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Synthesis, structure and properties of divalent bis(di-*tert*-butylcyclopentadienyl)ytterbium complexes with diethyl ether and 1,2-dimethoxyethane

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Abstract

The reaction between YbI$_2$ and 1,3-^{t}Bu$_2$C$_5$H$_3$Na containing some 1,2-^{t}Bu$_2$C$_5$H$_3$Na in diethyl ether or 1,2-dimethoxyethane afforded (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$ (**1**), (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·DME (**2**) and (1,2-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·DME (**2a**). The crystal structures of **1** and **2a** were determined. Crystals of **1** are monoclinic: $a = 11.302(2)$ Å, $b = 19.018(4)$ Å, $c = 14.404(3)$ Å, $\beta = 90.41(3)°$, $d_{\text{calc}} = 1.291$ g cm^{-3}, space group $P2_1/n$, $z = 4$. Mean bond distances Yb–C, Yb–O and the bond angle Cp–Yb–Cp are 2.69(2) Å, 2.430(14) Å, and 133.0°, respectively. Crystals of **2a** are monoclinic: $a = 13.782(3)$ Å, $b = 10.299(2)$ Å, $c = 10.849(2)$ Å, $\beta = 95.04(3)°$, $d_{\text{calc}} = 1.337$ g cm^{-3}, space group C2, $z = 2$. Mean bond distances Yb–C, Yb–O and the bond angle Cp–Yb–Cp are 2.72(2) Å, 2.53(2) Å, and 143.2°, respectively. The ether-free complex (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb (**3**) displays low catalytic activity in the polymerization of ethene. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ytterbium(+2); Metallocenes; Substituted cyclopentadienyls; Ethene polymerization

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1. Introduction

Complexes of transition metals with non-bridged and *ansa*-bound cyclopentadienyl ligands having bulky *tert*-butyl and trimethylsilyl substituents are of much current interest [1–6]. These complexes differ markedly in composition, structure, solubility in organic solvents, reactivity, and catalytic activity from the corresponding unsubstituted metallocenes. For example, complexes of divalent organolanthanides with sterically unhindered cyclopentadienyl ligands were isolated from solutions as disolvates [5,7–11], whereas complexes with two or more bulky substituents usually crystallize with one molecule of a monodentate solvent [3,12,13] although the metal atom has one or two vacant orbitals. Moreover, for the unsolvated complexes {[(1,3-SiMe$_3$)$_2$C$_5$H$_3$]$_2$Ln}$_\infty$ (Ln = Eu, Yb) [4] the intra- and intermolecular agostic hydrogen bonds have been localized in their crystal structures. In addition, some racemic forms of *ansa*-bound metallocenes with bulky substituents in cyclopentadienyl rings show unique catalytic activity in the stereospecific polymerization of olefins [14].

Starting from YbI$_2$(THF)$_x$ and ^{t}Bu$_2$C$_5$H$_3$Na in THF, we previously isolated the stable mono- and unstable disolvate of bis(1,3-di-*tert*-butylcyclopentadienyl)ytterbium(+2). Their catalytic activity was studied in hexene-1 hydrogenation and styrene polymerization [15,16]. However, all our attempts to determine the crystal structure of the monosolvate failed. In this paper, we report on the synthesis and

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structure of bis(di-*tert*-butylcyclopentadienyl)ytterbium(+2) solvated by diethyl ether and 1,2-dimethoxyethane.

2. Experimental

All manipulations involved in the synthesis were carried out in vacuum or argon atmosphere with the use of the standard Schlenk technique. The solvents were refluxed with $LiAlH_4$ for 3 h and then distilled. 1,3-^{t}$Bu_2C_5H_4$ [17] and 1,3-^{t}$Bu_2C_5H_3Na$ [18] were prepared according to the literature procedures. ^{1}H-NMR spectra were recorded using a Varian VXR-300 spectrometer.

YbI_2 was obtained by desolvation of $YbI_2 \cdot THF_x$ at 180°C in vacuum (10^{-2} torr). Found, (%): Yb-40.7; I-59.1. Calculated for YbI_2 (%): Yb-40.5; I-59.5.

2.1. *(1,3-tert-$Bu_2C_5H_3)_2Yb \cdot OEt_2$ (**1**)*

To a stirred suspension of YbI_2 (3.1 g, 7.3 mmol) in diethyl ether (200 ml) 1,3-^{t}$Bu_2C_5H_3Na$ (2.9 g, 14.5 mmol) was slowly added. The mixture was held for 24 h with vigorous stirring. The white NaI precipitate was filtered off, and concentration of the green filtrate in vacuum afforded green crystals of **1** (yield 70%). Found, (%): C-59.75; H-8.70; Yb-28.6. Calculated for $C_{30}H_{52}OYb$, (%): C-59.88; H-8.71; Yb-28.8.

Table 1
Crystal data and structure refinement for (1,3-^{t}$Bu_2C_5H_3)_2Yb \cdot OEt_2$ (1) and (1,2-^{t}$Bu_2C_5H_3)_2Yb \cdot DME$ (2a)

Compound	(1,3-*t*-$Bu_2C_5H_3)_2$ $Yb \cdot OEt_2$	(1,2-*t*-$Bu_2C_5H_3)_2$ $Yb \cdot DME$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2$
Unit cell dimensions		
a (Å)	11.302(2)	13.782(3)
b (Å)	19.018(4)	10.299(2)
c (Å)	14.404(3)	10.849(2)
β (°)	90.41(3)	95.04(3)
V (Å^3)	3095.9(11)	1534.0(5)
D_{calc} (mg m^{-3})	1.291	1.337
Wavelength (Å)	0.71073	0.71069
Temperature (K)	293(2)	293(2)
Z	4	2
Diffractometer	CAD-4	Nicolet R3
Collection method	$\theta/2\theta$	$\theta/2\theta$
Radiation type	Mo–K_α	Mo–K_α
Radiation monochromator	Beta-filter	Graphite
Absorption coefficient (mm^{-1})	3.038	3.069
Crystal size (mm)	$0.25 \times 0.19 \times 0.14$	$0.23 \times 0.25 \times 0.10$
Theta range for data collection (°)	1.77–22.46	1.88–22.48
Reflections collected	1482	798
Independent reflections	1406	798
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $wR_2 = 0.0981$	$R_1 = 0.0432$, $wR_2 = 0.1121$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for (1,3-^{t}$Bu_2C_5H_3)_2Yb \cdot OEt_2$ (**1**)

Atom	*x*	*y*	*z*	U_{eq}
Yb	6160(1)	2267(1)	3061(1)	55(1)
O	6281(12)	1932(9)	1436(9)	88(5)
C(1)	8475(16)	2670(15)	3299(14)	60(5)
C(2)	8479(18)	1932(14)	3279(14)	62(6)
C(3)	7920(17)	1679(12)	4064(14)	65(6)
C(4)	7541(15)	2238(16)	4533(13)	69(5)
C(5)	7849(20)	2861(13)	4079(16)	83(8)
C(6)	9091(16)	3159(14)	2609(15)	84(7)
C(7)	10 057(52)	2880(34)	2217(57)	481(69)
C(8)	8406(30)	3417(29)	1936(29)	260(28)
C(9)	9602(77)	3702(35)	3066(29)	430(59)
C(10)	7844(21)	943(15)	4398(18)	92(7)
C(11)	8861(29)	681(18)	4727(42)	321(36)
C(12)	7014(40)	829(22)	5095(32)	249(25)
C(13)	7397(50)	514(16)	3686(33)	279(32)
C(14)	4322(19)	3091(12)	3476(15)	67(6)
C(15)	3846(18)	2642(16)	2830(13)	71(7)
C(16)	3791(19)	1915(14)	3207(14)	69(6)
C(17)	4243(20)	2008(12)	4100(16)	77(7)
C(18)	4570(15)	2707(17)	4268(13)	74(6)
C(19)	4378(19)	3875(13)	3358(16)	85(7)
C(20)	5012(36)	4213(16)	4142(31)	214(19)
C(21)	5063(32)	4060(13)	2543(26)	182(16)
C(22)	3199(24)	4219(15)	3340(27)	166(14)
C(23)	3224(18)	1290(11)	2774(16)	74(6)
C(24)	2841(29)	1393(16)	1783(20)	152(12)
C(25)	2099(23)	1109(14)	3317(21)	139(11)
C(26)	3969(22)	671(16)	2823(21)	129(10)
C(27)	7056(31)	1435(20)	1090(19)	138(12)
C(28)	6631(35)	763(22)	869(23)	185(16)
C(29)	5561(26)	2223(22)	707(18)	147(13)
C(30)	6031(27)	2666(21)	180(26)	167(14)

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

^{1}H-NMR (300 MHz, δ C_6D_6, 298 K): 0.93 (t, 6H), 1.40 (br. s, 36H), 3.39 (q, 4H), 5.73 (t, 2H), 6.17 (d, 4H).

2.2. *(1,3-tert-$Bu_2C_5H_3)_2Yb \cdot DME$ (**2**)*

1,2-Dimethoxyethane (150 ml) was added to a dry mixture of YbI_2 (5.0 g, 11.7 mmol) and 1,3-^{t}$Bu_2C_5H_3Na$ (4.7 g, 23.5 mmol). The resultant blue solution was stirred for 3 h. Next, solvent was removed in vacuum, toluene (100 ml) was added to the dry residue, NaI was separated, and the filtrate was concentrated 5-fold and left to stand. Violet crystals of (1,2-^{t}$Bu_2C_5H_3)_2Yb \cdot DME$ (**2a**) (yield 3%) formed after 24 h. The remaining product, (1,3-^{t}$Bu_2CH_3)_2Yb \cdot DME$ (**2**) (yield 85%), was isolated as bluish green crystals from

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for (1,2-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·DME (**2a**)

Atom	x	y	z	U_{eq}
Yb	0	0	0	59(1)
C(1)	1793(17)	722(29)	−109(23)	63(7)
C(2)	1369(15)	1727(22)	479(30)	78(9)
C(3)	1224(13)	1418(22)	1707(17)	51(5)
C(4)	1606(12)	−60(75)	1866(16)	59(6)
C(5)	1950(14)	−48(64)	733(26)	156(32)
C(6)	1875(18)	−685(25)	3005(23)	69(6)
C(7)	2848(19)	−299(38)	3612(22)	88(17)
C(8)	1117(23)	−722(32)	3986(24)	92(8)
C(9)	1939(22)	−2172(29)	2666(26)	93(9)
C(10)	822(19)	2434(28)	2533(27)	92(9)
C(11)	1513(21)	2725(36)	3668(29)	101(10)
C(12)	−172(19)	1916(27)	2966(22)	83(7)
C(13)	640(22)	3719(24)	1946(27)	94(8)
O	408(13)	−2101(21)	−1047(28)	125(9)
C(14)	416(31)	−3213(37)	−328(52)	174(26)
C(15)	1147(27)	−2119(50)	−1918(37)	149(18)

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

hexane solution. Found, (%): C-58.49; H-8.31; Yb-27.7. Calculated for $C_{30}H_{52}O_2Yb$, (%): C-58.33, H-8.48, Yb-28.0.

2.3. (1,3-*tert*-Bu$_2$C$_5$H$_3$)$_2$Yb (**3**)

Green crystals of **1** were dissolved in toluene and the solvent was removed under argon (1 atm). The residue was again dissolved in toluene. Black crystals of **3** were obtained by cooling the dark-green solution. Yield 50%. Found (%): C-59.34; H-8.17; Yb-32.5. Calculated for $C_{26}H_{42}Yb$, (%): C-59.18; H-8.02; Yb-32.8.

^{1}H-NMR (300 MHz, δ $_6D_6$, 298 K): 1.35 (br s, 36H), 5.64 (t, 2H, $J_{H-H} = 12$ MHz), 5.97 (d, 4H, $J_{H-H} = 15$ MHz).

The complexes obtained were tested for catalytic activity in ethene polymerization as 10^{-3} M toluene solutions at 20°C and an ethene pressure of 1 atm with the use of Schlenk reactor.

2.4. X-ray structure determination

Unit cell determination, data collection and structure refinement are detailed in Table 1. Experimental data were processed using the PROFIT procedure [19]. As soon as the experiment has been taken from a formless crystal sealed in a capillary, the correct absorption correction could not be applied. The structure was solved by heavy atom technique and refined by full-matrix anisotropic least-squares method. Hydrogen atoms

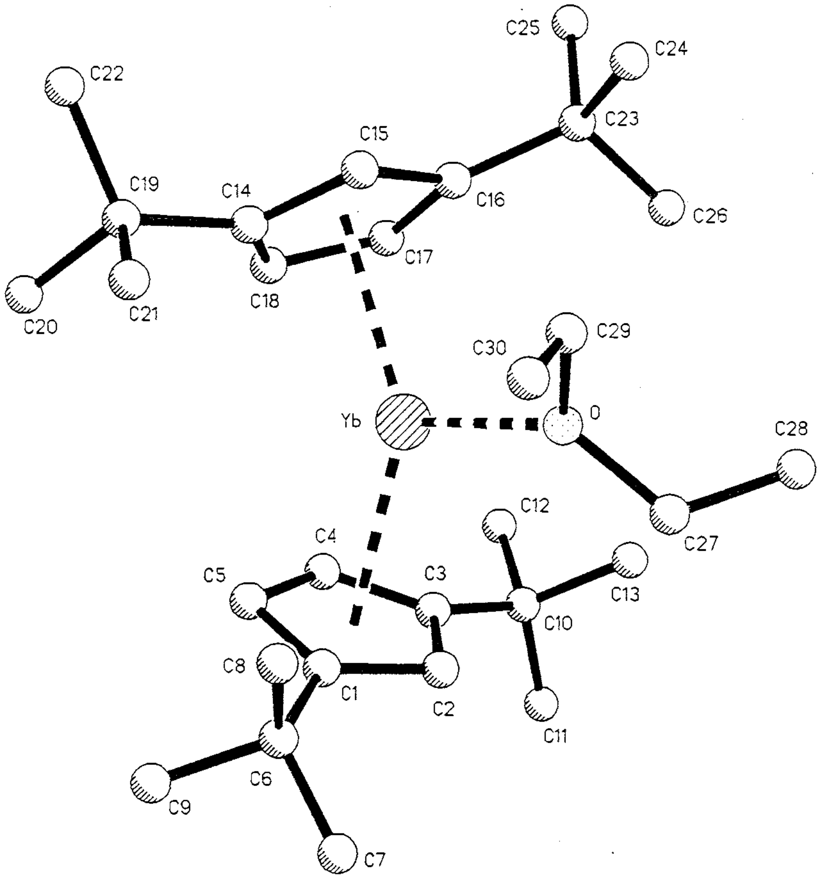


Fig. 1. Molecular structure of (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$ (**1**).

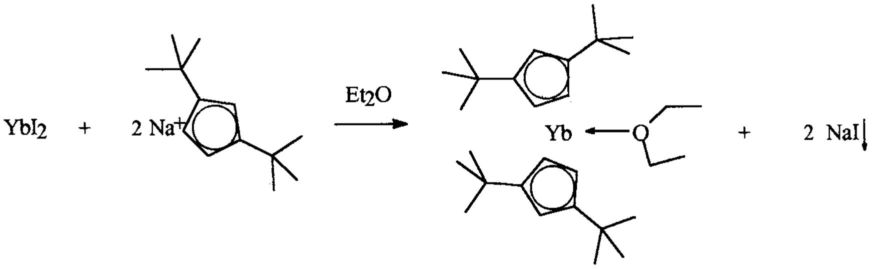
positions were found from difference synthesis, their positional and isotropic thermal parameters were included into refinement fixed. The anisotropic thermal parameters of the carbon atoms of *tert*-butyl groups show strong thermal vibration of these groups. Structure solution and refinement were performed using SHELXTL-81 [20] and SHELXL-93 [21] packages, respectively. Atomic coordinates for **1** and **2a** are given in Tables 2 and 3, respectively.

3. Results and discussion

Ytterbium(+ 2) iodide, which is obtained from the metal and iodine in THF [15], is isolated as a solvate with a variable number of coordinated solvent molecules [22]. This makes difficult or even impossible the preparation of ytterbium cyclopentadienyl complexes with bases weaker than THF. Therefore, it is more advantageous to use unsolvated YbI_2, which, like SmI_2 [23], forms readily upon heating of $YbI_2\cdot THF_x$ in vacuum:

$$\mathrm{YbI_2\cdot THF_x} \xrightarrow[180^{o}\mathrm{C}]{10^{-2}\ \mathrm{mm\ Hg}} \mathrm{YbI_2} + \mathrm{x\ THF}\uparrow \qquad (1)$$

The ether complex of $(1,3\text{-}^t\mathrm{Bu_2c_5H_3})_2\mathrm{Yb}$ forms via Eq. 2 and, as could be expected, crystallizes with one solvent molecule.



(2)

Table 4
Selected bond lengths (Å) and angles (°) for $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb\cdot OEt_2}$ (**1**)

Bond	*d* (Å)	Angle	*ω* (°)
Yb–O	2.430(14)	C(27)–O–C(29)	111(2)
Yb–C(1)	2.75(2)	C(5)–C(1)–C(2)	106(2)
Yb–C(2)	2.71(2)	C(5)–C(1)–C(6)	127(3)
Yb–C(3)	2.69(2)	C(2)–C(1)–C(6)	126(2)
Yb–C(4)	2.62(2)	C(3)–C(2)–C(1)	109(2)
Yb–C(5)	2.65(2)	C(4)–C(3)–C(2)	107(2)
Yb–C(14)	2.67(2)	C(4)–C(3)–C(10)	125(2)
Yb–C(15)	2.73(2)	C(2)–C(3)–C(10)	128(2)
Yb–C(16)	2.77(2)	C(3)–C(4)–C(5)	111(2)
Yb–C(17)	2.69(2)	C(1)–C(5)–C(4)	107(2)
Yb–C(18)	2.65(2)	C(15)–C(14)–C(18)	108(2)
O–C(27)	1.38(3)	C(15)–C(14)–C(19)	124(2)
O–C(29)	1.43(3)	C(18)–C(14)–C(19)	128(2)
C(1)–C(5)	1.38(3)	C(14)–C(15)–C(16)	110(2)
C(1)–C(2)	1.40(2)	C(17)–C(16)–C(15)	102(2)
C(1)–C(6)	1.53(3)	C(17)–C(16)–C(23)	130(2)
C(2)–C(3)	1.39(3)	C(15)–C(16)–C(23)	128(2)
C(3)–C(4)	1.33(3)	C(16)–C(17)–C(18)	112(2)
C(3)–C(10)	1.48(3)	C(14)–C(18)–C(17)	108(2)
C(4)–C(5)	1.40(3)	O–C(27)–C(28)	119(3)
C(14)–C(15)	1.37(3)	C(30)–C(29)–O	118(3)
C(14)–C(18)	1.38(3)		
C(14)–C(19)	1.50(3)		
C(15)–C(16)	1.49(3)		
C(16)–C(17)	1.39(3)		
C(16)–C(23)	1.49(3)		
C(17)–C(18)	1.40(3)		
C(27)–C(28)	1.40(4)		
C(29)–C(30)	1.25(4)		

Insolubility of NaI in ether is both an advantage and disadvantage of this solvent. On one hand, the reaction time and yield depend on the dispersity of $1,3\text{-}^t\mathrm{Bu_2C_5H_3Na}$ and intensity of stirring. On the other, additional operations such as solvent removal and extraction of the goal product from its mixture with NaI, which are necessary in the case of THF solvent [15], are excluded.

The structure of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb\cdot OEt_2}$ (**1**) (Fig. 1, Table 4) is similar to those of the related compounds (Table 5). The ytterbium atom of **1** has a distorted-trigonal environment. The bond angles Cp(1)–Yb–O and Cp(2)–Yb–O are 113.6 and 113.4°, respectively. The bond angle Cp–Yb–Cp is 133.0°; and this value lies between the values found for substituted and unsubstituted cyclopentadienyl ytterbium solvates (Table 5). The mean distance between the cyclopentadienyl carbons and ytterbium (2.69 Å), as well as the distance between the latter and the center of the rings (2.42 Å), is close to or the same as that in the related complexes $[\mathrm{C_5H_4(CH_2)_3C_5H_4}]\mathrm{Yb\cdot(THF)_2}$ (2.70, 2.42 Å) [9], $(\mathrm{C_5H_5})_2\mathrm{Yb\cdot(THF)_2}$ (2.69, 2.43 Å) [8], $(\mathrm{C_5Me_4Et})_2\mathrm{Yb\cdot THF}$ (2.69, 2.41 Å) [12] and $[1,3\text{-}(\mathrm{SiMe_3})_2\mathrm{C_5H_3}]_2\mathrm{Yb\cdot THF}$ (2.67, 2.39 Å) [3]. The oxygen atom of **1** is out of the Cp(1)–Yb–Cp(2) plane by 0.12 Å. The Yb–O bond distance (2.43(1) Å) is nearly identical to that in the disolvate $(^t\mathrm{BuC_5H_4})_2\mathrm{Yb\cdot(THF)_2}$ (2.43(8) Å) [5] and much longer than that in the monosolvate $[1,3\text{-}(\mathrm{SiMe_3})_2\mathrm{C_5H_3})]_2\mathrm{Yb\cdot THF}$ (2.34(1) Å) [3]. This is explicable by the fact that diethyl ether requires more space and is less basic than THF. This explanation is consistent with the finding that (1,3-

Table 5
Geometric parameters of some cyclopentadienyl ytterbium complexes

Complex	Angle Cp–M–Cp (°)	M–C (range) (Å)	M–C$_{av}$ (Å)	M–O (Å)	M–Cp (Å)	Reference
$(1,3\text{-}{}^{t}Bu_2C_5H_3)_2Yb\cdot OEt_2$	133.0	2.62–2.77	2.69	2.430	2.42	This work
$(C_5H_4(CH_2)_3C_5H_4)Yb\cdot(THF)_2$	127	2.67–2.73	2.70	2.42, 2.41	2.42	[9]
$(C_5H_5)_2Yb\cdot(THF)_2$	127.9	2.67–2.71	2.69	2.44	2.43	[8]
$(SiMe_3C_5H_4)_2Yb\cdot(THF)_2$	133	2.64–2.84	2.75	2.42	2.39	[10]
$({}^{t}BuC_5H_4)_2Yb\cdot(THF)_2$	134.4	2.645–2.807	2.723	2.43	2.44	[5]
$(1,3\text{-}(SiMe_3)_2C_5H_3)_2Yb\cdot THF$	136	2.65–2.70	2.67	2.34	2.39	[3]
$\{(1,3\text{-}(SiMe_3)_2C_5H_3)_2Yb\}_\infty$	138.0	2.642–2.684	2.66	–	2.37	[4]
$(C_5Me_5)_2Yb\cdot THF(NH_3)$	135.1, 139.3	2.72–2.84	2.78	2.46	2.51	[7]
$(C_5Me_5)_2Yb\cdot THF(1/2PhMe)$	143.5	2.643–2.680	2.66	2.412	2.37	[24]
$(C_5Me_4Et)_2Yb\cdot THF$	144.5	2.655–2.730	2.69	2.379	2.41	[12]

${}^{t}Bu_2C_5H_3)_2Yb\cdot OEt_2$ does not form the ether disolvate on being cooled and readily loses the single ether molecule on being heated.

Among unique structural features of $(1,3\text{-}{}^{t}Bu_2C_5H_3)_2Yb\cdot OEt_2$, note that the coordination sphere of the ytterbium is heavily 'loaded'. As a result, a noticeable distortion of the cyclopentadienyl ligands is observed (Table 4). The cyclopentadienyl ligands are gosh to each other (Fig. 2) and planar to within 0.03 Å (the dihedral angle between the ring planes is 52.3°). The quaternary atoms of the *tert*-butyl groups are out of the planes by 0.12–0.16 Å in the direction opposite to ytterbium. Similar effect, though not so strong, was observed with other compounds with bulky substituents in cyclopentadienyl rings, viz. $[1,3\text{-}(SiMe_3)_2C_5H_3]_2Yb\cdot THF$ (0.01 and 0.14 Å) [3] and $({}^{t}BuC_5H_4)_2Yb\cdot(THF)_2$ (0.03 Å) [5].

Like the THF solvate, complex **1** is highly soluble in organic solvents and sublimes at 10^{-2} mm Hg (70°C), retaining its composition. Note that $[1,3\text{-}(SiMe_3)_2C_5H_3]_2Yb\cdot OEt_2$ and $(C_5Me_5)_2Yb\cdot OEt_2$ do lose coordinated solvent molecules upon sublimation in vacuum [4]. The desolvation of **1** was only possible by removal of the ether from a boiling toluene solution of **1** under an argon pressure of 1 atm. Unfortunately, the crystals of $[(1,3\text{-}{}^{t}Bu_2C_5H_3)_2Yb]$ (**3**) thus obtained (its composition was deduced from analytical and ^{1}H-NMR data) were not suitable for direct X-ray structure

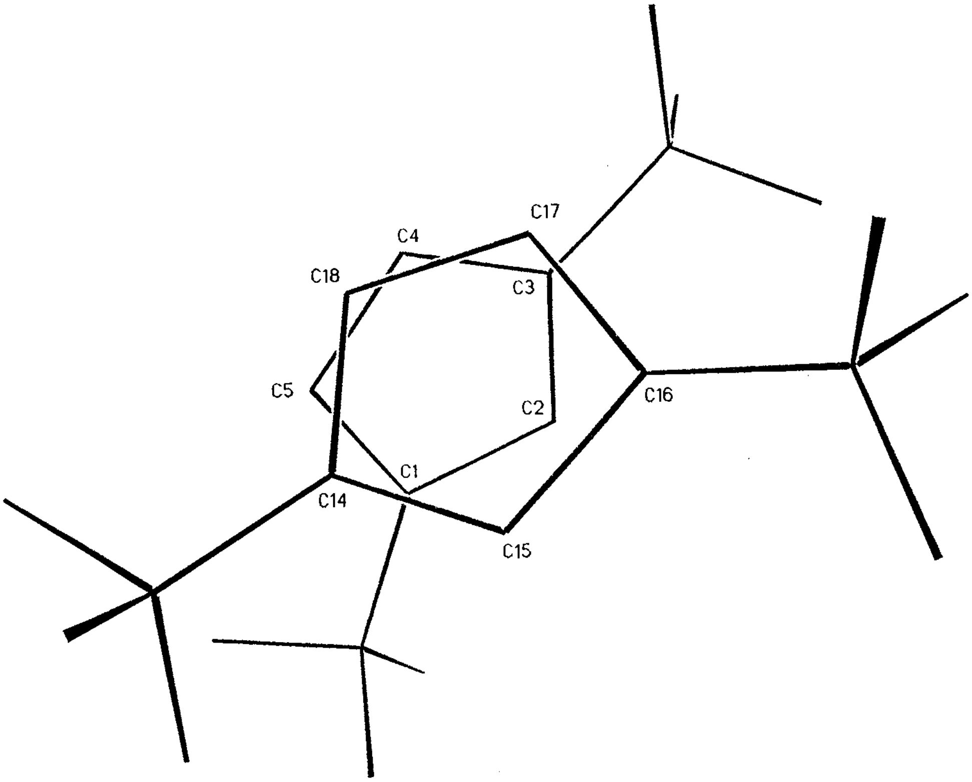


Fig. 2. Conformation of cyclopentadienyl rings of $(1,3\text{-}{}^{t}Bu_2C_5H_3)_2Yb\cdot OEt_2$ (**1**).

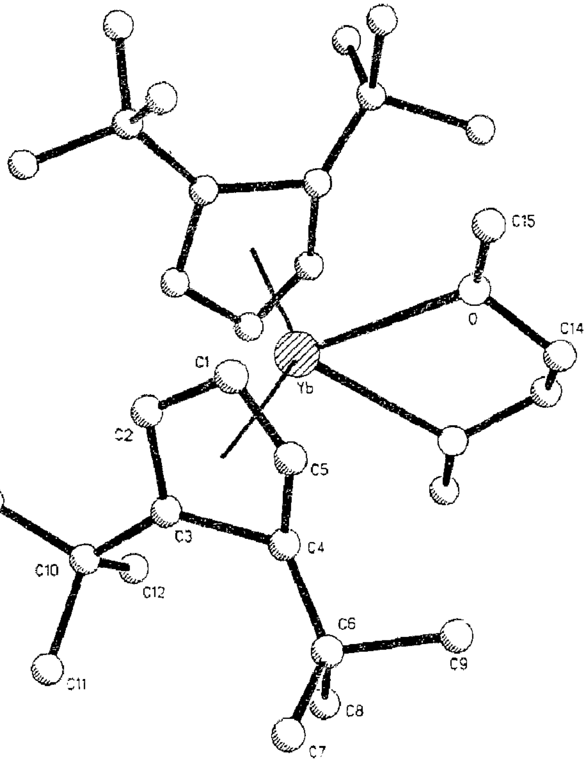
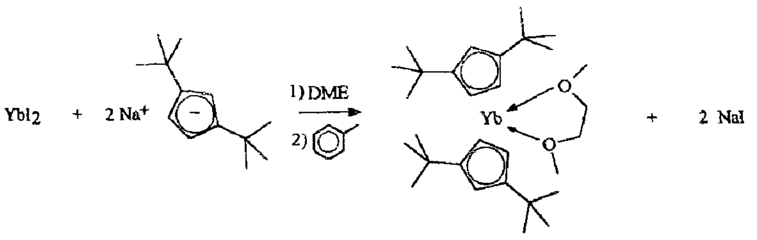


Fig. 3. Molecular structure of $(1,2\text{-}^{t}Bu_2C_5H_3)_2Yb \cdot DME$ (**2a**).

determination. However, the structural similarity of $(1,3\text{-}^{t}Bu_2C_5H_3)_2Yb \cdot OEt_2$ and $[1,3\text{-}(SiMe_3)_2C_5H_3]_2Yb \cdot THF$ [3] as well as their identical thermal behavior suggests the existence in **3** of an agostic C–H → Yb contact similar to that found in the solvent-free molecule $\{[1,3\text{-}(SiMe_3)_2C_5H_3]_2Yb\}_{\infty}$ [4].

Catalytic properties of monoether solvate **1** and solvent-free complex **3** are different. The former, unlike Sm(+ 2) complexes [25], is not oxidized by ethene and does not catalyze the ethene polymerization as well. On the other hand, **3** is very slowly oxidized by olefin in toluene (color change becomes noticeable in a few days) and displays a very low catalytic activity, affording a low-molecular PE. The high activity of divalent samarocenes in olefin polymerization was previously ascribed to the oxidation of Ln(+ 2) to the corresponding binuclear complex $Cp_2LnCH_2CH_2LnCp_2$, affording subsequently the hydride Cp_2LnH, which was found to be the true catalyst [25]. The very low rate of ethene polymerization induced by divalent ytterbocenes may be related to a low redox potential of Yb(+ 2)–Yb(+ 3) pair in comparison with that of the similar samarium pair and, as a consequence, to the formation a negligible amount of Cp'_2YbH.

The synthesis of $(1,3\text{-}^{t}Bu_2C_5H_3)_2Yb \cdot DME$ (**2**) (Eq. 3) is similar to that reported elsewhere [15] for the ytterbium complex with THF:



(3)

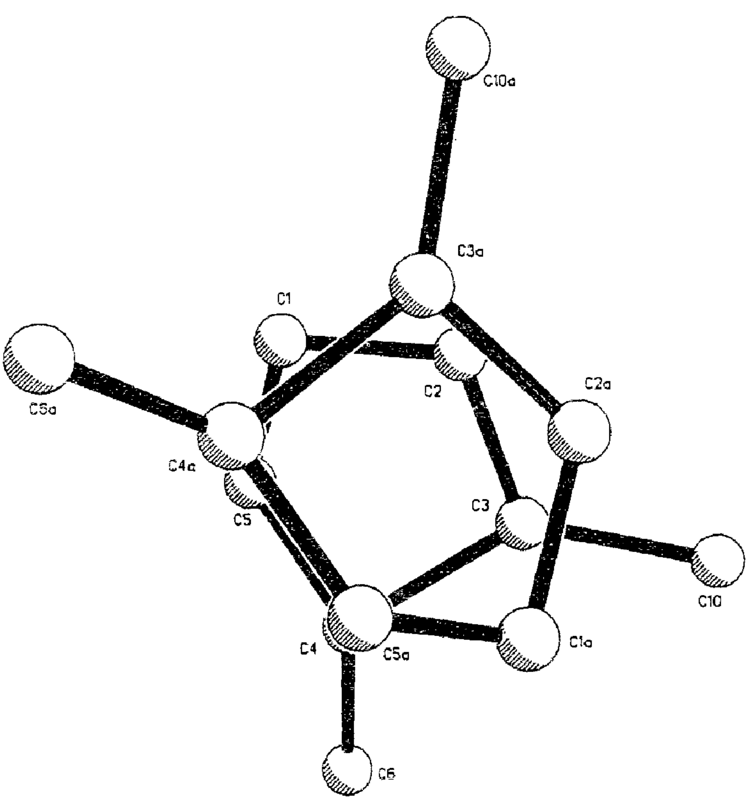


Fig. 4. Conformation of cyclopentadienyl rings of $(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2$Yb·DME (**2a**).

The dark blue solvate obtained by rapid crystallization was almost amorphous to X-rays. Slow (for 3–4 months) crystallization yielded large blue green crystals from a hexane solution. However, all attempts to determine the structure of this material using the cell parameters $a = 14.611$ Å, $b = 17.791$ Å, $c = 25.200$ Å,

Table 6
Selected bond lengths (Å) and angles (°) for $(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2$Yb·DME (**2a**)

Bond	d (Å)	Angle	ω (°)
Yb–O	2.53(2)	O–Yb–O*	62.4(14)
Yb–C(1)	2.59(2)	C(2)–C(1)–C(5)	101(3)
Yb–C(2)	2.61(2)	C(1)–C(2)–C(3)	112(2)
Yb–C(5)	2.73(2)	C(4)–C(3)–C(2)	104(2)
Yb–C(3)	2.80(2)	C(4)–C(3)–C(10)	136(2)
Yb–C(4)	2.87(2)	C(2)–C(3)–C(10)	120(2)
C(1)–C(2)	1.37(4)	C(5)–C(4)–C(3)	92(4)
C(1)–C(5)	1.21(5)	C(5)–C(4)–C(6)	135(4)
C(2)–C(3)	1.40(4)	C(3)–C(4)–C(6)	126(4)
C(3)–C(4)	1.62(8)	C(4)–C(5)–C(1)	129(5)
C(3)–C(10)	1.51(3)	C(14)–O–C(15)	113(3)
C(4)–C(5)	1.36(3)	C(14)–O–Yb	116(3)
C(4)–C(6)	1.41(4)	C(15)–O–Yb	120(2)
O–C(14)	1.39(5)	O–C(14)–C(14)*	109(3)
O–C(15)	1.45(5)		
C(14)–C(14)*	1.40(10)		

Table 7
Main geometric parameters of 1,2-di-*tert*-butyl substituted metallocenes

Substances	α (°)	Cp–M–Cp (°)	M–Cp (Å)	Reference
$(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2$Yb·DME	44.5	143.2	2.72	This work
$(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{TiCl}_2$	60.8	132.1	2.13	[2]
$(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{ZrCl}_2$	61.4	128.7	2.12 2.24	[2]
$(1,2\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{UCl}_2$	63.5	123.3	2.49 2.43	[2]

Table 8
Geometric parameters of some cyclopentadienyl complexes with 1,2-dimethoxyethane.

Substance	Angle Cp–M–Cp (°)	Angle O–M–O (°)	M–C (Å)	M–C_{av} (Å)	O–O (Å)	M–O (Å)	M–Cp (Å)	Reference
$(1,2\text{-}^tBu_2C_5H_3)_2$Yb·DME	143.2	62.4	2.59–2.87	2.72	2.62	2.53	2.46	This work
$(C_5H_4PPh_2)_2$Yb·DME	133.8	67.7	2.67–2.75	2.71	2.68	2.40	2.43	[30]
$(C_5H_5)_2$Yb·DME	133.9	69.3	2.65–2.67	–	2.81	2.47	2.41	[31]
$(C_5H_5)_2$Yb·DME	124–133	67.2	2.60–2.91	2.72	2.74	2.50 2.45	–	[27]
$(C_5Me_5)_2$Sm·DME	140	62.5	2.77–2.82	2.79	2.67	2.52 2.61	2.54	[32]

$\beta = 95.44°$, and space group *C*2 or *C*2/*m* failed. A possible reason is that crystals of **2** form intergrowths that are difficult to separate.

$(1,2\text{-}^tBu_2C_5H_3)_2$Yb·DME (**2a**) (Fig. 3), whose yield does not exceed 3%, is a by-product of reaction 3. Its formation is explained by the presence of $1,2\text{-}^tBu_2C_5H_3$ in the starting sodium salt of the ligand. The separation of isomers **2** and **2a** at a very low content of the latter is likely due to a very low solubility of the 1,2-substituted isomer compared to that of the 1,3-substituted one.

The structural data show that the all main geometric parameters of **2a** (Table 6) differ markedly not only from complexes with the 1,3-disubstituted cyclopentadienyl rings (Table 5) but also from the related molecules containing 1,2-disubstituted ligands (Table 7). In particular, the *tert*-butyl groups in **2a** are trans to each other (Fig. 4) as observed in the $(1,2\text{-}^tBuC_5H_3)_2$Fe molecule with parallel cyclopentadienyl ligands [26], and are out of the Cp ring by 0.33 (C6) and 0.16 (C10) Å. The Cp rings adopt an eclipsed conformation. The bond distances Yb–C and Yb–Cp in **2a** are normal; the dihedral angle α between the Cp planes is 44.5°, while the bond angle Cp–Yb–Cp is 143.2°. The parameters quoted distinguish complex **2a** from the complexes $(1,2\text{-}^tBu_2C_5H_3)_2MCl_2$, where M = Ti, Zr and U [2] (Table 7), whose Cp rings are eclipsed, while the substituents, though are turned with respect to each other, are directed to the same side.

The O–O distance, shortened to 2.62 Å, is lower than the sum of van der Waals radii of oxygen atoms [27]. The bond angle O–Yb–O is 62.4°, while the Yb–O distance is increased to 2.53 Å (Table 8). It is believed that 1,2-dimethoxyethane is pushed out of the coordination sphere of ytterbium, whereas the geometry of the metallocene fragment becomes similar to the geometry of the monodentate organometallic complexes $(C_5Me_5)_2Yb(\mu\text{-}Me)Be(C_5Me_5)$ [28] (Cp–M–Cp = 145°) and $(C_5Me_5)_2Yb(\mu\text{-}Et)AlEt_2$ [29] (Cp–M–Cp = 142.8°).

4. Supplementary material

Anisotropic temperature factors, hydrogen atom parameters, and the complete set of bond distances and angles for complexes **1** and **2a** can be received from the authors on request.

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