

Syntheses and crystal structures of two ytterbocene complexes $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ and $[\text{Yb}(\eta\text{-Cp}'')_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$ $(\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3})$

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Received 20 May 2000; accepted 22 July 2000

Abstract

The ytterbocene(III) iodide $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (**1**) ($\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}$) was synthesized by the reaction of two equivalents of $\text{Na}(\text{Cp}'')$ with $\text{YbI}_3(\text{THF})_2$ (obtained from Yb and an excess of $(\text{ICH}_2)_2$ in THF). The heterobimetallic complex $[\text{Yb}(\eta\text{-Cp}'')_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$ (**2**) was prepared from two equivalents of $\text{Li}(\text{Cp}'')$ with YbCl_3 . The crystal structures of **1** and **2** have been determined. The formation of the ytterbium(II) complex $[\text{Yb}(\eta\text{-Cp}'')(\text{OAr})(\text{THF})_x]$ (**3**) ($\text{OAr} = \text{OC}_6\text{H}_2\text{Bu}_5\text{-2,6-Me-4}$) was observed (^1H - and ^{171}Yb -NMR spectroscopy) during the reaction of either $\text{Na}(\text{Cp}'')$ or $[\text{Yb}(\eta\text{-Cp}'')_2(\text{THF})]$ with $[\text{Yb}(\text{OAr})_2(\text{THF})_3]$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ytterbium; Lanthanide(III) halides; Heteroleptic lanthanide(II) complexes

1. Introduction

In the organometallic chemistry of the 4f elements [1], the lanthanocene(III) halides are important precursors for a variety of lanthanocene(III) derivatives such as alkyls, hydrides or amides. These have shown unique characteristics as catalysts in hydrogenation [2], oligomerization [3], polymerization [4], hydroamination [5], hydrosilylation [6], silanolytic chain transfer [7] and hydroboration [8] of α -olefins.

Lanthanocene(III) halides are available as crystalline solvent-free, dimeric compounds $[\{\text{Ln}(\eta\text{-cp})_2\text{X}\}_2]$ (cp is C_5H_5 ($\equiv \text{Cp}$) or a derivative thereof) [9]. Monomeric lanthanocene(III) halide complexes, $[\text{Ln}(\eta\text{-cp})_2\text{X}(\text{THF})]$ are well known. For $\text{Ln} = \text{Eu}$, Sm or Yb , they are invariably prepared by the oxidation of the appropriate lanthanocene(II) complex by a suitable alkyl halide [10]. Heterobimetallic $\text{Ln(III)}\text{--M}$ complexes ($\text{M} = \text{an}$

alkali metal) are accessible from LnCl_3 and two equivalents of the alkali metal (M) cyclopentadienyl in an aprotic donor solvent [11]. Sublimation of the latter generally gave lanthanocene(III) halides $[\{\text{Ln}(\eta\text{-cp})_2\text{X}\}_2]$ [9a,b,c,e], MCl being eliminated.

Homoleptic lanthanide(II) complexes are numerous, but somewhat fewer heteroleptic analogues have been reported [12]. In some instances this was due to their lability with respect to redistribution into homoleptic partners. However, the following heteroleptic lanthanide(II) complexes have been structurally characterized by X-ray diffraction: $[\{\text{Yb}_6(\eta\text{-C}_5\text{Me}_4\text{-}(\text{SiMe}_2\text{Bu}')_6\text{I}_8)\{\text{Li}(\text{THF})_4\}_2]$ [12a], $[\{\text{Yb}(\eta\text{-Cp}^*)(\mu\text{-I})(\text{THF})_2\}_2]$ [12a], $[\{\text{Yb}(\eta\text{-Cp}^*)(\mu\text{-I})(\text{DME})_2\}_2]$ [12a], $[\text{Yb}(\text{Tp})\text{I}(\text{THF})]$ [12b,c], $[\text{Yb}(\text{Tp})\text{I}(3,5\text{-lutidine})_2]$ [12c], $[\{\text{YbI}(\mu\text{-OCPh}_3)(\text{DME})_2\}_2]$ [12d], $[\{\text{YbI}(\mu\text{-OMe})(\text{DME})_2\}_2]$ [12d], $[\{\text{Sm}(\text{NR}_2)(\mu\text{-I})(\text{THF})(\text{DME})\}_2]$ [12e], $[\{\text{Sm}(\eta\text{-Cp}^*)(\mu\text{-I})(\text{THF})_2\}_2]$ [12f], $[\{\text{Yb}(\text{CR}_3)(\mu\text{-I})(\text{OEt}_2)_2\}_2]$ [12g], $[\{\text{Yb}(\text{NR}_2)(\mu\text{-OCBu}_3')_2\}_2]$ [12h,i], $[\text{Yb}(\text{Tp})(\text{NR}_2)]$ [12b], $[\{\text{Yb}(\text{CR}_3)(\mu\text{-OEt})(\text{OEt}_2)_2\}_2]$ [12j,k], $[\{\text{Sm}(\eta\text{-Cp}^*)(\mu\text{-OC}_6\text{H}_2\text{Bu}_5\text{-2,4,6})_2\}_2]$ [12l], $[\text{Yb}(\text{Tp})(\text{CHR}_2)]$ [12b], $[\text{Yb}(\eta\text{-Cp}^*)(\text{SiR}_3)(\text{THF})_2]$ [12m], $[\{\text{Eu}(\eta\text{-Cp}^*)(\mu\text{-C} \equiv \text{CPh})(\text{THF})_2\}_2]$ [12n] and $[\text{Yb}(\eta\text{-C}_5\text{H}_4\text{R})(\text{Tp})]$ [12o] ($\text{R} = \text{SiMe}_3$, $\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Tp} = \text{hydrotris}(3\text{-tert-butyl-5-methylpyrazolyl})\text{borate}$).

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Heteroleptic lanthanide(II) complexes $\text{Ln}(\text{X})(\text{Y})$ are accessible by the following routes (i)–(iii): (i) $\text{LnX}_2 + \text{Y}^-$; (ii) $\text{LnX}_2 + \text{LnY}_2$; or (iii) $\text{LnX}_2 + \text{HY}$.

2. Results and discussion

2.1. Synthesis of $\text{YbI}_3(\text{THF})_2$

The iodide $\text{YbI}_3(\text{THF})_2$ was prepared in a similar manner to its ytterbium(II) analogue [13], except that an excess of $\text{ICH}_2\text{CH}_2\text{I}$ was used (Eq. (1)). Normally in the reactions leading to $\text{YbI}_2(\text{L})_n$ (L being a neutral donor), an excess of the metal is used in order to prevent subsequent $\text{Yb}(\text{II}) \rightarrow \text{Yb}(\text{III})$ oxidation. The title compound was isolated as a pink solid and the quantitative yield indicated a bis-THF adduct, as evident also from the analytical data.

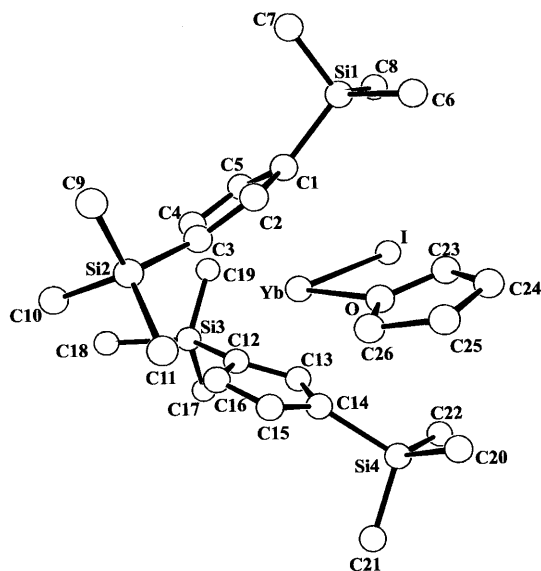


Fig. 1. Molecular structure and atom-labelling scheme for $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (**1**).

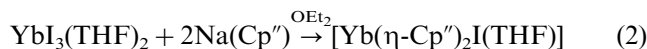
Table 1
Selected bond lengths (Å) and angles (°) for complex **1**^a

Yb–Cent(1)	2.321	Yb–I	2.925(2)
Yb–Cent(2)	2.330	Yb–O	2.303(13)
Cent(1)–Yb–Cent(2)	129.7	Cent(2)–Yb–I	105.7
Cent(1)–Yb–I	110.0	Cent(2)–Yb–O	107.8
Cent(1)–Yb–O	104.3	I–Yb–O	93.3(3)

^a Cent(1) and Cent(2) are the centroids of the C(1)–C(5) and C(12)–C(16) rings, respectively.

2.2. Synthesis of $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (**1**)

The reaction of two equivalents of $\text{Na}(\text{Cp}'')$ with $\text{YbI}_3(\text{THF})_2$ in diethyl ether yielded $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (**1**) as the sole product, Eq. (2). This is surprising, since generally the reaction of $\text{M}(\text{cp})$ with LnX_3 gives as the principal product the heterobimetallic complex $[\text{Ln}(\eta\text{-cp})_2(\mu\text{-X})_2\text{M}(\text{L})_2]$. For example, from YCl_3 and $\text{K}(\text{Cp}^*)$ in THF, $[\text{Y}(\eta\text{-Cp}^*)_2\text{Cl}(\text{THF})]$ was isolated only as a minor product alongside $[\text{Y}(\eta\text{-Cp}^*)_2(\mu\text{-Cl})_2\text{K}(\text{THF})_2]$ [10]. We attribute our finding to steric constraints, the Yb(II) radius being small and the Cp''^- and I^- ligands being sterically demanding. Consistent with this interpretation, we note the recent reports on the monomeric homometallic lanthanocene(III) halide complexes $[\text{Ln}(\eta\text{-C}_5\text{Me}_4\text{Pr}')_2\text{Cl}(\text{THF})]$ (Ln = Y, Sm or Lu) [14] and $[\text{Sm}\{(\eta\text{-C}_5\text{Me}_4)_2\text{SiMe}_2\}\text{I}(\text{THF})]$ [15], obtained by a similar procedure. The conventional pathway to such compounds is via oxidation of the lanthanocene(II) or the metal by an alkyl halide as for the following compounds which were prepared in this manner; $[\text{Sm}(\eta\text{-Cp}^*)_2\text{X}(\text{THF})]$ (X = Cl or I) [10] or $[\text{Yb}(\eta\text{-Cp})_2\text{X}(\text{THF})]$ (X = Cl, Br or I) [16]; while $[\text{Ln}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (Ln = Sm, Y, Er or Lu) or $[\text{Lu}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta\text{-Cp}'')\text{I}(\text{THF})]$ were obtained from the appropriate LnCl_3 , $\text{Na}(\text{Cp}'')$, $\text{Na}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and NaI in THF [17].



2.3. X-ray crystal structure of $[\text{Yb}(\eta\text{-Cp}'')_2\text{I}(\text{THF})]$ (**1**)

The molecular structure and atom numbering scheme for the crystalline complex **1** are shown in Fig. 1. Selected bond lengths and angles are in Table 1. The structure of **1** is typical of a bent metallocene complex with two additional ligands. Thus **1** adopts a distorted tetrahedral geometry about the metal, with angles decreasing in the sequence $\text{Cent}(1)\text{--Yb--Cent}(2) > \text{Cent}(1 \text{ or } 2)\text{--Yb--O} \geq \text{Cent}(1 \text{ or } 2)\text{--Yb--I} > \text{I--Yb--O}$ [Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(12)–C(16) rings, respectively]. The Yb–C bond distances range from 2.59(2) to 2.69(2) Å. The bond length of Yb–I 2.925(2) Å can be compared with the Yb–I 3.013(1) Å for the ytterbium(II) complex $[\text{YbI}_2(\text{THF})_4]$ [12p]. Selected data can be compared with those other monomeric ether adducts of lanthanocene halide complexes, Table 2.

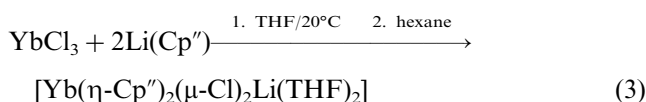
2.4. Synthesis of $[\text{Yb}(\eta\text{-Cp}'')_2(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$ (**2**)

Compound **2** was prepared by the addition of two equivalents of LiCp'' to YbCl_3 in THF, Eq. (3) [19]. Recrystallisation from hexane gave red, X-ray-quality crystals.

Table 2

Selected bond lengths and angles for monomeric yttrium and lanthanocene(III) halide complexes

Complex	Ln ionic radius (Å) [18]	Ln–C _{av} (Å)	Ln–X (Å)	Ln–O (Å)	Cp–Ln–Cp' (°)	X–M–O (°)	Reference
[Y(η-Cp*) ₂ Cl(THF)]	1.015	2.655	2.578(3)	2.410(7)	136.4(4)	90.1(2)	[10]
[Y(η-Cp'') ₂ I(THF)]	1.015	2.654	2.969(1)	2.350(4)	130.4	94.2(1)	[17]
[Sm(η-Cp*) ₂ Cl(THF)]	1.09	2.72	2.737(8)	2.46(2)	135(1)	91.0(5)	[10]
[Sm(η-Cp*) ₂ I(THF)]	1.09	2.725	3.048(2)	2.45(1)	137(1)	89.7(3)	[10]
[Sm(η-Cp'') ₂ I(THF)]	1.09	2.714	3.007(1)	2.411(9)	129.4	94.0(2)	[17]
[Sm{(η-C ₅ Me ₄) ₂ SiMe ₂ }I(THF)]	1.09	2.702	3.0485(4)	2.427(2)	123.3	93.24(5)	[15]
[Er(η-Cp'') ₂ I(THF)]	1.00	2.640	2.931(1)	2.335(7)	130.5	94.1(2)	[17]
[Yb(η-Cp'') ₂ I(THF)]	0.98	2.565	2.9316(7)	2.311(5)	129.8	91.96(12)	[16]
[Yb(η-Cp'') ₂ I(THF)] (1)	0.98	2.62	2.925(2)	2.303(13)	129.7	93.3(3)	This work
[Lu(η-C ₅ Me ₄ Pr') ₂ Cl(THF)]	0.97	2.645	2.516(2)	2.314(5)	137.22(11)	87.17(12)	[14]
[Lu(η-C ₅ H ₄ SiMe ₃)(η-Cp'')I(THF)]	0.97	2.605	2.914(2)	2.310(10)	131.3	93.5(3)	[17]
[Lu(η-Cp'') ₂ I(THF)]	0.97	2.611	2.896(1)	2.307(7)	130.7	93.8(2)	[17]



2.5. X-ray crystal structure of [Yb(η-Cp'')₂(μ-Cl)₂Li(THF)₂] (2)²

The molecular structure and atom numbering scheme for the crystalline complex **2** are shown in Fig. 2. Selected bond lengths and angles are in Table 3 and are available for comparison with those for [Nd(η-Cp'')₂(μ-Cl)₂Li(THF)₂] [9a]. Complex **2** has a distorted tetrahedral geometry about both the ytterbium and lithium atoms, these being bridged by two chloride ligands. The central Yb–Cl(1)–Li–Cl(2) unit is essentially planar. The cyclopentadienyl rings are incorporated in the typical bent metallocene arrangement. The angles about the ytterbium atom decrease in the sequence Cent(1)–Yb–Cent(2) > Cent(1 or 2)–Yb–Cl(2 or 1) > Cent(2 or 1)–Yb–Cl(1 or 2) > Cl(1)–Yb–Cl(2), while those about the lithium atom fall off in the sequence Cl(1 or 2)–Yb–O(1 or 2) > Cl(1 or 2)–Yb–O(2 or 1) ≈ O(1)–Li–O(2) > Cl(1)–Yb–Cl(2) [Cent(1) and Cent(2) are the centroids of C(1)–C(5) and C(12)–C(16) rings, respectively]. The Yb–C bond lengths range from 2.581(2) to 2.677(6) Å.

2.6. Formation of [Yb(η-Cp'')(OAr)(THF)_x] (3) (OAr = OC₆H₂Bu'₂-2,6-Me-4)

The use of ¹⁷¹Yb-NMR spectroscopy in the study of ytterbium(II) complexes [20] has allowed us to monitor the formation of complex **3** via two synthetic pathways.

Initially we observed that treatment of Na(Cp'') with [Yb(OAr)₂(THF)₃] afforded **3** (δ [¹⁷¹Yb] 206.1), but the product was shown to be a mixture containing additionally [Yb(η-Cp'')₂(THF)₂] (δ [¹⁷¹Yb] 172.0) and [Yb(OAr)₂(THF)₃] (δ [¹⁷¹Yb] 237.7) [21]. A further minor product is believed to have been [Na(THF)_x][Yb(η-Cp'')(OAr)₂] (δ [¹⁷¹Yb] 328.0). Synthesis of the complex [K(THF)₂][Yb(η-Cp'')₂(OAr)], by the reaction of two equivalents of K(Cp*) with [Sm(OAr)₂(THF)₃], has been reported [12].

The reaction of excess [Yb(OAr)₂(THF)₃] with [Yb(η-Cp'')₂(THF)] in THF was studied by ¹⁷¹Yb-NMR spectroscopy. The spectra recorded at 304 K showed that [Yb(η-Cp'')₂(THF)₂] [20] was still present

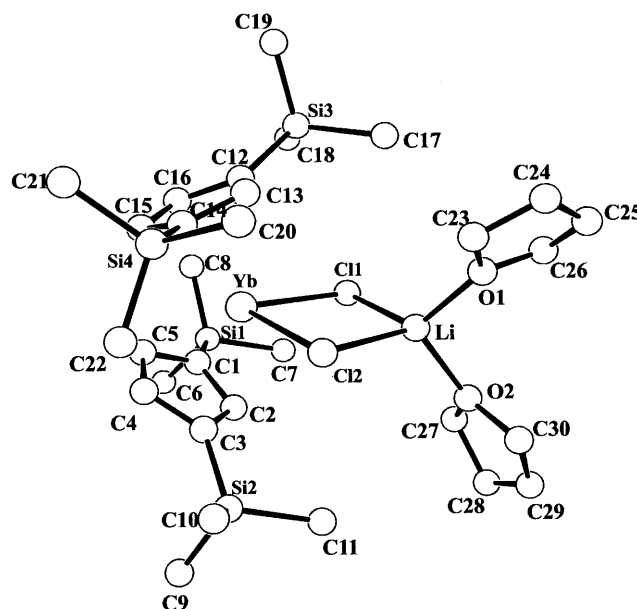


Fig. 2. Molecular structure and atom-labelling scheme [Yb(η-Cp'')₂(μ-Cl)₂Li(THF)₂] (**2**).

² Note added in proof: crystals of **2** have independently been X-ray-characterised in a paper which appeared after the submission of this manuscript. The results are close to those reported here [27].

Table 3

Selected bond lengths (Å) and angles (°) for complex **2**^a

Yb–Cent(1)	2.331	Yb–Cl(1)	2.575(2)
Yb–Cent(2)	2.339	Yb–Cl(2)	2.582(2)
Li–Cl(1)	2.337(14)	Li–O(1)	1.896(15)
Li–Cl(2)	2.330(13)	Li–O(2)	1.979(15)
Cent(1)–Yb–Cent(2)	127.7	Cent(2)–Yb–Cl(1)	110.5
Cent(1)–Yb–Cl(1)	107.3	Cent(2)–Yb–Cl(2)	107.1
Cent(1)–Yb–Cl(2)	110.9	Cl(1)–Yb–Cl(2)	85.15(5)
Cl(1)–Li–Cl(2)	95.7(5)	Cl(1)–Li–O(1)	123.2(7)
Cl(1)–Li–O(2)	104.9(6)	Cl(2)–Li–O(1)	108.3(6)
Cl(2)–Li–O(2)	119.7(6)	O(1)–Li–O(2)	106.0(7)
Yb–Cl(1)–Li	89.1(3)	Yb–Cl(1)–Li	89.9(3)

^a Cent(1) and Cent(2) are the centroids of the C(1)–C(5) and C(12)–C(16) rings, respectively. Some comparisons with average bond lengths (Å) and angles (°) in [Nd(η-Cp'')₂(μ-Cl)₂Li(THF)₂]: Nd–Cl_{av} 2.744, Li–Cl_{av} 2.405, Cl–Nd–Cl' 82.1(3), Cl–Li–Cl' 97.2(9) [9a].

in solution (δ [¹⁷¹Yb] 172.0), along with **3** (δ [¹⁷¹Yb] 206.1) and the unreacted ytterbium aryloxide complex (δ [¹⁷¹Yb] 237.7). Even with an excess of one or other of the two starting components, ligand redistribution from complex **3** still seemed to be taking place, with **3** existing in equilibrium with its parent precursor complexes. Such behaviour has also been reported for [Yb(OAr)I(THF)_x] [12p]. The minor product observed in the above preparative scale experiment was not observed.

3. Experimental

3.1. General procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by published procedures: Na(Cp'') [22], [Yb(OAr)₂(THF)₃] [23] and [Yb(η-Cp'')₂(THF)] [24]. Ytterbium metal and YbCl₃ were donated by Johnson Matthey PLC. Microanalyses were carried out in the micro-analytical department of the University of Sussex. NMR Spectra were recorded using Bruker WM360 or Bruker 500 spectrometers.

3.2. Preparation of YbI₃(THF)₂

Ytterbium metal powder (0.47 g, 2.72 mmol) was added as a solid to a solution of ICH₂CH₂I (3.86 g, 13.70 mmol) in THF (250 ml); the mixture was stirred for 20 h at 20°C, then filtered to give the pink precipitate which was dried under vacuum to afford the free-flowing powder of YbI₃(THF)₂ (1.83 g, 96%). Anal. Found: C, 13.4; H, 2.22. Calc. for C₈H₁₆I₃O₂Yb: C, 13.8; H, 2.31%.

3.3. Preparation of [Yb(η-Cp'')₂I(THF)] (**1**)

YbI₃(THF)₂ (1.83 g, 2.62 mmol) was added as a solid to a suspension of Na(Cp'') (1.22 g, 5.24 mmol) in diethyl ether (200 ml); the mixture was stirred for 20 h at 20°C. The red suspension was filtered and the solvent removed from the filtrate in vacuo to give a brown solid which was extracted into hexane (50 ml). Cooling this solution to –30°C afforded brown X-ray-quality single crystals of **1** (1.53 g, 74%). Anal. Found: C, 39.2; H, 6.39. Calc. for C₂₆H₅₀ISi₄Yb: C, 39.5; H, 6.37%.

3.4. Preparation of [Yb(η-Cp'')₂(μ-Cl)₂Li(THF)₂] (**2**)

Ytterbium(III) chloride (0.93 g, 3.33 mmol) was added to a solution of Li(Cp'') (1.45 g, 6.72 mmol) in THF (250 ml). The resultant mixture was stirred for 20 h at 20°C. The volatiles were removed in vacuo, to give a red solid which was extracted into hexane (100 ml). The extract was concentrated to ca. 50 ml. Cooling to –30°C yielded X-ray quality crystals of **2** (1.76 g, 65%). Anal. Found: C, 44.1; H, 7.17. Calc. for C₃₀H₅₈Cl₂LiO₂Si₄Yb: C, 44.3; H, 7.18%.

3.5. Preparation of [Yb(η-Cp'')(OAr)(THF)_x] (**3**)

Method A. To a solution of [Yb(OAr)₂(THF)₃] (2.36 g, 3.03 mmol) in THF (200 ml), a molar equivalent of Na(Cp'') (0.69 g, 2.97 mmol) was added and the resultant mixture was stirred for 8 h at 20°C. The suspension was filtered and solvent removed from the filtrate in vacuo to yield a red oil.

Method B. [Yb(OAr)₂(THF)₃] (2.53 g, 3.06 mmol) in THF (100 ml) was added to a solution of [Yb(η-Cp'')₂(THF)] (0.41 g, 0.62 mmol) in THF (100 ml). The solution was stirred for 8 h at 20 °C and solvent was removed under reduced pressure to yield a red oil.

[Yb(η-Cp'')(OAr)(THF)_x] (**3**) NMR: ¹H (C₄H₈O–C₆D₅CD₃, 250.13 MHz), δ 0.16 (s, 18H, SiMe₃), 1.32 (s, 18H, Bu'), 1.58 (br s, β-CH₂ (THF)), 2.19 (s, 3H, Me), 3.74 (br s, α-CH₂ (THF)), 6.76 (m, 1H, C₅H₃), 6.84 (m, 2H, C₅H₃), 7.01 (s, 2H, C₆H₂); ¹⁷¹Yb–{¹H} (C₄H₈O–C₆D₅CD₃, 87.51 MHz, 25°C), δ 206.1.

[Yb(η-Cp'')₂(THF)₂] NMR: ¹H (C₄H₈O–C₆D₅CD₃, 250.13 MHz), δ 0.22 (s, 36H, SiMe₃), 1.58 (br s, β-CH₂ (THF)), 3.74 (br s, α-CH₂ (THF)), 6.92 (m, 2H, C₅H₃), 6.98 (m, 4H, C₅H₃); ¹⁷¹Yb–{¹H} (C₄H₈O–C₆D₅CD₃, 87.51 MHz, 25°C), δ 172.0.

[Yb(OAr)₂(THF)₃] NMR: ¹H (C₄H₈O–C₆D₅CD₃, 250.13 MHz), δ 1.35 (s, 36H, Bu'), 1.58 (br s, β-CH₂ (THF)), 2.26 (s, 6H, Me), 3.74 (br s, α-CH₂ (THF)), 6.92 (s, 4H, C₆H₂); ¹⁷¹Yb–{¹H} (C₄H₈O–C₆D₅CD₃, 87.51 MHz, 25°C), δ 237.7.

3.6. X-ray structure determinations for $[Yb(\eta-Cp'')_2I(THF)]$ (**1**) and $[Yb(\eta-Cp'')_2(\mu-Cl)_2Li(THF)_2]$ (**2**)

In both cases unique data were collected, using a crystal sealed in a capillary under argon on an Enraf–Nonius CAD4 diffractometer in the $\theta - 2\theta$ mode with monochromated Mo–K $_{\alpha}$ radiation ($\lambda = 0.71069$ Å). For **1** two standard reflections showed a decrease in intensity of 9.2% and a correction for this was applied. Data were corrected for Lorentz and polarisation effects and also for absorption using DIFABS [25] after isotropic refinement. Reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$ were considered observed. The structure was solved using the heavy atom routines of SHELXS-86 [26]. Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3 U_{eq}$ for the parent atom.

For **1**, non-hydrogen atoms were refined with isotropic thermal parameters by full-matrix least-squares, with Yb and I anisotropic, using programs from the Enraf–Nonius SDP-PLUS package. For **2**, non-hydrogen atoms were refined anisotropically by full-matrix least-squares, except for the C atoms of the THF groups which became non-positive and were therefore refined isotropically. This probably reflects slight conformational disorder in the THF groups. Further details are given in Table 4.

Table 4
Crystal data and structure refinement

	$[Yb(\eta-Cp'')_2I(THF)]$ (1)	$[Yb(\eta-Cp'')_2(\mu-Cl)_2Li(THF)_2]$ (2)
Empirical formula	C ₂₆ H ₅₀ IOSi ₄ Yb	C ₃₀ H ₅₈ Cl ₂ LiO ₂ Si ₄ Yb
Formula weight	791.0	814.0
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_1$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	10.930(2)	12.932(5)
<i>b</i> (Å)	16.244(5)	19.530(5)
<i>c</i> (Å)	20.033(5)	16.739(3)
β (°)		99.22(2)
<i>V</i> (Å ³)	3556.9	4224.3
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ^{−3})	1.48	1.28
μ (Mo–K $_{\alpha}$) (cm ^{−1})	36.3	24.7
<i>F</i> (000)	1572	1668
Crystal size (mm)	0.3 × 0.3 × 0.2	0.8 × 0.4 × 0.4
Total unique reflections	3518	7668
θ_{max} (°)	25	25
Significant reflections	2111	4797
$ F^2 > 3\sigma F^2 $		
Variables	143	321
<i>R</i> , <i>R'</i> ^a	0.047, 0.059	0.031, 0.043

^a $R = \Sigma w(|F_o| - |F_c|) / (\Sigma w|F_o|)$; $R' = [\Sigma w(|F_o| - |F_c|)^2 / (\Sigma w|F_o|^2)]^{1/2}$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144235 for compound **1** and CCDC no. 144236 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Johnson Matthey PLC for gifts of YbCl₃ and ytterbium metal and for a CASE award for S.P., SERC for financial support, Dr G.A. Lawless for recording ¹⁷¹Yb-NMR spectra, and Drs I. López-Solera and A.M. Rodriguez for useful discussion.

References

- [1] For recent leading organolanthanide reviews, see: (a) R. Anwander, W.A. Herrmann, in: Topics in Current Chemistry, vol. 179, Springer-Verlag, Berlin, 1996, pp. 1–32. (b) F.T. Edelmann, in: Topics in Current Chemistry, vol. 179, Springer-Verlag, Berlin, 1996, pp. 247–276. (c) F.T. Edelmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol.4, Pergamon Press, Oxford, 1995, pp. 11–212. (d) F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466. (e) H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865. (f) C.J. Schaverien, Adv. Organomet. Chem. 36 (1994) 283. (g) G.A. Molander, Chemtracts: Org. Chem. 11 (1998) 237.
- [2] (a) P.W. Roesky, U. Denninger, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 4486. (b) G.A. Molander, J.O. Hoberg, J. Org. Chem. 57 (1992) 3266. (c) G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091. (d) W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 105 (1983) 1401.
- [3] (a) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203. (b) W.E. Piers, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 9406. (c) K.H. den Hann, Y. Wielstra, J.H. Teuben, Organometallics 6 (1987) 2053. (d) G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103. (e) H.J. Heeres, J.H. Teuben, Organometallics 10 (1991) 1980.
- [4] (a) P.L. Watson, J. Am. Chem. Soc. 105 (1983) 6491. (b) P.L. Watson, D.C. Roe, J. Am. Chem. Soc. 104 (1982) 6471. (c) G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8111. (d) C.J. Schaverien, Organometallics 13 (1994) 69. (e) W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett. (1990) 74. (f) P.J. Shapiro, E.E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867. (g) R.E. Marsh, W.P. Schaefer, E.B. Caughlin, J.E. Bercaw, Acta Cryst. C48 (1992) 1773. (h) M.A. Giardello, Y. Yamamoto, L. Brard, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 3276. (i) X. Yang, A.M. Seyam, P.-F. Fu, T.J. Marks, Macromolecules 27 (1994) 4625. (j) H. Yasuda, E. Ihara, Macromol. Chem. Phys.

- 196 (1995) 2417. (k) E. Ihara, M. Nodono, H. Yasuda, *Macromol. Chem. Phys.* 197 (1996) 1909.
- [5] (a) M.R. Gagné, C.L. Stern, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 275. (b) Y. Li, T.J. Marks, *J. Am. Chem. Soc.* 118 (1996) 9295. (c) M.A. Giardello, V.P. Conticello, L. Brard, M.R. Gagné, T.J. Marks, *J. Am. Chem. Soc.* 116 (1994) 10241. (d) M.R. Gagné, L. Brard, V.P. Conticello, M.A. Giardello, C.L. Stern, T.J. Marks, *Organometallics* 11 (1992) 2003. (e) Y. Li, T.J. Marks, *Organometallics* 15 (1996) 3770. (f) Y. Li, T.J. Marks, *J. Am. Chem. Soc.* 118 (1996) 707. (g) G.A. Molander, E.D. Dowdy, *J. Org. Chem.* 63 (1998) 8983. (h) V.M. Arredondo, F.E. McDonald, T.J. Marks, *J. Am. Chem. Soc.* 120 (1998) 4871. (i) Y. Li, T.J. Marks, *J. Am. Chem. Soc.* 120 (1998) 1757. (j) P.W. Roesky, C.L. Stern, T.J. Marks, *Organometallics* 16 (1997) 4705. (k) S. Tian, V.M. Arredondo, F.E. McDonald, T.J. Marks, *Organometallics* 18 (1999) 2568. (l) V.M. Arredondo, S. Tian, F.E. McDonald, T.J. Marks, *J. Am. Chem. Soc.* 121 (1999) 3633.
- [6] (a) G.A. Molander, W.H. Retsch, *Organometallics* 14 (1995) 4570. (b) P.-F. Fu, L. Brard, Y. Li, T.J. Marks, *J. Am. Chem. Soc.* 117 (1995) 7157. (c) G.A. Molander, M. Julius, *J. Org. Chem.* 57 (1992) 6347. (d) T. Sakakura, H.-J. Lautenschlager, M. Tanaka, *J. Chem. Soc. Chem. Commun.* (1991) 40.
- [7] (a) P.-F. Fu, T.J. Marks, *J. Am. Chem. Soc.* 117 (1995) 10747. (b) K. Koo, P.-F. Fu, T.J. Marks, *Macromolecules* 32 (1999) 981.
- [8] (a) K.N. Harrison, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 9220. (b) E.A. Bijpost, R. Duchateau, J.H. Teuben, *J. Mol. Catal.* 95 (1995) 121.
- [9] (a) M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, *J. Chem. Soc. Chem. Commun.* (1981) 1190. (b) R.E. Maginn, S. Manastyrskij, M. Dubeck, *J. Am. Chem. Soc.* 85 (1963) 672. (c) J.N. John, M. Tsutsui, *Inorg. Chem.* 20 (1981) 1602. (d) T.J. Marks, G.W. Gryniewicz, *Inorg. Chem.* 15 (1976) 1302. (e) E. Dornberger, R. Klenze, B. Kanellakopulos, *Inorg. Nucl. Chem. Lett.* 14 (1978) 319. (f) M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir, *J. Chem. Soc. Chem. Commun.* (1980) 987. (g) W.J. Evans, R. Dominguez, T.P. Hanusa, *Organometallics* 5 (1986) 1291. (h) H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal, K. Handrick, *Inorg. Chim. Acta* 156 (1989) 119. (i) W. Lamberts, H. Lueken, B. Hassner, *Inorg. Chim. Acta* 134 (1987) 155. (j) H. Lueken, W. Lamberts, P. Hannibal, *Inorg. Chim. Acta* 132 (1987) 111. (k) W. Lamberts, H. Lueken, U. Elsenhans, *Inorg. Chim. Acta* 121 (1986) 81.
- [10] W.J. Evans, J.W. Grate, K.R. Levan, I. Bloom, T.T. Peterson, R.J. Doedens, H. Zhang, J.L. Atwood, *Inorg. Chem.* 25 (1986) 3614.
- [11] (a) M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, *J. Chem. Soc. Chem. Commun.* (1981) 1191. (b) J.L. Atwood, W.E. Hunter, R.D. Rogers, J. Holton, J. McMeeking, R. Pearce, M.F. Lappert, *J. Chem. Soc. Chem. Commun.* (1978) 140. (c) T.D. Tilley, R.A. Andersen, *Inorg. Chem.* 20 (1981) 3267. (d) P.L. Watson, J.F. Whitney, R.L. Harlow, *Inorg. Chem.* 20 (1981) 3271.
- [12] (a) S.P. Constantine, G.M. De Lima, P.B. Hitchcock, J.M. Keates, G.A. Lawless, *Chem. Commun.* (1996) 2421. (b) L. Hasinoff, J. Takats, X.W. Zhang, *J. Am. Chem. Soc.* 116 (1994) 8833. (c) G.H. Maunder, A. Sella, D.A. Tocher, *J. Chem. Soc. Chem. Commun.* (1994) 2689. (d) D.J. Duncalf, P.B. Hitchcock, G.A. Lawless, *Chem. Commun.* (1996) 269. (e) W.J. Evans, D.K. Drummond, H. Zhang, J.L. Atwood, *Inorg. Chem.* 27 (1988) 575. (f) W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter, J.L. Atwood, *J. Am. Chem. Soc.* 107 (1985) 941.
- (g) C. Eaborn, P.B. Hitchcock, K. Izod, J.D. Smith, *J. Am. Chem. Soc.* 116 (1994) 12071. (h) J.R. van den Hende, P.B. Hitchcock, M.F. Lappert, *J. Chem. Soc. Chem. Commun.* (1994) 1413. (i) J.R. van den Hende, P.B. Hitchcock, M.F. Lappert, *J. Chem. Soc. Dalton Trans.* (1995) 2251. (j) P.B. Hitchcock, S.A. Holmes, M.F. Lappert, S. Tian, *J. Chem. Soc. Chem. Commun.* (1994) 2691. (k) J.R. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, *J. Chem. Soc. Dalton Trans.* (1995) 3933. (l) Z. Hou, Y. Zhang, T. Yoshimura, Y. Wakatsuki, *Organometallics* 16 (1997) 2963. (m) M.M. Corradi, A.D. Frankland, P.B. Hitchcock, M.F. Lappert, G.A. Lawless, *Chem. Commun.* (1996) 2323. (n) J.M. Boncella, T.D. Tilley, R.A. Andersen, *J. Chem. Soc. Chem. Commun.* (1984) 710. (o) G.M. Ferrence, R. McDonald, M. Morissette, J. Takats, *J. Organomet. Chem.* 596 (2000) 95. (p) J.R. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, W.-P. Leung, T.C.W. Mak, S. Prashar, *J. Chem. Soc. Dalton Trans.* (1995) 1427. (q) J.R. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, *J. Chem. Soc. Dalton Trans.* (1995) 1435. (r) L.N. Bochkarev, M.N. Kholodilova, S.F. Zhiltsov, T.V. Guseva, M.N. Bochkarev, G. Razuvaev, A. Zh. Obshch. Khim. 56(3) (1986) 723. (s) F.G.N. Cloke, C.I. Dalby, P.B. Hitchcock, H. Karamallakis, G.A. Lawless, *J. Chem. Soc. Chem. Commun.* (1991) 779. (t) S.J. Swamy, H. Schumann, *J. Organomet. Chem.* 334 (1987) 1. (u) D.F. Evans, G.V. Fazakerley, R.F. Phillips, *J. Chem. Soc. Chem. Commun.* (1970) 244.
- [13] (a) P.L. Watson, T.H. Tulip, I. Williams, *Organometallics* 9 (1990) 1999. (b) P. Girard, J.L. Namy, H.B. Kagan, *J. Am. Chem. Soc.* 102 (1980) 2693.
- [14] H. Schumann, M.R. Keitsch, J. Winterfeld, S. Mühle, G.A. Molander, *J. Organomet. Chem.* 559 (1998) 181.
- [15] W.J. Evans, D.A. Cano, M.A. Greci, J.W. Ziller, *Organometallics* 18 (1999) 1381.
- [16] G.B. Deacon, S.C. Harris, G. Meyer, D. Stellfeldt, D.L. Wilkinson, G. Zelesny, *J. Organomet. Chem.* 525 (1996) 247.
- [17] Z. Xie, Z. Liu, F. Xue, Z. Zhang, T.C.W. Mak, *J. Organomet. Chem.* 542 (1997) 285.
- [18] D.R. Lide (Ed.), *C.R.C. Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, 78th ed., Boca Raton, Florida, 1997–98, pp. 4–121.
- [19] M.F. Lappert, A. Singh, *Inorg. Synth.* 27 (1990) 168.
- [20] A.G. Avent, M.A. Edelman, M.F. Lappert, G.A. Lawless, *J. Am. Chem. Soc.* 111 (1989) 3423.
- [21] $[\text{Yb}(\eta\text{-Cp}^{\prime\prime})_2(\text{THF})]$ in THF forms the bis-THF adduct $[\text{Yb}(\eta\text{-Cp}^{\prime\prime})_2(\text{THF})_2]$ in a reversible process similar to that previously observed for $[\text{Sm}(\eta\text{-Cp}^{\prime\prime})_2(\text{THF})]$. P.B. Hitchcock, M.F. Lappert, S. Prashar, *J. Organomet. Chem.* 413 (1991) 79.
- [22] P.B. Hitchcock, J.A.K. Howard, M.F. Lappert, S. Prashar, *J. Organomet. Chem.* 437 (1992) 177.
- [23] G.B. Deacon, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, P.I. MacKinnon, R.H. Newnham, *J. Chem. Soc. Chem. Commun.* (1989) 935.
- [24] P.B. Hitchcock, M.F. Lappert, S. Prashar, J.A.K. Howard, in: W.A. Herrmann (Ed.), *Synthetic Methods of Organometallic Chemistry*, vol. 6, Thieme Verlag, Stuttgart, 1997, pp. 60–62 Chapter 2.
- [25] N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* 39 (1983) 158.
- [26] G.M. Sheldrick, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), *Crystallographic Computing 3*, Oxford University Press, London, 1985, pp. 175–189.
- [27] H.-S. Chan, Q. Yang, T.C.W. Mak, Z. Xie, *J. Organomet. Chem.* 601 (2000) 160.