_2$ (**2**). Complex **1** reacts with $LiBH_4$ in diethyl ether, yielding the borohydride complex *meso*-$(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2YbBH_4(THF)$ (**3**) with a tridentate BH_4 group. The structures of **2** and **3** were determined by X-ray structural analysis.

Keywords: Ytterbium(+ 3); ansa-Metallocenes; Borohydride; Crystal structure

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1. Introduction

According to the data of the Cambridge Structural Data Bank, lanthanidocene(+ 3) derivatives, particularly halides, have a rather wide variety of structures, and it is the halides that define the structural types in the lanthanidocene family. The following *ansa*-lanthanidocene halides were structurally characterised:

1. ionic *ate* complex $[Me_4C_2(C_5H_4)_2YbCl_2]^-$ $[Mg_2Cl_3{\cdot}6THF]^+{\cdot}THF$ [1] and molecular *ate* complexes $[Me_2Si(C_5Me_4)_2NdCl]_2ClLi(THF)_2$ [2], *rac*-$Me_2Si(2\text{-}Me_3Si\text{-}4\text{-}Bu^tC_5H_2)_2YCl_2Li(THF)_2$ [3], (R)-(+)-$Me_2Si(C_5H_4)((neomenthyl)C_5H_3)LuCl_2Li(Et_2O)_2$ [4], *rac*-$Me_2Si(2,4\text{-}(Me_3Si)_2C_5H_2)_2SmCl_2Li(THF)_2$ [5], and *rac*-$Me_2C(3\text{-}Me_3EC_5H_3)_2YbCl_2Li(OEt_2)_2$ (E = Si [6], C [7]);
2. solvated monomers *meso*-$Me_2Si(Me_2SiOSiMe_2)(3\text{-}Me_3SiC_5H_2)_2YCl(THF)$ [5] and *meso*-$Me_2Si[3\text{-}Me_3SiC_5H_3]_2YbCl(THF)$ [7]; and
3. unsolvated dimers $[\mu_2\text{-}(Me_2Si(C_5H_4)_2)YbX]_2$ (X = Cl [8], Br [9]), in which one *ansa*-bound ligand is coordinated to two metal atoms.

Borohydride analogues of the lanthanidocene halides are less studied. Six bis(cyclopentadienyl) complexes with non-bonded ligands were structurally characterised: unsolvated monomer $((Me_3Si)_2C_5H_3)_2ScBH_4$ [10], unsolvated dimers $[(^tBu_2C_5H_3)_2LnBH_4]_2$ (Ln = Ce [11], Sm [12]), and monomeric ‘inner’ solvates $(C_5H_4CH_2CH_2OMe)_2LnBH_4$ (Ln = Y [13], Pr [14], Nd [14]). The only known *ansa*-lanthanidocene borohydride is $\{rac\text{-}Me_2C(3\text{-}Me_3SiC_5H_3)_2Yb(BH_4)_2Li(THF)_2\}_\infty$ [6], a heterometallic complex of *ansa*-ytterbocene with lithium borohydride.

In this paper, we report the structures of the *ansa*-ytterbocenes(+ 3) $[meso\text{-}(CH_3)_2Si[3\text{-}(CH_3)_3SiC_5H_3]_2Yb(\mu_2\text{-}Cl)]_2$ (dimeric unsolvated chloride) and *meso*-$(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2Yb[(\mu_2\text{-}H)_3BH](THF)$ (monomeric solvated borohydride).

2. Experimental

All manipulations involved in the pretreatment of the starting reagents, synthesis, and study of reaction products were performed under flowing argon or in vacuo with the use of Schlenk techniques. Solvents were

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boiled over $LiAlH_4$ for 2 h and then distilled. $LiBH_4$ was recrystallised from ether. *meso*-$(CH_3)_2Si(3-(CH_3)_3Si-C_5H_3)_2YbCl(THF)$ (**1**) was prepared by the known [7] procedure.

2.1. *[meso-$(CH_3)_2Si[3-(CH_3)_3SiC_5H_3]_2Yb(\mu_2-Cl)]_2$* (**2**)

Complex **1** (0.50 g, 0.82 mmol) was dissolved in 100 ml of toluene. The solvent was removed in vacuo at 70°C until crystallisation commenced. The resulting crystals were dissolved with heating and left to slowly cool. Red crystals of **2** (0.14 g) were thus obtained. Yield: 31%. Found (%): C, 40.18; H, 5.55; Yb, 16.2. Anal. Calc. for $C_{36}H_{60}Cl_2Si_6Yb_2$: C, 40.09; H, 5.61; Yb, 16.05.

2.2. *meso-$(CH_3)_2Si(3-(CH_3)_3SiC_5H_3)_2YbBH_4(THF)$* (**3**)

To a red solution of **1** (0.25 g, 0.41 mmol) in diethyl ether (50 ml), 11 ml of 0.04 M $LiBH_4$ solution in diethyl ether was added with stirring to obtain a red solution with a white precipitate. The mixture was stirred for 1 day. The precipitate was then filtered off, and the solution was evaporated to dryness. Recrystallisation of the resultant solid from benzene yielded 0.10 g of red crystals of **3**. Yield: 41%. Found (%): C, 44.62; H, 7.01; Yb, 29.3. Anal. Calc. for $C_{22}H_{42}BOSi_3Yb$ (%):C, 44.73; H, 7.17; Yb, 29.29. IR (Nujol, KBr, cm^{-1}): 470 (s), 490 (s), 635 (s), 652(s), 674 (s), 680 (sh), 750–880 (broad band with maxima at 765, 785, 795, 815, 840, and 855), 930 (s), 1015 (s), 1045 (sh), 1060 (sh), 1085 (s), 1110 (sh), 1195 (s), 1210 (sh), 1250 (s), 1315 (w), 1340 (w), 1375 (w), 1405 (w), 1440 (s), 1455 (sh), 2125 (s), 2195 (s), 2240–2385 (broad band with maxima at 2250, 2280, 2310, and 2370), and 2475 (s) (see also Fig. 3).

2.3. *X-ray structure determination*

Unit cell determination, data collection, and structure refinement are detailed in Table 1. Structures were solved by direct methods, and non-hydrogen atoms were refined by anisotropic full-matrix least squares. Hydride hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The other hydrogen atoms were placed geometrically and refined in a riding model. All calculations were carried out with the use of the SHELXTL PLUS and SHELXL-93 programs. At room temperature unexpected strong thermal vibrations of the atoms have not allowed the crystal structure of complex **2** to be refined. As a consequence, the data have been collected at 193 K.

3. Results and discussion

Complexes **2** and **3** were synthesised by standard procedures, and no anomalies were observed during the syntheses. It is somewhat surprising that complex **1** undergoes desolvation at a temperature as low as 70°C. Usually, desolvation of such a complex requires either prolonged boiling of its solution in a high-boiling solvent with simultaneous removal of the solvent or vacuum sublimation with heating. On heating borohyride complex **3** decomposes giving hydride compound and then products of unknown composition.

In the crystal structure of **2** (Fig. 1, Table 2), Cp rings are flat to an accuracy of 0.0017 Å. The Si(2) atom is off the ring plane by 7°, the Si(3) atom by 9°, and the Si(1) atom by 20 and 19°. The Yb–Cl distances in **2** (2.631(3), 2.681(4) Å) are much longer than that in the starting monomeric solvated complex **1** (2.496(2) Å [7]) but are nearly equal to those in the other known dimeric chlorides: $[\mu_2-(Me_2Si(C_5H_4)_2)YbCl]_2$, 2.636 Å [15]; $[(C_5H_5)_2YbCl]_2$, 2.639(3) and 2.645(3) Å [16]; $[(C_5H_4Me)_2YbCl]_2$, 2.64 Å [17]; $[((Me_3Si)_2C_5H_3)_2YbCl]_2$, 2.65 Å [18]; and $[(Ph_2PC_5H_4)_2YbCl]_2$, 2.627(5)–2.676(5) Å [19]. The parameters of the metallocene fragment of **2** are identical to those of **1** [7].

Table 1
Crystal data and structure refinement for [*meso*-$(CH_3)_2Si[3-(CH_3)_3SiC_5H_3]_2Yb(\mu_2-Cl)]_2$ (**2**) and *meso*-$(CH_3)_2Si(3-(CH_3)_3SiC_5H_3)_2-YbBH_4(THF)$ (**3**)

Compound	2	3
Colour	Red	Red
Habit	Rhombohedron	Rhombohedron
Crystal size (mm)	0.1 × 0.2 × 0.1	0.2 × 0.4 × 0.2
Unit cell dimensions		
a (Å)	9.920(9)	10.791(4)
b (Å)	11.639(9)	23.529(8)
c (Å)	11.701(7)	12.234(4)
α (°)	94.05(6)	90
β (°)	107.45(6)	116.12(2)
γ (°)	116.26(7)	90
Wavelength (Å)	0.71073	0.71073
Radiation type	Mo–K_α	Mo–K_α
Radiation monochromator	Graphite	Graphite
Temperature (K)	193(2)	298(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Z	1	4
Volume (Å^3)	1123(1)	2789(2)
Diffractometer	Syntex $P2_1$	Siemens P3/PC
Collection method	$\theta/2\theta$	$\theta/2\theta$
Theta range for data collection (°)	1.88–25.05	1.73–26.06
Absorption coefficient (mm^{-1})	4.441	3.492
Reflections collected	3959	5800
Independent reflections	3959	5505
Refinement method	Full-matrix-block least-squares on F^2	Full-matrix-block least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0903$, $wR_2 = 0.2469$	$R_1 = 0.0379$, $wR_2 = 0.0727$

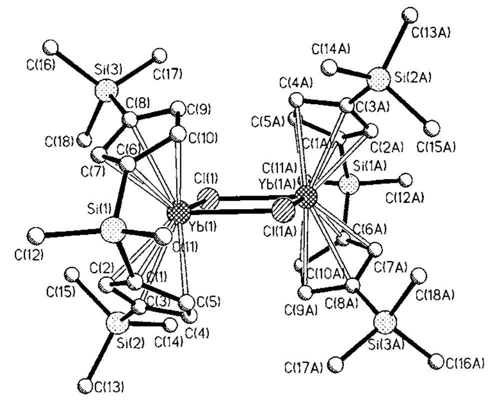

Fig. 1. Molecular structure of the complex [*meso*-$(CH_3)_2Si[3-(CH_3)_3SiC_5H_3]_2YbCl]_2$ (**2**).

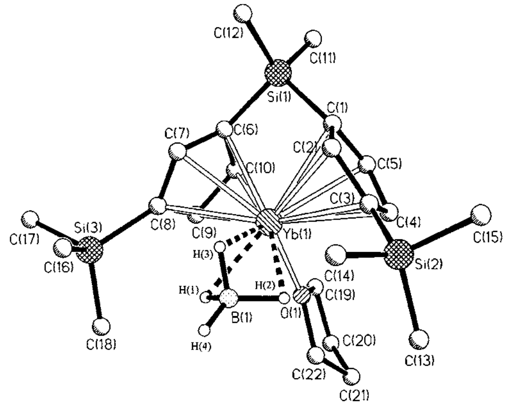

Fig. 2. Molecular structure of the complex *meso*-$(CH_3)_2Si(3-(CH_3)_3SiC_5H_3)_2YbBH_4(THF)$ (**3**).

In the structure of complex **3** (Fig. 2, Table 3), which was obtained by the reaction of **1** with $LiBH_4$ in diethyl ether followed by crystallisation of the product from benzene, the borohydride group is tridentate, while in many other metallocenes (e.g. $Me_2C(C_5H_4)_2Nb(\eta^2\text{-}BH_4)$ [20], $[(C_5H_4Me)_2Zr(\eta^2\text{-}BH_4)(THF)][BPh_4]$ [21], $[(Me_3Si)_2C_5H_3]_2Sc(\eta^2\text{-}BH_4)$ [10]), this group is bidentate. The Yb—B distance in **3** (2.470(8) Å) is consistent with reported [22] size of the tridentate borohydride group and is shorter than those in the complex $\{rac\text{-}Me_2C(3\text{-}Me_3SiC_5H_3)_2Yb(BH_4)_2Li(THF)_2\}_\infty$ (2.587(11), 2.592(10) Å [6]), where two borohydride groups are η^2-coordinated to the ytterbium atom. The Yb–H distances in **3** (2.06(5), 2.22(5), 2.25(5) Å) fall within the range of the Yb–H distances in $\{rac\text{-}(CH_3)_2C(3\text{-}(CH_3)_3SiC_5H_3)_2Yb(BH_4)_2\text{-}Li(THF)_2\}_\infty$ (2.1(1)–2.4(1) Å [6]). The observed range of the B–H bond lengths (1.09–1.20(5) Å) is typical for such compounds. For example, the B–H distance is 1.05–1.19 Å in $(CH_3CN)_4Yb[(\mu\text{-}H)_3BH]_2$ [23], 1.19 Å in $[(Me_3Si)_2C_5H_3]_2Sc(\mu_2\text{-}H)_2BH_2$ [10], and 0.94–1.40 Å in $\{(\eta^5\text{-}{}^tBu_2C_5H_3)_2Ce[\mu{:}\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ [11]. The Yb–O distance in **3** (2.328(4) Å) is similar to that in the starting complex **1** (2.316(8) Å [7]).

In **3**, Cp rings are flat to an accuracy of 0.009 Å. The Si(2) atom is off the ring plane by 8°, the Si(3) atom by 7°, and the Si(1) atom by 16°. The Yb–C_{av} distance (2.647(5) Å) is somewhat longer, and the Cp1–Yb(1)–Cp2 angle (121.5(2)°) is smaller than those found in **1** (2.617(8) Å, 122.5(3)°) [7].

The IR spectrum of complex **3** in the range of B–H vibrations (Fig. 3) is rather uncommon. However, because complex **3** is highly soluble in all inert organic media, the complexity of the recorded spectrum can be explained by the superimposition of the spectra of solid complex **3** and its Nujol solution. Dissolution of **3** is supposedly accompanied by a change in the denticity of the borohydride group, and a band at 2125 cm^{-1}, characteristic of the η^2-bound BH_4 group, appears as a result.

Table 2
Selected bond lengths (Å) and angles (°) for [*meso*-$(CH_3)_2Si[3-(CH_3)_3SiC_5H_3]_2Yb(\mu_2\text{-}Cl)]_2$ (**2**)

Bond distances			
Yb(1)–Cl(1)	2.631(3)	Yb(1)–C(10)	2.615(13)
Yb(1)–Cl(1A)	2.681(4)	Yb(1)–C(9)	2.632(13)
Cl(1)–Yb(1A)	2.681(4)	Yb(1)–C(8)	2.669(13)
Yb(1)–C(1)	2.537(12)	Yb(1)–C(3)	2.685(11)
Yb(1)–C(7)	2.54(2)	Si(1)–C(6)	1.867(14)
Yb(1)–C(2)	2.562(12)	Si(1)–C(1)	1.897(14)
Yb(1)–C(5)	2.579(12)	Si(2)–C(3)	1.857(12)
Yb(1)–C(6)	2.575(13)	Si(3)–C(8)	1.875(12)
Yb(1)–C(4)	2.601(13)		
Bond angles			
Cl(1)–Yb(1)–Cl(1A)	82.15(12)	C(6)–Si(1)–C(1)	97.7(5)
Yb(1)–Cl(1)–Yb(1A)	97.85(12)	Cp1–Yb(1)–Cp2	122.6(4)
Cp1/Cp2	63.0(4)		

Table 3
Selected bond lengths (Å) and angles (°) for *meso*-$(CH_3)_2Si(3-(CH_3)_3SiC_5H_3)_2YbBH_4(THF)$ (**3**)

Bond distances			
Yb(1)–O(1)	2.328(4)	Yb(1)–C(3)	2.741(5)
Yb(1)–B(1)	2.470(8)	Si(1)–C(6)	1.863(5)
Yb(1)–C(10)	2.586(5)	Si(1)–C(1)	1.867(5)
Yb(1)–C(5)	2.594(6)	Si(2)–C(3)	1.867(5)
Yb(1)–C(6)	2.595(5)	Si(3)–C(8)	1.864(6)
Yb(1)–C(1)	2.600(5)	Yb(1)–H(1)	2.25(5)
Yb(1)–C(7)	2.626(5)	Yb(1)–H(2)	2.22(5)
Yb(1)–C(2)	2.632(5)	Yb(1)–H(3)	2.06(5)
Yb(1)–C(9)	2.678(5)	B(1)–H(1)	1.15(5)
Yb(1)–C(4)	2.685(5)	B(1)–H(2)	1.20(5)
Yb(1)–C(8)	2.732(5)	B(1)–H(3)	1.09(5)
		B(1)–H(4)	1.10(5)
Bond angles			
O(1)–Yb(1)–B(1)	93.4(2)	H(1)–B(1)–H(2)	109(3)
C(6)–Si(1)–C(1)	98.2(2)	H(1)–B(1)–H(3)	88(3)
Cp1–Yb(1)–Cp2	121.5(2)	H(1)–B(1)–H(4)	113(3)
Yb(1)–H(1)–B(1)	87(3)	H(2)–B(1)–H(3)	100(3)
Yb(1)–H(2)–B(1)	87(3)	H(2)–B(1)–H(4)	122(3)
Yb(1)–H(3)–B(1)	98(3)	H(3)–B(1)–H(4)	117(3)

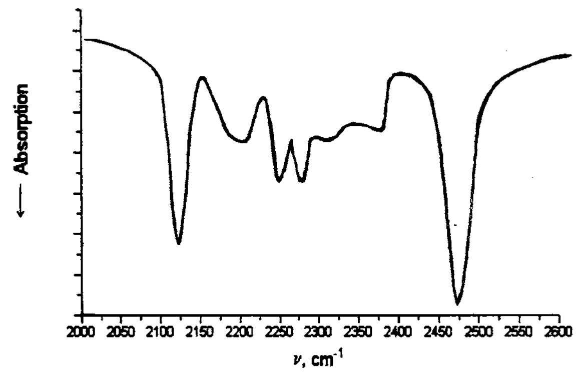

Fig. 3. IR spectrum of the complex **3** in the range of B–H vibrations.

Thus, in the lanthanide range the denticity of the borohydride group is determined by many factors: radius of central atom, volume and quantity of ring substituents, length of bridge group and nature of bridge atoms. This multifactor influence makes a forecast of the structure of borohydride (as well as alumohydride) complexes of lanthanide uncertain.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 118925 for compound **2** and no. 118926 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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References

[1] P. Yan, N. Hu, Z. Jin, W. Chen, J. Organomet. Chem. 391 (1990) 313.
[2] G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103.
[3] E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606.
[4] M.A. Giardello, V.P. Conticello, L. Brard, M. Sabat, A.L. Rheingold, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10212.
[5] H. Yasuda, E. Ihara, Macromol. Chem. Phys. 196 (1995) 2417.
[6] A.V. Khvostov, V.K. Belsky, A.I. Sizov, B.M. Bulychev, N.B. Ivchenko, J. Organomet. Chem. 564 (1998) 5.
[7] A.V. Khvostov, V.K. Belsky, B.M. Bulychev, A.I. Sizov, B.B. Ustinov, J. Organomet. Chem. 571 (1998) 243.
[8] N. Höck, W. Oroschin, G. Paolucci, R.D. Fisher, Angew. Chem. 98 (1986) 748.
[9] T. Akhnoukh, J. Müller, K. Qiao, X.-F. Li, R.D. Fisher, J. Organomet. Chem. 408 (1991) 47.
[10] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Chem. Commun. (1983) 206.
[11] E.B. Lobkovsky, Yu.K. Gun'ko, B.M. Bulychev, V.K. Belsky, G.L. Soloveichik, M.Yu. Antipin, J. Organomet. Chem. 406 (1991) 343.
[12] Yu.K. Gun'ko, B.M. Bulychev, G.L. Soloveichik, V.K. Belsky, J. Organomet. Chem. 424 (1992) 289.
[13] D.A. Laske, R. Duchateau, J.H. Teuben, A.L. Spek, J. Organomet. Chem. 462 (1993) 149.
[14] D. Deng, X. Zheng, C. Qian, J. Sun, L. Zhang, J. Organomet. Chem. 466 (1994) 95.
[15] N. Höck, W. Oroschin, G. Paolucci, R.D. Fisher, Angew. Chem. 98 (1986) 748.
[16] H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal, K. Handrick, Inorg. Chim. Acta 156 (1989) 119.
[17] E.C. Baker, L.D. Brown, K.N. Raymond, Inorg. Chem. 14 (1975) 1376.
[18] M.F. Lappert, A. Singh, J.L. Atwood et al., J. Chem. Soc. Chem. Commun. (1981) 1190.
[19] G.B. Deacon, G.D. Fallon, C.M. Forsyth, J. Organomet. Chem. 462 (1993) 183.
[20] N.J. Bailey, M.L.H. Green, M.A. Leech, J.F. Saunders, H.M. Tidswell, J. Organomet. Chem. 538 (1997) 111.
[21] R. Choukroun, B. Douziech, B. Donnadieu, Organometallics 16 (1997) 5517.
[22] N. Edelstein, Inorg. Chem. 20 (1981) 297.
[23] J.P. White, H. Deng, S.G. Shore, Inorg. Chem. 30 (1991) 2337.