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bis-(di-*tert*-Butylcyclopentadienyl)ytterbium(II): reactions with triisobutylaluminum and aluminium deuteride. Crystal structures of the complex $(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_3\text{Yb}$ and the complex $(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}(\mu\text{-D})_2\text{Al}(\eta^2\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)$ with allyl → Al extra bonding

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Abstract

The reaction of $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}\cdot\text{OEt}_2$ with Al^iBu_3 in the presence of hexene-1 and hydrogen gave in high yield $(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_3\text{Yb}$ (**1**). The treatment of $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}\cdot\text{OEt}_2$ with $\text{AlD}_3\cdot\text{Et}_2\text{O}$ or $\text{AlD}_2(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\cdot\text{Et}_2\text{O}$ in diethyl ether yielded the novel hetero-metallic complex $(\eta^5\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}(\mu\text{-D})_2\text{Al}(\eta^2\text{-}1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)$ (**2**). The crystal structures of complexes **1** and **2** are reported. The containing an Yb(+2) and a three-coordinate Al atoms complex **2** is supposed to be stable due to interaction of π-electrons of the 'allyl' group of the η^2-bonded Cp ring with unoccupied orbitals of the aluminium atom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ytterbium; Aluminium; Metallocenes; Hydrides; Binuclear complexes

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1. Introduction

Lanthanide(II) compounds are particularly interesting among the cyclopentadienyl complexes of rare-earth elements [1]. As the compounds are both strong Lewis acids and strong reducing agents, their reactions with Brönsted acids and various Lewis bases can be easily predicted unlike their reactions with Lewis acids with reducing properties. For example, reactions of $\text{Cp}''_2\text{Sm}$ with AlAlk_3 [2,3] and $\text{AlH}_3\cdot\text{L}$ [4] ($\text{Cp}'' = \text{C}_5\text{Me}_5$, $\text{C}_5\text{H}_3\text{R}_2$; $\text{L} = \text{Et}_2\text{O}$, THF, NEt_3, etc.) proceed with oxidation of the samarium atom, yielding first products $\text{Cp}''_2\text{SmAlk}$ and $\text{Cp}''_2\text{SmH}$, respectively, and then binuclear complexes (monomeric $\text{Cp}''_2\text{Sm}^{+3}\text{Et}_2\text{AlEt}_2\cdot\text{L}$ [3]; dimeric $[\text{Cp}''_2\text{SmMe}_2\text{AlMe}_2]_2$ [2], $[\text{Cp}''_2\text{SmH}_2\text{AlH}_2]_2$ [4]). The reaction of $\text{Cp}''_2\text{Sm}$ with AlD_3TMEDA allows to isolate the $\text{Cp}''_2\text{Sm}^{+2}\text{D}_2\text{AlD}\cdot\text{TMEDA}$ intermediate [4], which is result of pure donor–acceptor interaction and is stable apparently due to isotopic effect. Stability to oxidation for such compounds is supposed to increase in the row Sm < Yb < Eu, because of decreasing $\text{Ln}^{+3}/\text{Ln}^{+2}$ reduction potential. However, only a few lanthanide(+2) bimetallic complexes (e.g. $\text{Cp}^*_2\text{YbEtAlEt}_2\cdot\text{THF}$ [5], $\text{Cp}^*_2\text{Yb(CH}_3\text{)BeCp}^*$ [6], where $\text{Cp}^* = \text{C}_5\text{Me}_5$) have been structurally characterised.

Investigation of such compounds is expected to discover new metallocene catalysts for olefin transformations and to provide better understanding of catalysis by Group III and IVB metals compounds. It was already found that the system $(\text{C}_5\text{Me}_5)_2\text{Yb}\cdot\text{THF-AlEt}_3$ [5] and complexes $(^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{YbH}_2\text{AlH}\cdot\text{L}$ [7] are catalytically active in polymerisation of ethylene and styrene, respectively.

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We now report two reactions of (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$ with Al^{i}Bu$_3$ (in the presence of hexene-1 and hydrogen) and AlD$_3$·OEt$_2$, as well as the structures of two resulting compounds.

2. Results and discussion

We reported previously [8], that weak catalytic activity of the ytterbium(II) mononuclear complex (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$ in homogeneous hydrogenation of hexene-1 are explained by the slow formation of ytterbocene(+ 3) hydride during the catalytic reaction. It was expected that introducing an organoaluminum cocatalyst in the (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb-hexene-1-H$_2$ system would cause rapid oxidation of the ytterbium atom (as in the case samarocene(+ 2) [2,3]), formation of the alkyl or hydride derivative of ytterbocene(+ 3) and, as a consequence, an increase of catalytic activity. In fact, the estimated at 15 mmol H$_2$/(mol Yb·h) hydrogenation rate of hexene-1 in the presence of Al^{i}Bu$_3$ (Yb: Al = 1: 1–1: 10) differs a bit from that with the pure mononuclear complex (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$. However, whether the redox reactions do proceed in the system is unclear. One of these reactions gives tris-[di-(*tert*-butyl)-cyclopentadienyl]ytterbium(+ 3) (**1**).

The crystalline **1** consist of separated molecules (Fig. 1, Table 1), with metal atoms are located almost precisely in the same planes as ring centroids (off-plane displacement does not exceed 0.008 Å). The average deviations of quaternary carbon atoms of *tert*-butyl groups from Cp-ring planes are 0.41 Å. This value is more than twice as large as that found for (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$ [9].

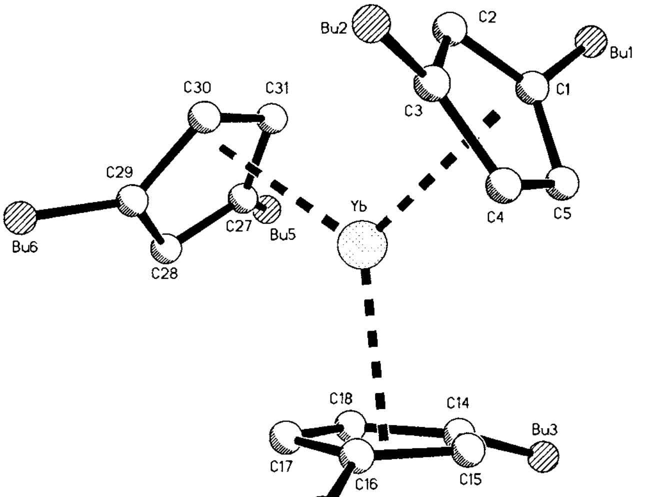


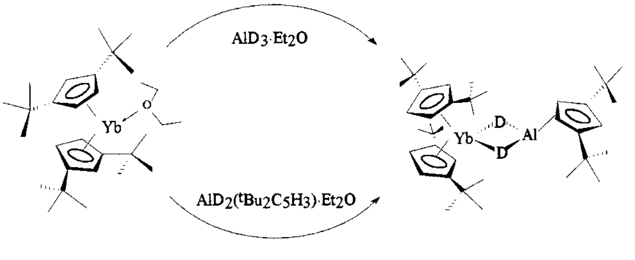
Fig. 1. Molecular structure of the complex (η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)$_3$Yb (**1**). Carbon atoms of *tert*-butyl groups are not shown.

Table 1
Selected bond lengths (Å) and bond angles (°) for (η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)$_3$Yb (1) with estimated standard deviations

Bond distances			
Yb–Cp1	2.44(1)	C(4)–C(5)	1.39(1)
Yb–Cp2	2.41(1)	C(2)–C(3)	1.40(1)
Yb–Cp3	2.55(1)	C(1)–C(5)	1.40(1)
Yb–C(4)	2.55(1)	C(3)–C(4)	1.41(1)
Yb–C(5)	2.56(1)	C(1)–C(2)	1.42(1)
Yb–C(3)	2.79(1)	C(16)–C(17)	1.39(1)
Yb–C(1)	2.82(1)	C(14)–C(18)	1.40(1)
Yb–C(2)	2.86(1)	C(14)–C(15)	1.40(1)
Yb–C(17)	2.54(1)	C(15)–C(16)	1.40(1)
Yb–C(18)	2.55(1)	C(17)–C(18)	1.43(1)
Yb–C(16)	2.76(1)	C(27)–C(28)	1.37(1)
Yb–C(14)	2.76(1)	C(29)–C(30)	1.38(1)
Yb–C(15)	2.83(1)	C(28)–C(29)	1.40(1)
Yb–C(30)	2.54(1)	C(30)–C(31)	1.41(1)
Yb–C(31)	2.55(1)	C(27)–C(31)	1.40(2)
Yb–C(27)	2.94(1)		
Yb–C(29)	2.95(1)		
Yb–C(28)	3.06(1)		
Bond angles			
Cp1–Yb–Cp2	122.7(8)	Cp3–Yb–Cp2	116.5(8)
Cp1–Yb–Cp3	120.8(8)		

Yb–C distances in **1** vary in a wide range (between 2.55 and 3.06 Å). Their mean value varies from one Cp ring to another: Yb–C$^{\mathrm{Cp1}}_{\mathrm{mean}}$ = 2.71 Å, Yb–C$^{\mathrm{Cp2}}_{\mathrm{mean}}$ = 2.69 Å and Yb–C$^{\mathrm{Cp3}}_{\mathrm{mean}}$ = 2.81 Å. These distances are much longer than Yb–C$^{\mathrm{Cp}}$ distances in (η^5-C$_5$H$_5$)$_3$Yb (2.64 Å) [10] and (η^5-CH$_3$C$_5$H$_4$)$_3$Yb (2.65 Å) [11]. The correspondent distance between the Yb atom and Cp-ring centroid ranges from 2.41 to 2.55 Å in **1**; from 2.35 to 2.36 Å in (η^5-C$_5$H$_5$)$_3$Yb [10]; and, as determined for two independent molecules, from 2.29 to 2.38 Å or from 2.32 to 2.40 Å in (η^5-CH$_3$C$_5$H$_4$)$_3$Yb [11].

In the complex **1**, as in {1,3-(Me$_3$Si)$_2$C$_5$H$_3$}$_3$Sm [12], located between *tert*-butyl substituents carbon atoms (C2, C15, C28) are most distant from the metal atom. In contrast, not bonded with substituents carbon atoms (C4, C5, C17, C18, C30, C31) are located most closely to the metal centre. The atom C28 is 0.08 Å off the plane formed by four other carbons of the ring. The bend angle in this 'envelope' structure is 5.8°. In {η^5-1,3-^{t}Bu$_2$C$_5$H$_3$}$_3$Ce [13], {η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$}$_3$Ce [14], {η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$}$_3$Sm [12] and {η^5-1,3-



Scheme 1.

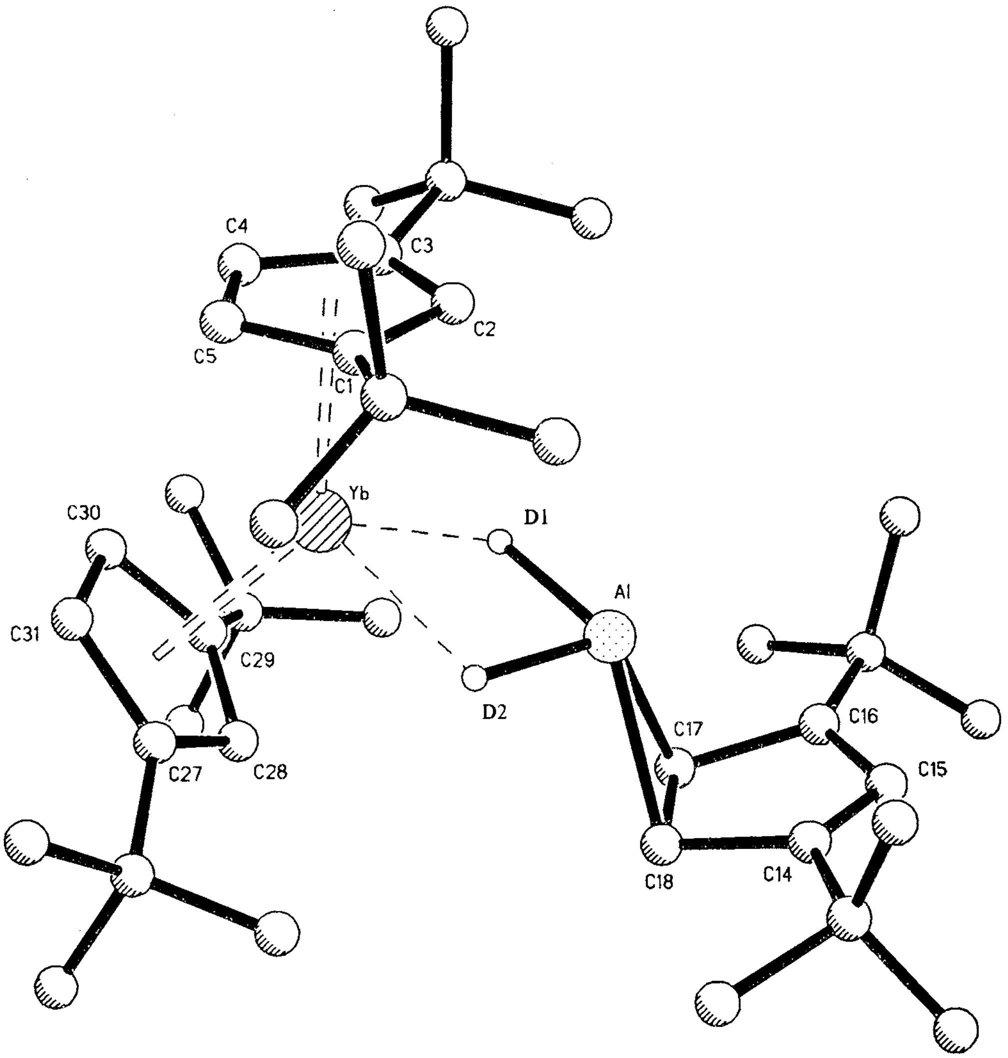


Fig. 2. Molecular structure of the complex (η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb(μ-D)$_2$Al(η^2-1,3-^{t}Bu$_2$C$_5$H$_3$) (**2**).

(Me$_3$Si)$_2$C$_5$H$_3$}$_3$Th [15], where the metal has a larger ionic radius [16] then Yb^{+3}, the difference between 'long' and 'short' distances is 0.10–0.15 Å, while this difference in **1** is 0.25–0.50 Å (Table 1). Therefore the coordination of all three Cp ligands in **1** could formally be considered as η^2-type. However, because of the absence of a fragment with shortened ('allyl') C–C distances in Cp rings (the one more distinctive feature of η^2-bonding), it is more appropriate to consider the Yb–Cp bond in the complex **1** as η^5-type and explain all structural anomalies by the presence of six bulky *tert*-butyl substituents. This conclusion conforms with the earlier one [17] finding that the use of the more bulky 1,3-bis(trimethylsilyl)cyclopentadienyl ligand does not allow the synthesis of the tris-Cp″ ytterbium complex by a simple metathesis method.

Isolation of the complex **1** in relatively high yield from the (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$-Al^{i}Bu$_3$-hexene-1-H$_2$ system is rather surprising. Apparently, it is similar on the unexpected isolation of samarium tris(cyclopentadienyl) complexes (1,3-(Me$_3$Si)$_2$C$_5$H$_3$)$_3$Sm [12] and (Me$_5$C$_5$)$_3$Sm [18] upon reactions of (1,3-(Me$_3$Si)$_2$C$_5$H$_3$)$_2$Sm·THF and CO and of (Me$_5$C$_5$)$_2$Sm and cyclooctatetraene, respectively. A wide variety of processes, including not only ligand exchange between organometallic components, but also oxidative addition of the olefin and hydrogenolysis of the alkyl derivative, can occur in the considered system. All these reactions (or one of them) apparently yield **1**, which precipitates as well formed crystals because it has lower solubility and higher stability than mono and bis Cp-complexes [19] and it crystallises better. For example, it was reported [20] that tris(cyclopentadienyl) complexes of lutetium and neodymium react with isobutyllithium to give first alkyl complexes of lanthanidocenes and then the corresponding hydrides. The decomposition of lutetiecene hydride yielding (Me$_5$C$_5$)$_3$Lu was observed in other study [21]. It is apparently complicated processes in the (1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Yb·OEt$_2$-Al^{i}Bu$_3$-H$_2$-hexene-1 system that not only make possible isolation of **1**, but are also responsible for a low hydrogenation rate of the olefin even in the presence of the organoaluminium compound.

Reactions of ytterbocenes(+2) containing bulky ligands with aluminium hydride complexes $\text{AlH}_3\cdot\text{L}$ were studied earlier [7], but products were not characterised structurally. It was only noted that the resulting bimetallic complexes are more stable to oxidation than analogous samarocene(+2) complexes. A binuclear complex with even higher oxidation stability can be obtained by using deuterium-substituted aluminium hydride $\text{AlD}_3\cdot\text{TMEDA}$ [4]. This reagent does not affect even the valence of samarium in samarocene(+2): the reaction is limited to an acid-base interaction and terminated after the initial step.

The analogous reaction of complex $(1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}\cdot\text{OEt}_2$ and $\text{AlD}_3\cdot\text{Et}_2\text{O}$ (Scheme 1) yields a binuclear complex $(\eta^5\text{-}1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}(\mu\text{-D})_2\text{Al}(\eta^2\text{-}1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)$ (**2**) (Fig. 2), which can be considered as a product of donor-acceptor interaction between $(1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}\cdot\text{OEt}_2$ and $\text{D}_2\text{Al}(\eta^2\text{-}1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)$. The formation of **2** in this reaction system indicates again to the occurrence of complicated equilibrium, including ligand exchange between metals. Since ligand exchange is well known for both metallocenes [19,20] and aluminium hydride [22] and obviously involved in the formation of complex **1**, we believe that this process is also possible in the metallocene-aluminium deuteride system. However, the structure and some physical properties of complex **2** are very unusual and deserve detailed consideration.

First of all, this compound is red-orange, while ytterbocenes(+2) with substituted Cp rings and one organic ligand are green. It is also remarkable that very short distances Yb–C with average of 2.58 Å and Yb–Cp of 2.29 Å (Table 2) are more typical for Yb(+3) bis(cyclopentadienyl) complexes (normally, 2.60–2.65 Å) than for ytterbocenes(+2) (normally, 2.66–2.69 Å). However, it was previously reported [8] that coordination of second THF molecule to $(1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}\cdot\text{THF}$ with the increasing of Yb coordination number to four caused a reversible changing of colour from green to red. Since the Yb atom in **2** has the same coordination number, red colour of this complex is not surprising. Then, the EPR spectrum of **2** in toluene solution at 298 K shows no signals from paramagnetic species, although it does not prove absolutely the absence of paramagnetic ion Yb(+3) in the system in the case of rare-earth elements. It has to be stressed that neither EPR nor even NMR and IR spectroscopy are sufficiently effective for characterisation of complex **2**. The presence of Al atom in this complex does not permit to obtain qualitative ^{1}H-NMR spectrum using standard technique.

Table 2
Selected bond lengths (Å) and bond angles (°) for $(\eta^5\text{-}1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}(\mu\text{-D})_2\text{Al}(\eta^2\text{-}1,3\text{-}{}^t\text{Bu}_2\text{C}_5\text{H}_3)$ (2) with estimated standard deviations

Bond distances			
Al–D(1)	1.6(1)	$\text{Yb–Cp}^{\text{cnt}}_{\text{av.}}$	2.29(2)
Al–D(2)	1.6(1)	Yb–C(5)	2.52(2)
Al–C(18)	2.04(2)	Yb–C(4)	2.53(2)
Al–C(17)	2.10(1)	Yb–C(1)	2.61(1)
Yb...Al	2.985(4)	Yb–C(3)	2.62(1)
Yb–D(1)	2.0(1)	Yb–C(2)	2.62(1)
Yb–D(2)	2.1(1)	Yb–C(30)	2.52(2)
C(15)–C(16)	1.36(2)	Yb–C(31)	2.53(1)
C(14)–C(15)	1.36(2)	Yb–C(28)	2.62(2)
C(17)–C(18)	1.46(2)	Yb–C(27)	2.61(1)
C(16)–C(17)	1.50(2)	Yb–C(29)	2.64(1)
C(14)–C(18)	1.54(2)		
Bond angles			
C(18)–Al–C(17)	41.3(6)	αCp(1)Cp(3)	48.5(7)
Cp(1)–Yb–Cp(3)	138.0(5)		

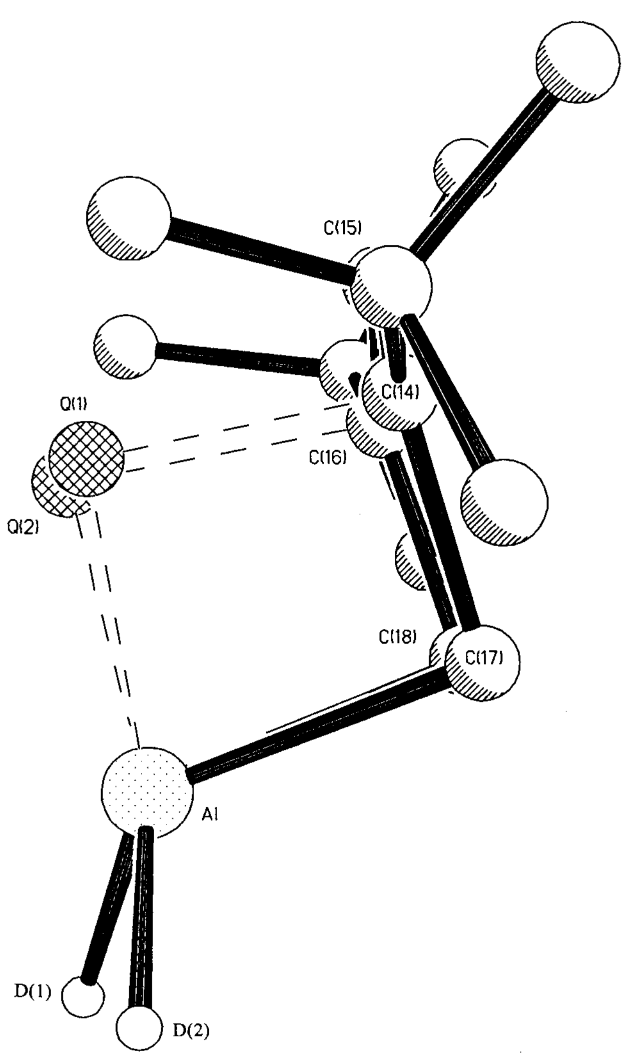


Fig. 3. Fragment of the molecular structure of complex **2** with the electron-density maxima Q(1) and Q(2).

We found that three ligands are co-ordinated to the aluminium atom in complex **2**. Three is rather rare coordination number for complexes with bulky ligands, which protect the central atom from attack by other donor ligands. This condition formally occurs in complex **2**. In the complex the aluminium atom is bound to the ytterbium atom via two deuterium bridges and with one cyclopentadienyl ligand by η^2-bond. The interatomic distance Yb...Al in **2**, 2.96 Å, is much shorter than that in $[Cp_2Yb^{+3}H_2AlH_2 \cdot NEt_3]_2$ (3.26 Å) [23] and it is comparable with the Sm...Al distance in $Cp''_2Sm^{+}2D_2AlD \cdot TMEDA$ (2.92 Å) [4]. The Al–C bond lengths in **2** of 2.04 and 2.10 Å, are shorter than those in the sterically strained structure $(\eta^2\text{-}C_5H_5)_2AlCH_3$ (2.11–2.19 Å) [24] but similar to those in the more shielded molecule $(\eta^2\text{-}C_5H_5)(\eta^{1,5}\text{-}C_5H_5)_2Al$ (2.05–2.09 Å) [25]. The C(14)–C(15) and C(15)–C(16) bond lengths are strong evidence of 'allyl' bonding in this fragment.

The dihedral angle between the D(1)–Al–D(2) and C(17)–Al–C(18) planes in **2** is 122.5°. As a consequence, the aluminium atom is 'bare' from the one side and, although protected by bulky *tert*-butyl groups, can accommodate one more ligand, as is the case of the samarium analogue [4] and aluminium cyclopentadienyl complexes [23,24]. If the aluminium atom in **2** had an additional ligand, it would imply that the ytterbium atom is in the oxidation state + 3. This would remove some ambiguity in the structural description of this compound. However, no atom or group was found near the bisector plane of the D_2Al/AlC_2 angle. On the other hand, differential synthesis indicates electron density maxima Q(1) and Q(2) (ca. 1e $Å^{-3}$), which are 1.8–1.9 Å distant from C(14) and C(15) atoms, 1.9–2.1 Å distant from the aluminium atom, and separated by 1.6 Å from each other (Fig. 3). From chemical and stereochemical considerations, these Q may be due to only hydrogen (deuterium) atom statistically ordered over two positions. However, the refinement of structure **2** under this assumption, the thermal parameter U_{iso} of hypothetical Q atoms tends to zero. Therefore, these maxima are not attributable to hydrogen atoms. The polyhedron formed by Al, C(14), C(16), C(18), and C(17), Q(1) and Q(2) has the dihedral angles $AlC_2/AlQ_2 = 93°$ and $AlC_2/C_2C_2 = 96°$ and above-quoted inter-atomic distances. This geometry does not allow the assignment of Q(1) and Q(2) maxima to any chemical

Table 3
Crystal data and structure refinement for $(\eta^5\text{–}1,3\text{-}^tBu_2C_5H_3)_3Yb$ (1) and $(\eta^5\text{-}1,3\text{-}^tBu_2C_5H_3)_2Yb(\mu\text{-}D)_2Al(\eta^2\text{-}1,3\text{-}^tBu_2C_5H_3)$ (2)

Compound	1	2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.873(2)	10.674(2)
b (Å)	19.810(4)	20.362(4)
c (Å)	17.770(4)	19.083(4)
β (°)	104.88(3)	104.40(3)
V (Å^3)	3699.2(13)	4017.3(14)
Z	4	4
$D_{calc.}$ (mg m^{-3})	1.266	1.233
Wavelength (Å)	0.71073	0.71073
Temperature (K)	293(2)	293(2)
Diffractometer	CAD-4	CAD-4
Collection method	$\theta/2\theta$	$\theta/2\theta$
Radiation type	Mo–K$_\alpha$	Mo–K$_\alpha$
Radiation monochromator	Graphite	β-filter
Absorption coefficient (mm^{-1})	2.551	2.373
Crystal size (mm)	0.32 × 0.25 × 0.20	0.16 × 0.22 × 0.40
Theta range for data collection (°)	2.00–21.96	2.20–22.46
Independent reflections	2184	2182
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0225$, $wR_2 = 0.0556$	$R_1 = 0.0398$, $wR_2 = 0.0968$

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

Atom	*x*	*y*	*z*	U_{eq}
Yb	6673(1)	7125(1)	5713(1)	48(1)
C(1)	5650(8)	8416(5)	5826(5)	44(3)
C(2)	6984(9)	8526(4)	6090(5)	38(2)
C(3)	7580(9)	8408(5)	5493(5)	47(3)
C(4)	6619(10)	8163(5)	4860(6)	55(3)
C(5)	5469(12)	8168(5)	5067(6)	58(3)
C(6)	4637(11)	8685(6)	6203(7)	64(3)
C(7)	4225(27)	9374(10)	5823(12)	136(8)
C(8)	3539(17)	8205(15)	6088(13)	135(10)
C(9)	5142(16)	8796(11)	7059(9)	93(5)
C(10)	8864(10)	8664(6)	5450(6)	62(3)
C(11)	8619(21)	9307(12)	4973(17)	129(9)
C(12)	9717(19)	8818(14)	6259(13)	100(6)
C(13)	9564(16)	8177(10)	5048(11)	89(5)
C(14)	4782(8)	6395(5)	4703(5)	38(2)
C(15)	5458(8)	6657(5)	4197(5)	41(2)
C(16)	6708(8)	6410(5)	4383(5)	38(2)
C(17)	6828(9)	6010(5)	5039(5)	42(2)
C(18)	5639(9)	5994(5)	5239(5)	45(2)
C(19)	3340(8)	6372(5)	4551(5)	48(3)
C(20)	2899(12)	6172(10)	5267(9)	99(5)
C(21)	2894(13)	5819(7)	3907(9)	75(4)
C(22)	2711(11)	7034(8)	4206(9)	79(4)
C(23)	7566(8)	6398(5)	3830(5)	42(3)
C(24)	7416(13)	7026(7)	3322(7)	66(3)
C(25)	7134(13)	5786(7)	3297(7)	64(3)
C(26)	8953(13)	6305(12)	4246(10)	82(4)
C(27)	6831(9)	6481(6)	7226(5)	42(3)
C(28)	7736(10)	6103(6)	7004(6)	54(3)
C(29)	8749(8)	6487(5)	6900(5)	42(2)
C(30)	8384(9)	7145(8)	6989(5)	54(3)
C(31)	7218(10)	7151(8)	7195(5)	57(3)
C(32)	5846(11)	6212(6)	7621(6)	59(3)
C(33)	6541(17)	6086(10)	8484(8)	95(5)
C(34)	4829(15)	6746(9)	7619(11)	99(5)
C(35)	5265(18)	5552(9)	7284(9)	90(5)
C(36)	10058(9)	6228(5)	6901(5)	51(3)
C(37)	10781(14)	6133(9)	7751(7)	88(4)
C(38)	10801(14)	6733(9)	6557(12)	81(4)
C(39)	10024(16)	5557(10)	6460(13)	81(5)

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

species. Otherwise, the maxima would be displaced from the Cp-ring plane toward the bisector plane of the $\mathrm{D_2Al/AlC_2}$ angle.

The location of Q(1) and Q(2) in the region of maximum 'allyl' electron density of C(14) and C(16) atoms suggests another interpretation of the observed phenomenon. The aluminium atom, which has an unsaturated coordination sphere (the maximum coordination number of Al is six), interacts with π-electrons of the allyl group of the Cp ring. Thereby the electron deficiency of aluminium atom is diminished. This effect is apparently responsible for the clear-out 'envelope' geometry of the η^2-bonds ring, where the atom C(15) is displaced from the C(14), C(16), C(17), C(18) plane by 0.16 Å in the direction opposite to 'atoms' Q(1) and Q(2) (bend angle, 13.2°).

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**

Atom	x	y	z	U_{eq}
Yb	742(1)	2388(1)	4617(1)	47(1)
Al	1914(4)	3370(2)	5753(2)	69(1)
C(1)	−1090(12)	3147(7)	3887(7)	56(4)
C(2)	74(13)	3462(7)	3857(8)	55(4)
C(3)	797(14)	3094(7)	3480(8)	65(4)
C(4)	57(16)	2542(8)	3259(9)	71(5)
C(5)	−1060(16)	2573(10)	3496(10)	84(6)
C(6)	−2245(13)	3421(8)	4119(9)	83(5)
C(7)	−3176(17)	3673(11)	3441(11)	146(8)
C(8)	−2899(19)	2903(11)	4444(14)	157(9)
C(9)	−1845(18)	4008(11)	4602(14)	153(9)
C(10)	2001(15)	3318(7)	3259(9)	73(4)
C(11)	1584(19)	3624(12)	2504(13)	156(10)
C(12)	2881(18)	2738(9)	3215(14)	141(8)
C(13)	2719(18)	3852(9)	3729(12)	134(7)
C(14)	2167(15)	3920(10)	7096(8)	93(6)
C(15)	3269(15)	4234(8)	7054(11)	62(5)
C(16)	4070(16)	3906(9)	6722(8)	95(6)
C(17)	3539(15)	3223(8)	6623(8)	88(5)
C(18)	2318(16)	3214(9)	6839(11)	109(6)
C(19)	1039(14)	4145(7)	7365(10)	74(4)
C(20)	241(32)	4585(18)	6934(20)	284(23)
C(21)	1516(21)	4387(18)	8075(16)	221(16)
C(22)	186(23)	3574(11)	7426(16)	182(11)
C(23)	5295(13)	4109(7)	6543(8)	64(4)
C(24)	6139(16)	4445(11)	7176(11)	136(8)
C(25)	5941(20)	3515(9)	6332(13)	148(8)
C(26)	5084(20)	4527(12)	5902(12)	154(9)
C(27)	350(13)	1346(6)	5329(11)	52(4)
C(28)	1651(17)	1453(8)	5549(13)	56(6)
C(29)	2233(13)	1347(6)	4995(10)	56(4)
C(30)	1214(22)	1208(7)	4386(12)	82(7)
C(31)	33(15)	1203(6)	4604(13)	71(5)
C(32)	−555(12)	1256(6)	5839(9)	69(4)
C(33)	−202(23)	641(9)	6262(14)	184(13)
C(34)	−457(19)	1826(9)	6347(13)	139(8)
C(35)	−1969(18)	1169(12)	5405(12)	162(9)
C(36)	3668(13)	1271(6)	5036(9)	71(4)
C(37)	4441(13)	1845(7)	5368(11)	119(7)
C(38)	3900(18)	1115(10)	4300(13)	141(8)
C(39)	4118(14)	673(8)	5504(11)	122(7)
D(1)	222(10)	296(5)	512(10)	47(10)
D(2)	068(10)	288(6)	559(10)	96(10)

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

The determined correctly structure is uncommon but suggests an apparent synthetic route to complex **2** via the direct reaction of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ and $\mathrm{D_2Al}(1,3\text{-}^t\mathrm{Bu_2C_5H_3})$. By this reaction, we obtained red-brown crystals, which are although coloured differently, but structurally identical to the resulted from reaction of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ and $\mathrm{AlD_3}\cdot\mathrm{Et_2O}$ crystals.

Thus, our data are best consistent with the assumption that the Yb atom in complex **2** is in the oxidation state $+2$ and that the Al atom is three-coordinated. However, very short Yb–C distances observed are not typical for Yb($+2$) complexes. This shortening requires additional consideration, if it can not be fully explained by the tendency of the aluminium atom with incomplete electronic shell to fill its unoccupied orbitals by all means (for example, by using an electronic capacity of the $\mathrm{Cp''_2Yb}$ fragment).

3. Experimental

All operations with starting materials and syntheses of compounds were carried out either under vacuum or under an argon atmosphere using standard Schlenk techniques. Solvents were boiled under reflux with $\mathrm{LiAlH_4}$ for 2 h and then distilled under argon. $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ [9], $\mathrm{AlD_3}\cdot\mathrm{Et_2O}$ [26], and $\mathrm{AlD_2Cl}\cdot\mathrm{Et_2O}$ [26] were synthesised by using known procedures.

3.1. Hydrogenation of hexene-1

Hexene-1 was added to the green solution of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ and $\mathrm{Al}^i\mathrm{Bu_3}$ in toluene (Yb: olefin ≥ 100; Yb: Al = 1:5, C_{Yb} ca. 10^{-3} M). The flask with the mixture was attached to filled with hydrogen gas-burettes. The solution absorbed hydrogen during the period of 2 days and gradually turned yellow. After completing of hydrogenation two thirds of the solvent were evaporated. The resulting solution was diluted with hexane and left to stand in a refrigerator. Orange crystals of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_3\mathrm{Yb}$ (**1**) (0.2 g, ca. 45%) precipitated in a few days. Anal. Found, (%): C, 66.50; H, 9.05; Yb, 24.56. Anal. Calc. for $\mathrm{C_{39}H_{63}Yb}$ (%): C, 66.45; H, 9.01; Yb, 24.54.

3.2. Synthesis of $(\eta^5\text{-}1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}(\mu\text{-D})_2\mathrm{Al}(\eta^2\text{-}1,3\text{-}^t\mathrm{Bu_2C_5H_3})$ (2)

3.2.1. Method 1

A total of 0.54 g (5.15 mmol) of $\mathrm{AlD_3}\cdot\mathrm{Et_2O}$ in 175 ml of diethyl ether was added to 3.1 g (5.15 mmol) of

$(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ in 70 ml of diethyl ether. During the mixing and subsequent 5-h stirring of the reagents, the solution retained green colour. Then the ether was slowly removed in vacuum, the solution gradually turned red and the red-orange substance precipitated. Simultaneously slight decomposition of aluminium deuteride or the product of reaction was occurred, that caused the formation of a thin aluminium metal deposit on the flask walls. The precipitate was extracted with 70 ml of benzene. The resulting red solution was filtered to remove the residual precipitate, and the solvent was evaporated to give red crystals (0.57 g, ca. 30%).

3.2.2. Method 2

A total of 0.67 g (3.34 mmol) of $1,3\text{-}^t\mathrm{Bu_2C_5H_3Na}$ was added to 0.47 g (3.34 mmol) of $\mathrm{AlD_2Cl}\cdot\mathrm{Et_2O}$ in 150 ml of diethyl ether. The mixture was stirred for 3 h at room temperature. The NaCl precipitate was filtered off and the filtrate was added to the solution of $(1,3\text{-}^t\mathrm{Bu_2C_5H_3})_2\mathrm{Yb}\cdot\mathrm{OEt_2}$ (2.00 g, 3.34 mmol) in 70 ml of ether. Colour change was not observed. The solvent was removed in vacuum. The residue was extracted with 50 ml of toluene, and 15 ml of 1,4-dioxane was added to the extract. The resulted dingy red solution was concentrated in vacuum to give red crystals of **2** (0.77 g, ca. 45%). Anal. Found (%): C, 63.97; H, 9.01; Al, 3.7; Yb, 23.7. Anal. Calc. for $\mathrm{C_{39}H_{65}AlYb}$ (%): C, 63.82; H, 8.93; Al, 3.68; Yb, 23.57.

3.3. X-ray structure determination

Crystal data for complexes **1** and **2** and data collection parameters are presented in Table 3. Experimental data were processed with the use of the PROFIT procedure [27]. Absorption corrections were not applied. Structures were solved by the heavy-atom method and refined by the full-matrix least-squares procedure with anisotropic thermal parameters for non-hydrogen atoms. Both the obtained by differential synthesis coordinates of hydride hydrogen atoms and calculated from geometric considerations ones of hydrogen atoms from organic ligands were refined isotropically. Structure solution and refinement were carried out by using SHELXTL-81 [28] and SHELXL-93 [29] programs, respectively. Atomic coordinates for complexes **1** and **2** are listed in Tables 4 and 5, respectively.

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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