ELSEVIER

Journal of Organometallic Chemistry 571 (1998) 243–249

Journal of Organometallic Chemistry

ansa-Ytterbocenes(+ 3) with a short bridge and bulky substituents: synthesis and crystal structure of *meso*-$(CH_3)_2Si[3\text{-}(CH_3)_3SiC_5H_3]_2YbCl(THF)$, *rac*-$(CH_3)_2C[3\text{-}{}^tBuC_5H_3]_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$, and [*meso*-$(CH_3)_2C[3\text{-}{}^tBuC_5H_3]_2Yb(\mu_2\text{-}OCH_3)]_2$

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

Received 28 May 1998; received in revised form 28 June 1998

Abstract

$(CH_3)_2E(3\text{-}(CH_3)_3EC_5H_3)_2Li_2$ (E = C, Si) compounds react with $YbCl_3$ to yield the *ate*-complex *rac*-$(CH_3)_2C(3\text{-}{}^tBuC_5H_3)_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$ (**1**) and the monosolvate *meso*-$(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2YbCl(THF)$ (**2**), respectively. The reaction between $(CH_3)_2C(3\text{-}{}^tBuC_5H_3)_2Li_2$ and YbI_2 in 1,2-dimethoxyethane (DME) proceeds with solvent decomposition, and the complex [*meso*-$(CH_3)_2C(3\text{-}{}^tBuC_5H_3)_2Yb(\mu_2\text{-}OCH_3)]_2$ (**3**) crystallises from a DME–hexane mixture. The structures of the compounds obtained were determined by X-ray structural analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ytterbium; *ansa*-Metallocenes; Crystal structure

1. Introduction

The optical isomers of a large number of Group IVB *ansa*-metallocenes [1], including those of zirconium complexes with $(CH_3)_2Si[3\text{-}Me_3SiC_5H_3]_2$ and $(CH_3)_2C[3\text{-}{}^tBuC_5H_3]_2$ ligands [2,3], have recently been synthesised by various methods and studied. Much less research has been given to analogous compounds of Group IIIB [4,5] although they are unique one-component catalysts of alkene polymerisation and are useful in investigation of polymerisation mechanism [6–8]. In the known *ansa*-metallocenes of these elements, either cyclopentadienyl ligands are linked by long hydrocarbon bridges [9], which do not allow the complex to take on a certain conformation in solution, or the cyclopentadienyl rings contain no bulky substituents [10], which could give rise to optical isomerism.

In this work, which continues the series of works devoted to the synthesis of the optical isomers of rare-earth complexes, we report on the synthesis and structure of ytterbium(+ 3) complexes with 2,2-bis-(η^5-3-(*tert*-butyl)cyclopentadienyl)propane and bis-(η^5-3-(trimethylsilyl)cyclopentadienyl)dimethylsilane ligands.

2. Experimental

All manipulations involved in the pre-treatment of the starting reagents, synthesis, and study of reaction products were performed under flowing argon or in

---

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

0022-328X/98/$ - see front matter © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00822-5

vacuo with the use of Schlenk techniques. Solvents were boiled over $LiAlH_4$ for 2 h and then distilled. $(CH_3)_2C[3\text{-}^tBuC_5H_3]_2Li_2$ and $(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2Li_2$ were prepared by the known [2,11] procedures. $YbCl_3$ was obtained by dehydration of $YbCl_3 \cdot 6H_2O$ in the presence of NH_4Cl [12], and YbI_2 by the reaction between ytterbium and iodine in THF with subsequent desolvation of the product in vacuum under heating [13].

2.1. *rac*-$(CH_3)_2C(3\text{-}^tBuC_5H_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**1**)

To a suspension of $YbCl_3$ (2.91 g, 10.42 mmol) in diethyl ether (100 ml), a suspension of $(CH_3)_2C[3\text{-}^tBuC_5H_3]_2Li_2$ (3.03 g, 10.17 mmol) in diethyl ether (100 ml) was added with stirring. The resulting green solution together with the precipitate was stirred for 3 days. Next, the mixture was filtered, and the precipitate washed until white. The ether fractions were combined, mixed with 30 ml of benzene, and boiled down to obtain 3.78 g of green crystals of **1**. Yield: 51%. Anal. Found (%): C, 51.15; H, 7.43; Yb, 25.5; Li, 1.1; Cl, 10.3. Calc. for $C_{29}H_{50}Cl_2O_2LiYb$ (%): C, 51.10; H, 7.39; Yb, 25.39; Li, 1.02; Cl, 10.40.

2.2. *meso*-$(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2YbCl(THF)$ (**2**)

To a suspension of $YbCl_3$ (0.85 g, 3.04 mmol) in diethyl ether (100 ml), a suspension of $(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2Li_2$ (0.93 g, 2.70 mmol) in diethyl ether (100 ml) was added with stirring. The resulting red solution together with the precipitate was stirred for a day. Next, the solution was filtered, and the solvent evaporated. To the resulting red oil, 3 ml of THF and 30 ml of toluene were added, and the solvents were evaporated until crystallisation commenced. This afforded 0.33 g of red crystals of **2**. Yield: 20%. Anal. Found (%): C, 43.25; H, 6.20; Yb, 28.2; Cl, 5.8. Calc. for $C_{22}H_{38}Si_3ClOYb$ (%): C, 43.23; H, 6.27; Yb, 28.31; Cl, 5.80.

2.3. [*meso*-$(CH_3)_2C(3\text{-}^tBuC_5H_3)_2Yb(\mu_2\text{-}OCH_3)]_2$ (**3**)

To a suspension of YbI_2 (2.40 g, 5.62 mmol) in 1,2-dimethoxyethane (DME) (100 ml), a suspension of $(CH_3)_2C[3\text{-}^tBuC_5H_3]_2Li_2$ (1.67 g, 5.61 mmol) in DME (100 ml) was added with stirring. The resulting red solution was evaporated to about 10 ml, and 30 ml of hexane was added. Upon storage for 2 months, dark red crystals of **3** (0.11 g) formed in the hexane layer. Yield: ca. 2%. Anal. Found (%): Yb, 35.5. Calc. for $C_{22}H_{33}OYb$ (%): Yb, 35.57.

2.4. X-ray structure determination

Unit cell determination, data collection and structure

Table 1
Crystal data and structure refinement for compounds **1**–**3**

Compound	1	2	3
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.664(2)	10.773(2)	11.093(2)
b (Å)	21.033(4)	23.347(5)	13.217(3)
c (Å)	13.751(3)	12.115(2)	15.533(3)
α (°)	—	—	77.32(3)
β (°)	99.31(3)	115.61(3)	78.19(3)
γ (°)	—	—	71.83(3)
Volume (Å^3)	3329.1(11)	2747.8(9)	2088.1(7)
$D_{calc.}$ (g cm^{-3})	1.360	1.478	1.548
Z	4	4	2
Diffractometer	CAD-4	Syntex P$\bar{1}$	CAD-4
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	293(2)	293(2)	293(2)
Collection method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Radiation type	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$
Radiation monochromator	β-Filter	β-Filter	β-Filter
Absorption coefficient (mm^{-1})	2.990	3.642	4.484
Crystal size (mm)	0.40 × 0.25 × 0.20	0.34 × 0.28 × 0.16	0.28 × 0.22 × 0.18
Theta range for data collection (°)	2.34–24.91	2.06–25.05	1.95–24.97
Reflections collected	6364	3134	7968
Independent reflections	2252	3134	4963
Refinement method	Full-matrix-block least-squares on F^2	Full-matrix-block least-squares on F^2	Full-matrix-block least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0297$, $wR_2 = 0.0743$	$R_1 = 0.0357$, $wR_2 = 0.0893$	$R_1 = 0.0333$, $wR_2 = 0.0839$

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

Atom	x	y	z	U_{eq}^{a}
Yb	4440(1)	1282(1)	2194(1)	33(1)
Cl	5697(2)	357(1)	2463(3)	63(1)
Si(1)	2274(2)	−128(1)	2307(2)	42(1)
Si(2)	8647(2)	1418(1)	3476(2)	45(1)
Si(3)	3734(2)	2236(1)	3946(2)	41(1)
C(1)	2732(8)	1621(3)	3033(7)	39(2)
C(2)	2001(8)	1611(4)	1734(8)	37(2)
C(3)	1772(8)	1041(4)	1328(8)	35(2)
C(4)	2423(7)	667(3)	2342(7)	35(2)
C(5)	3001(9)	1039(4)	3368(9)	37(2)
C(6)	5203(8)	2200(3)	3522(7)	39(2)
C(7)	5083(11)	2352(4)	2358(10)	41(2)
C(8)	6143(9)	2096(4)	2162(8)	44(2)
C(9)	6963(8)	1764(3)	3189(7)	38(2)
C(10)	6364(8)	1822(3)	4014(7)	36(2)
C(11)	3617(12)	−451(5)	3713(10)	62(3)
C(12)	2393(19)	−410(5)	926(11)	67(3)
C(13)	562(12)	−333(5)	2238(13)	67(3)
C(14)	9979(12)	1989(7)	4065(14)	83(4)
C(15)	9102(15)	856(7)	4669(15)	91(4)
C(16)	8574(15)	1140(6)	2026(12)	77(4)
C(17)	4212(13)	2114(6)	5579(11)	65(3)
C(18)	2831(14)	2932(5)	3459(16)	72(4)
O	3818(8)	1291(4)	110(7)	49(2)
C(19)	4460(24)	942(10)	−478(14)	108(7)
C(20)	4020(21)	1183(7)	−1720(13)	112(6)
C(21)	2746(20)	1477(9)	−1974(13)	113(7)
C(22)	2787(17)	1648(6)	−818(11)	79(4)

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

refinement are detailed in Table 1. Experimental data were processed using the PROFIT procedure [14]. Absorption correction was not applied. The structure was solved by heavy atom technique and refined by full-matrix anisotropic least-squares method. Hydrogen atoms positions were found from difference synthesis, their positional and isotropic thermal parameters were included into refinement fixed. Structure solution and refinement were performed using SHELXTL-81 [15] and SHELXL-93 [16] packages, respectively. Atomic coordinates for **2** and **3** are given in Tables 2 and 3, respectively.

3. Results and discussion

Reacting the dilithio salt of 2,2-bis(3′-*tert*-butylcyclopentadienyl)propane with ytterbium(III) chloride in ether, the method commonly used to prepare the *ate* complex of trivalent ytterbium, results in *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}{}^tBu)_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$ (**1**) in about 50% yield. A similar situation obtains with 2,2-bis-(3′-(trimethylsilyl)cyclopentadienyl)propane [17]. Successive crystallisation from an ether–benzene mixture did not afford the *meso* isomer of this complex, as was evident from lattice constant data. By contrast, the reaction of $YbCl_3$ with the dilithio salt of the silicon analogue, bis-(3-(trimethylsilyl)cyclopentadienyl)dim-

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

Atom	x	y	z	U_{eq}^{a}
Yb(1)	6288(1)	5365(1)	4253(1)	32(1)
O(1)	4237(5)	5955(4)	4716(4)	37(1)
C(1)	8546(8)	5488(7)	4199(5)	37(2)
C(2)	7817(8)	6574(7)	4074(6)	41(2)
C(3)	7030(8)	6815(6)	4861(5)	37(2)
C(4)	7212(9)	5862(7)	5487(6)	40(2)
C(5)	8158(8)	5042(6)	5084(6)	37(2)
C(6)	8144(8)	4762(7)	3036(5)	39(2)
C(7)	7546(8)	3923(7)	3291(5)	39(2)
C(8)	6365(9)	4282(8)	2974(6)	43(2)
C(9)	6216(9)	5332(7)	2503(5)	46(2)
C(10)	7277(9)	5625(8)	2556(6)	44(2)
C(11)	9257(8)	4849(7)	3429(6)	41(2)
C(12)	10060(11)	5502(9)	2742(8)	56(2)
C(13)	10094(11)	3747(9)	3778(9)	56(3)
C(14)	6241(9)	7953(7)	5033(6)	49(2)
C(15)	7135(13)	8438(10)	5360(12)	74(4)
C(16)	5091(12)	7917(8)	5764(8)	62(3)
C(17)	5775(13)	8655(8)	4187(8)	62(3)
C(18)	5192(10)	5968(9)	1899(6)	58(3)
C(19)	3927(13)	5682(15)	2249(11)	84(4)
C(20)	5711(16)	5665(18)	980(8)	86(4)
C(21)	4960(16)	7175(13)	1822(12)	81(4)
C(22)	3365(11)	6955(8)	4389(8)	55(2)
Yb(2)	423(1)	9649(1)	8911(1)	31(1)
O(2)	731(5)	9030(4)	10307(3)	34(1)
C(1A)	1294(8)	10231(6)	7276(5)	36(2)
C(2A)	1204(9)	11085(7)	7720(6)	41(2)
C(3A)	2189(9)	10734(7)	8266(6)	45(2)
C(4A)	2883(8)	9669(7)	8184(5)	39(2)
C(5A)	2335(8)	9361(7)	7573(5)	37(2)
C(6A)	−488(8)	9512(7)	7576(5)	40(2)
C(7A)	−1568(9)	9967(7)	8176(6)	44(2)
C(8A)	−1732(8)	9178(7)	8918(6)	44(2)
C(9A)	−790(8)	8194(7)	8786(5)	41(2)
C(10A)	−22(8)	8424(6)	7965(5)	36(2)
C(11A)	277(9)	10108(7)	6810(5)	45(2)
C(12A)	−541(13)	11212(10)	6421(8)	62(3)
C(13A)	871(12)	9440(10)	6063(7)	55(2)
C(14A)	4146(9)	9047(8)	8508(6)	49(2)
C(15A)	5263(14)	9357(15)	7834(11)	74(4)
C(16A)	4234(13)	9327(12)	9395(8)	68(3)
C(17A)	4352(13)	7841(10)	8602(9)	64(3)
C(18A)	−743(10)	7093(7)	9310(6)	50(2)
C(19A)	−1263(14)	7141(11)	10299(7)	62(3)
C(20A)	−1631(14)	6634(10)	8961(9)	70(3)
C(21A)	630(14)	6342(9)	9218(10)	67(3)
C(22A)	1515(12)	8036(8)	10671(8)	50(2)

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

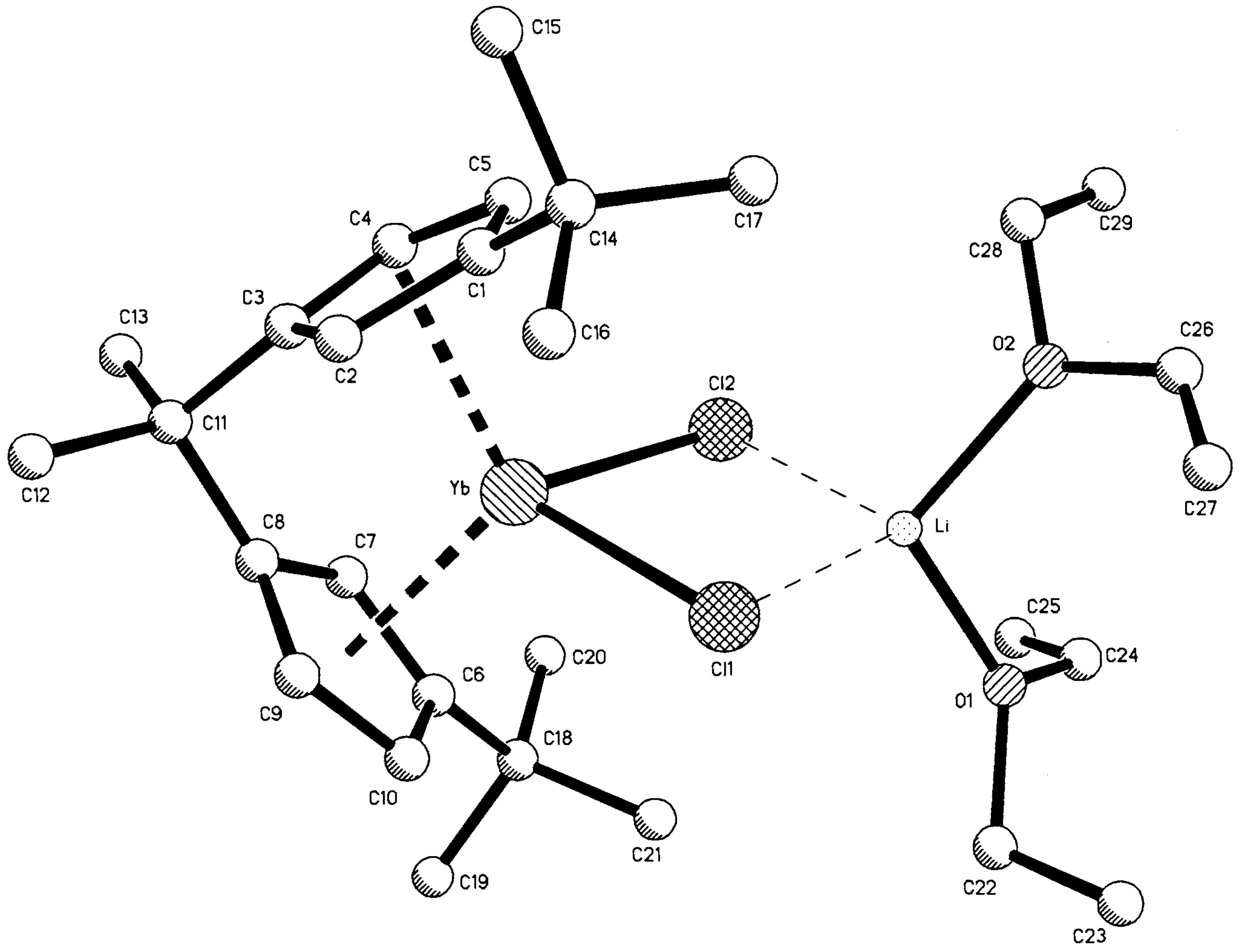

Fig. 1. Molecular structure of *rac*-$(CH_3)_2C(^tBuC_5H_3)_2Yb(\mu_2\text{-}Cl)_2Li(OEt_2)_2$ (**1**). Selected bond lengths (Å) and angles (°): Yb–Cp^1 2.31(1), Yb–Cp^2 2.32(1), Yb–C_{av}^{Cp1} 2.60(1), Yb–C_{av}^{Cp2} 2.61(1), Yb–Cl(1) 2.574(3), Yb–Cl(2) 2.578(3) Å; Cp^1–Yb–Cp^2 113.4(3), Cp^1/Cp^2 76.8(3), Cl(1)–Yb–Cl(2) 86.12(9), (Cp^1–Yb–Cp^2)/(Cl^1–Yb–Cl^2) 87.0(1), C(3)–C(11)–C(8) 102.0(8)°.

ethylsilane, gives the *meso* form of $(CH_3)_2Si(3\text{-}(CH_3)_3SiC_5H_3)_2YbCl(THF)$ (**2**). Such compounds usually crystallise as dimers of composition $(Cp'_2YbCl)_2$ [18] although unsubstituted *ansa*-ytterbocenes with a dimethylsilyl bridge give a compound where the *ansa* ligand is bridging rather than chelating, that is, binds two metal atoms [19]. Crystallisation of the monomer **2** in our case is likely due to the presence of bulky trimethylsilyl groups in cyclopentadienyl rings.

An attempt to synthesise an *ansa*-ytterbocene (+2) with the 2,2-bis-(η^5-3-*tert*-butylcyclopentadienyl)propane ligand in DME resulted in a non-crystallising oil, which apparently consisted of a mixture of isomers. Upon prolonged keeping of this substance in a DME–hexane mixture, the ytterbium atom oxidises, and DME decomposes to form [*meso*-$(CH_3)_2C(3\text{-}^tBuC_5H_3)_2Yb(\mu_2\text{-}OCH_3)]_2$ (**3**). Destruction of the DME molecule occurs rather often in the systems containing strong reductants [20–22]. Moreover, the ytterbium(+ 2) complex with the $(SiMe_3)_3C$ ligand even causes decomposition of diethyl ether [23]. Therefore, the observed formation of methoxoytterbocene(+ 3) was not surprising.

The crystal structure of the *ate* complex **1** (Fig. 1) is typical for such compounds [24] and similar to the structure of the complex *rac*-$(CH_3)_2C(C_5H_3\text{-}3\text{-}Si(CH_3)_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**) [17], containing trimethylsilyl substituents. In these structures, main angles (Cp–Yb–Cp, Cl–Yb–Cl) and distances (Yb–Cp, Yb–Cl) are nearly identical. Note only that, in the structure of **1**, the angle between the cyclopentadienyl rings is a little (by about 3°) increased, and the geometry of the bridge between the Cp ligands is slightly distorted. The bridging atom C11 in **1** is 0.30 and 0.35 Å off the ring planes, making angles of 11.9 and 13.4°, respectively. In **4**, the corresponding distances are 0.33 and 0.43 Å, and the angles, 12.7 and 15.8°, respectively.

The molecular structure of complex **2** (Fig. 2) and that of $(^tBuC_5H_4)_2YbCl(THF)$ [25] are similar in geometry, Yb–C_{av} bond length (2.617(8) and 2.63(1) Å, respectively), Yb–O bond length (2.316(8), 2.333(6) Å), and Cp1–Yb–Cp2 angle (122.5(3), 121.3(3)°). However, the Yb–Cl distance in **2** (2.496(2) Å) is smaller than not only that in $(^tBuC_5H_4)_2YbCl(THF)$ but also those in $(C_5Me_5)_2YbCl(THF)$ (2.539(4) Å) [26], $(C_5Me_5)_2YbCl$(1,1-bis(dimethylphosphino)methane) (2.532(8) Å) [27], and $(CH_3OCH_2CH_2C_5H_4)_2YbCl$ (2.588(6) Å) [28]. It is natural that the Cp–Yb–Cp′ and C^{Cp}–Si^{br}–$C^{Cp'}$ angles are much smaller in the structure of **2** (122.5(3) and 98.4(3)°, respectively), where the *ansa* ligand is chelating, than in the structure of $[\mu\text{-}(CH_3)_2Si(C_5H_4)_2Yb(\mu\text{-}Cl)]_2$ (135.5 and 118.7°, respectively) [19] with a bridging *ansa* ligand. In both complexes, the Yb–C_{av} distance is 2.617 Å. In addition, the Cp–Yb–Cp′ angle falls in the range of the values found for Me_2Si-bridged *ansa*-lanthanidocenes (*meso*-$Me_2Si(Me_2SiOSiMe_2)(3\text{-}^tBuC_5H_2)_2Sm(THF)_2$ 116.7° [8], *rac*-$Me_2Si(2,4\text{-}(SiMe_3)_2C_5H_2)_2SmCl_2Li(THF)_2$ 117° [6], *rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}^tBuC_5H_2)_2Sm(THF)_2$ 117.1° [8], $Me_2Si(2(3),4\text{-}(SiMe_3)_2C_5H_2)_2SmCH(SiMe_3)_2$ 118° [6], (*S*)-(+)-$LSmN(SiMe_3)_2$ 119.3°, (*R*)-(+)-$LSmCH(SiMe_3)_2$ 120.6, 121.1°, (*S*)-(−)-$LSmN(SiMe_3)_2$ 121.3°, (*R*)-(−)-$LYN(SiMe_3)_2$ 122.1, 122.4°, (*R*)-(−)-$LYCH(SiMe_3)_2$ 124.3, 123.5°, (*R*)-(+)-$LLuCl_2Li(Et_2O)_2$ 125.4°, (*R*)-(+)-$LYCH(SiMe_3)_2$ 125.5°, (*S*)-(+)-$LYCH(SiMe_3)_2$ 130.0° (L = (*R* or *S*)-$Me_2Si(C_5H_4)$[(+ or −)-(neomenthyl or menthyl)-C_5H_3]) [4]).

The *ansa*-metallocene fragment of complex **2** differs in geometry from that of **1** because the bridging silicon atom is larger than the bridging carbon atom. In passing from **1** to **2**, the Cp1–Yb–Cp2 angle increases from 113.4 to 122.5°, and the Cp1/Cp2 and C^{Cp1}–E^{br}–C^{Cp2} angles decrease from 76.8 to 63.8° and from 102.0 to 98.4°, respectively, while the Yb–Cp distance remains essentially constant. The Si1 and Si2 atoms of trimethylsilyl groups are off the Cp1 and Cp2 planes by 0.20 and 0.26 Å, respectively, and the bridging atom Si3, by 0.53 and 0.56 Å, respectively.

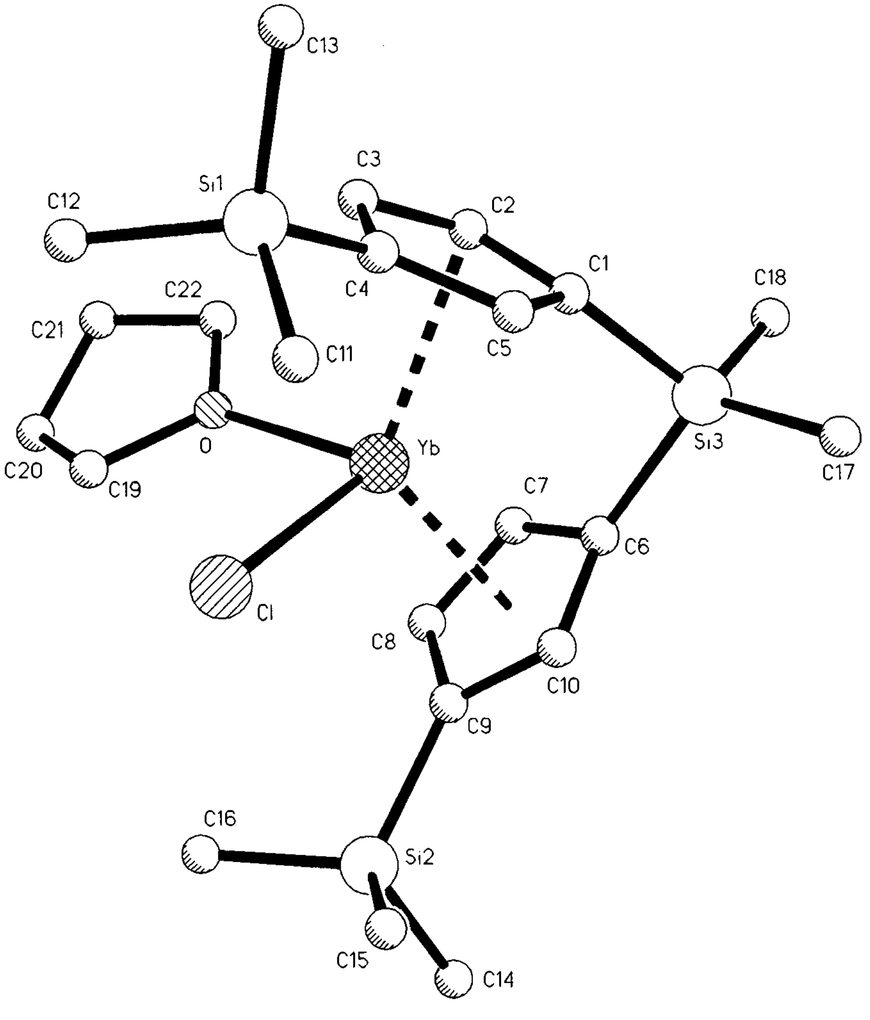

Fig. 2. Molecular structure of *meso*-$(CH_3)_2Si((CH_3)_3SiC_5H_3)_2YbCl(THF)$ (**2**). Selected bond lengths (Å) and angles (°): Yb–Cp^1 2.316(7), Yb–Cp^2 2.335(7), Yb–C_{av}^{Cp1} 2.610(8), Yb–C_{av}^{Cp2} 2.624(8), Yb–Cl 2.496(2), Yb–O 2.316(8) Å; Cp^1–Yb–Cp^2 122.5(3), Cp^1/Cp^2 63.8(3), O–Yb–Cl 92.0(2), C(1)–Si(3)–C(6) 98.4(3)°.

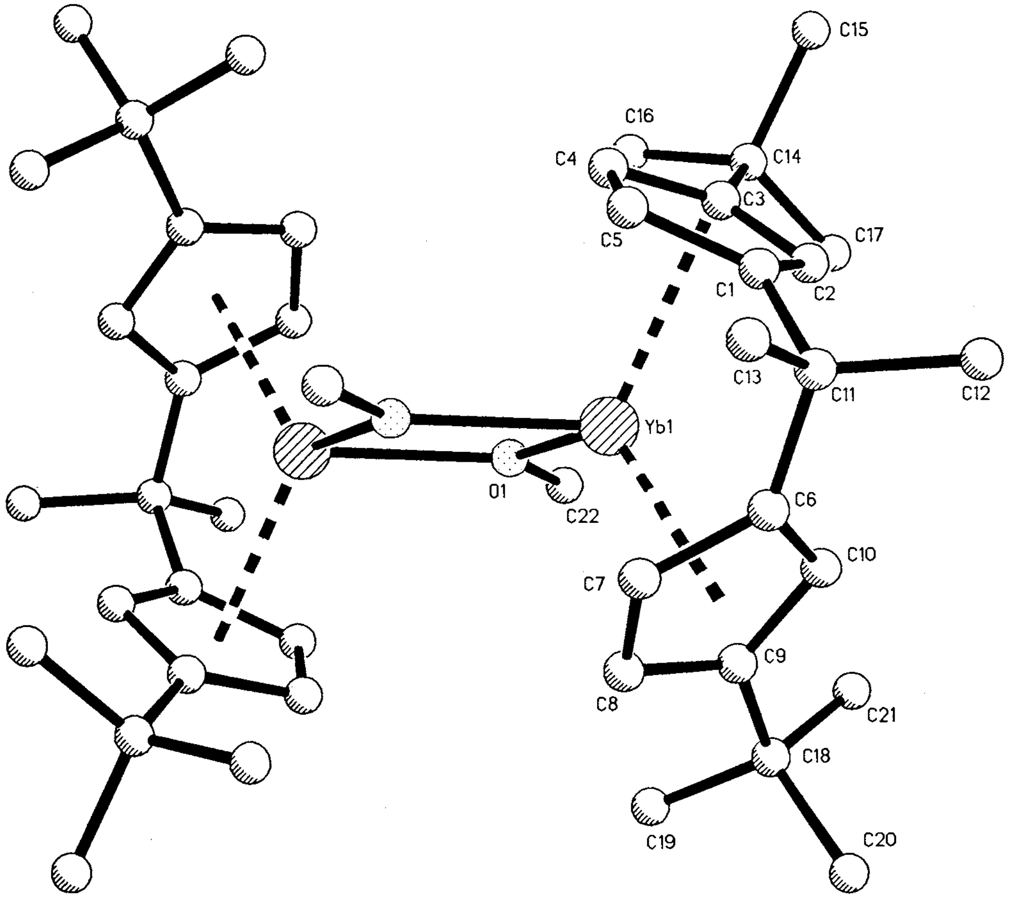

Fig. 3. Molecular structure of [*meso*-$(CH_3)_2C(^tBuC_5H_3)_2Yb(\mu_2\text{-}OCH_3)]_2$ (**3**). Selected bond lengths (Å) and angles (°) for two independent molecules: Yb–Cp^1 2.32(1), 2.35(1); Yb–Cp^2 2.35(1), 2.33(1); Yb–C_{av}^{Cp1} 2.606(9), 2.641(9); Yb–C_{av}^{Cp2} 2.630(9), 2.622(9); Yb(1)–O(1) 2.185(6), 2.201(5); Yb(1)–O′(1) 2.230(6), 2.250(5); O(1)–C(22) 1.43(1), 1.40(1) Å; Cp^1–Yb(1)–Cp^2 111.3(2), 110.8(2); $Cp^{1\perp}$–Yb(1)–$Cp^{2\perp}$ 103.7(2), 103.2(2); Cp^1/Cp^2 76.3(3), 76.8(3); O(1)–Yb′(1) 2.230(6), 2.250(5); O(1)–Yb(1)–O′(1) 73.5(2), 73.4(2); Yb(1)–O(1)–Yb′(1) 106.5(2), 106.6(2); (Cp^1–Yb–Cp^2)/(Yb–O–Yb′) 89.9(2), 90.2(2); C(6)–C(11)–C(1) 102.1(6), 101.8(6)°.

The structure of complex **3** is composed of two crystallographically-independent [*meso*-$(CH_3)_2C(3\text{-}^tBuC_5H_3)_2Yb(\mu_2\text{-}OCH_3)]_2$ molecules (Fig. 3). The Yb–O distances (2.185(6) and 2.201(5) Å) and O–Yb–O angle (73.5(2)°) are smaller than those in $[(C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$ (2.29(2) Å, 77.9(7)°) [29]. However, the Yb–O distances are nearly equal to that in$[Yb(paphy)(OH_2)_3(OH)]_2Cl_4 \cdot 4H_2O$ (2.19(1) Å) [30] and fall in the range of the M–O bond lengths found for various lanthanide and yttrium bis(cyclopentadienyl) complexes ($(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$, 2.08(1) Å [31]; $(C_5Me_5)_2Y)_2(\mu\text{-}OCH_2CH_2O)(THF)_2$, 2.042(4) Å [32]; $(C_5H_4SiMe_3)_2Y(\mu\text{-}OC(CH_3)_3)_2Li(THF)_2$, 2.148(10) and 2.157(11) Å [33]; $[(C_5Me_5)_2Y)_2(\mu\text{-}OCCH_3{=}CHC(OC_2H_5)O)]_2$, 2.179(2) Å [34]; $(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, 2.217(3) and 2.233(3) Å [35]; $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$, 2.275(3) and 2.290(3) Å [36], $(C_5Me_5)_2Nd(\mu\text{-}OCH_3)_2Na(DME)_2$, 2.248 Å [21]; $(C_5H_3^tBu_2)_2Ce(\mu\text{-}OMe)]_2$, 2.366(4) and 2.386(4) Å [20]).

Because complexes **1** and **3** contain the same *ansa* ligand, the geometric parameters of their *ansa*-metallocene fragments (Yb–Cp distances and Cp1/Cp2 angles) differ little despite the fact that the complexes are of different types (*ate* complex with lithium chloride and dimer with oxo bridges) and contain ligands in different conformations (*rac* and *meso* forms).

Crystallisation of the *meso* form of **3** is rather surprising for the methoxo group has a larger volume than the chlorine atom. This suggests that the *meso* form of the *ansa* ligand is ‘inherited’ by **3** from the starting ytterbocene(+ 2), for which steric hindrance is less important.

4. Supplementary material

Listings of anisotropic temperature factors, hydrogen atom parameters, complete bond distances and angles of complexes **1**, **2**, **3** and atomic coordinates with equivalent isotropic displacement parameters for complex **1** can be obtained from the authors on request.

Acknowledgements

Financial support from the Russian Foundation for Basic Research (RFBR, grant no.'s 98-03-32704 and 97-03-37776) and the US Civilian Research and Development Foundation (CRDF, grant RC1-276) is gratefully acknowledged.

References

[1] For example, see recent articles: (a) A. Vogel, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 527 (1997) 297. (b) A.Z. Voskoboynikov, A.Yu. Agarkov, E.A. Chernyshev, I.P. Beletskaya, A.V. Churakov, L.G. Kuz'mina, J. Organomet. Chem. 530 (1997) 75. (c) J.T. Park, B.W. Woo, S.C. Yoon, S.C. Shim, J. Organomet. Chem. 535 (1997) 29. (d) S.C. Yoon, T.K. Han, B.W. Woo, H. Song, S.I. Woo, J.T. Park, J. Organomet. Chem. 534 (1997) 81. (e) V. Varga, J. Hiller, R. Gyepes, M. Polášek, P. Sedmera, U. Thewalt, K. Mach, J. Organomet. Chem. 538 (1997) 63. (f) Y. Obora, C.L. Stern, T.J. Marks, P.N. Nickias, Organometallics 16 (1997) 2503. (g) K. Schmidt, A. Reinmuth, U. Rief, J. Diebold, H.H. Brintzinger, Organometallics 16 (1997) 1724. (h) A. Steinhorst, G. Erker, M. Grehl, R. Fröhlich, J. Organomet. Chem. 542 (1997) 191. (i) A.M. Barriola, A.M. Cano, T. Cuenca, F.J. Fernández, P. Gómez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 542 (1997) 247. (j) M.E. Huttenloch, B. Dorer, U. Rief, M.-H. Prosenc, K. Schmidt, H.H. Brintzinger, J. Organomet. Chem. 541 (1997) 219. (k) J.R. Butchard, O.J. Curnow, S.J. Smail, J. Organomet. Chem. 541 (1997) 407.

[2] H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz, H.-H. Brintzinger, J. Organomet. Chem. 369 (1989) 359.

[3] I.E. Nifant'ev, P.V. Ivchenko, Organometallics 16 (1997) 713 and references therein.

[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] (a) G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103. (b) T. Akhnoukh, J. Müller, K. Qiao, X.-F. Li, R.D. Fischer, J. Organomet. Chem. 408 (1991) 47 and references therein. (c) W.A. Herrmann, J. Eppinger, M. Spiegler, O. Runte, R. Anwander, Organometallics 16 (1997) 1813. (d) M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagné, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10241.

[6] H. Yasuda, E. Ihara, Macromol. Chem. Phys. 196 (1995) 2417.

[7] (a) E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606. (b) J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045. (c) H. Yasuda, E. Ihara, Tetrahedron 51 (1995) 4563.

[8] E. Ihara, M. Nodono, H. Yasuda, N. Kanehisa, Y. Kai, Macromol. Chem. Phys. 197 (1996) 1909.

[9] (a) J.N. John, M. Tsutsui, J. Coord. Chem. 10 (1980) 177. (b) J.N. John, M. Tsutsui, Inorg. Chem. 20 (1981) 1602. (c) C. Qian, C. Ye, H. Lu, Y. Li, Y. Huang, J. Organomet. Chem. 263 (1984) 333. (d) S.J. Swamy, J. Loebel, H. Schumann, J. Organomet. Chem. 379 (1989) 51. (e) C. Qian, G. Zou, L. Gao, J. Organomet. Chem. 525 (1996) 23 and references therein.

[10] (a) P. Yan, N. Hu, Z. Jin, W. Chen, J. Organomet. Chem. 391 (1990) 313. (b) F.T. Edelmann, M. Rieckhoff, I. Haiduc, I. Silaghi-Dumitrescu, J. Organomet. Chem. 447 (1993) 203.

[11] I.E. Nifant'ev, P.V. Ivchenko, L.G. Kuz'mina, Y.N. Luzikov, A.A. Sitnikov, O.E. Sizan, Synthesis 4 (1997) 469 and references therein.

[12] M.D. Taylor, P.C. Carter, J. Inorg. Nucl. Chem. 24 (1962) 387.

[13] A.V. Khvostov, A.I. Sizov, B.M. Bulychev, S. Ya. Knjazhanski, V.K. Belsky, J. Organomet. Chem. 559 (1998) 97.

[14] V.A. Streltsov, V.E. Zavodnik, Sov. Phys. Crystallogr. 34 (1989) 824.

[15] G.M. Sheldrick, SHELXTL User Manual, Nicolet XRD Corp., USA, 1981.

[16] G.M. Sheldrick, SHELXL-93 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

[17] A.V. Khvostov, V.K. Belsky, A.I. Sizov, B.M. Bulychev, N.B. Ivchenko, J. Organomet. Chem. 564 (1998) 5.

[18] (a) H. Lueken, J. Schmitz, W. Lamberts, et al., Inorg. Chim. Acta 156 (1989) 119. (b) E.C. Baker, L.D. Brown, K.N. Raymond, Inorg. Chem. 14 (1975) 1376. (c) M.F. Lappert, A. Singh, J.L. Atwood, et al., J. Chem. Soc. Chem. Commun. (1981) 1190.

[19] N. Höck, W. Oroschin, G. Paolucci, R.D. Risher, Angew. Chem. 98 (1986) 748.

[20] Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, J. Organomet. Chem. 499 (1995) 213.

[21] Y.-H. Lin, D.-S. Zeng, O. Shen, J. Rare Earths., Chin. Soc. Rare Earths 10 (1992) 170.

[22] V.K. Belsky, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik, Koord. Khim. 11 (1985) 1003.

[23] (a) C. Eaborn, P.B. Hitchcock, K. Izod, J.D. Smith, J. Am. Chem. Soc. 116 (1994) 12071. (b) P.B. Hitchcock, S.A. Holmes, M.F. Lappert, S. Tian, J. Chem. Soc. Chem. Commun. (1994) 2691.

[24] P.L. Watson, J.F. Whithey, R.L. Harlow, Inorg. Chem. 20 (1981) 3271.

[25] Q. Shen, M. Qi, J. Guan, Y. Lin, J. Organomet. Chem. 406 (1991) 353.

[26] H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura, Chem. Lett. (1989) 1309.

[27] T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin, D.H. Templeton, Inorg. Chem. 19 (1980) 2999.

[28] C. Qian, B. Wang, D. Deng, J. Hu, J. Chen, G. Wu, P. Zheng, Inorg. Chem. 33 (1994) 3382.

[29] P.B. Hitchcock, M.F. Lappert, S. Prashar, J. Organomet. Chem. 413 (1991) 79.

[30] E. Baraniak, R.St.L. Bruce, H.C. Freeman, N.J. Hair, J. James, Inorg. Chem. 15 (1976) 2226.

[31] W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller, D. Alvarez, Organometallics 9 (1990) 2124.

[32] B.-J. Deelman, M. Booij, A. Meetsma, J.H. Teuben, H. Kooijman, A.L. Spek, Organometallics 14 (1995) 2306.

[33] W.J. Evans, T.J. Boyle, J.W. Ziller, Organometallics 12 (1993) 3998.

[34] B.-J. Deelman, F. Wierda, A. Meetsma, J.H. Teuben, Appl. Organomet. Chem. 9 (1995) 483.

[35] W.J. Evans, M.S. Sollberger, J.L. Shreeve, J.M. Olofson, J.H. Hain, J.W. Ziller, Inorg. Chem. 31 (1992) 2492.

[36] W.J. Evans, R. Dominguez, T.P. Hanusa, Organometallics 5 (1986) 1291.