[$(C_9H_7)YbI(DME)_2$], the First Indenyl Half-Sandwich Complex of Divalent Ytterbium

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The reaction of the naphthalene ytterbium(II) complex (μ-$C_{10}H_8$)[$YbI(DME)_2$]$_2$ (**1**) with indene proved to be a convenient synthetic route to the novel indenyl half-sandwich ytterbium(II) complex [$(C_9H_7)YbI(DME)_2$] (**2**), which is a monomer in the solid state and stable in DME solution, although it rearranges in THF to give the symmetric derivatives [$(C_9H_7)_2Yb(THF)_2$] and [$YbI_2(THF)_2$]. The reaction of **2** with equimolar amounts of C_5H_5Na in DME yields [$(C_5H_5)_2Yb(DME)$] and [$(C_9H_7)_2Yb(DME)$].

Introduction

Although the first tris(indenyl)lanthanide complexes were synthesized more than 30 years ago,[1] the interest in indenyllanthanide compounds, especially concerning the nature of the metal-ligand bond and the characteristics of their molecular structures, still continued in the following decades. In the last years, a new wave of interest in this class of compounds was caused by the numerous reports on the high catalytic activity of analogous complexes of the early d-transition metals in α-olefin polymerization.[2,3]

Despite the attention which Ln^{II} complexes with η^5-bonded aromatic carbocyclic ligands attracted as prospective catalysts for the polymerization of both non-polar and polar monomers,[4–7] the number of indenyllanthanide(II) complexes is still very limited and their catalytic potential only scarcely investigated.

Although the synthesis of the first indenyl complex of divalent ytterbium, [$(C_9H_7)_2Yb(THF)_2$], obtained by ligand exchange between $(C_6F_5)_2Yb$ and indene was described in 1985,[8] the structure of this complex was not determined until 1993.[9] The corresponding DME-coordinated complex [$(C_9H_7)_2Yb(DME)$] was isolated as an unexpected product in 98% yield from the reaction of [$(CH_3)_2C(1$-$C_9H_6)_2$]Na_2 with $YbCl_3$, although the authors were actually intending to synthesize the $(CH_3)_2C$-bridged *ansa*-bis(indenyl) complex [$(CH_3)_2C(1$-$C_9H_6)_2YbCl$].[10] The ethylene-bridged *ansa*-bis(indenyl) complexes *rac*-[$(CH_2)_2(1$-$C_9H_6)_2Yb(THF)_2$] and *rac*-[$(CH_2)_2\{1$-$(4,7$-$(CH_3)_2C_9H_4\}_2$-$Yb(THF)_2$] have been isolated in poor yields starting from $YbCl_3$ and [$(CH_2)_2(1$-$Ind)_2$]Li_2 [Ind = C_9H_6, 4,7-$(CH_3)_2C_9H_4$], and subsequent reduction of the product by sodium metal.[10] The ytterbocenes [$\{1$-$(HSiR_2)$-2-R'-$C_9H_5\}_2Yb(L)_2$] (R = Me, Ph; R′ = H, Me; L = donor ligand), obtained by a silylamine elimination reaction from $HSiR_2$-substituted indenes and $Yb[N(SiMe_3)_2]_2(THF)_2$ as well as their fluxional behaviour in solution have also been described.[11] A structurally characterized bisindenyl complex of divalent samarium, [$(C_9H_7)_2Sm(THF)$], was prepared in high yields by metathesis of $SmI_2(THF)_2$ and C_9H_7K.[12] The Yb^{II} and Sm^{II} derivatives, $(Me_2NCH_2CH_2C_9H_6)_2Ln$ (Ln = Sm, Yb) containing the donor-functionalized 2-dimethylaminoethylindenyl ligands were synthesized by Qian et al.[13]

Halogen-functionalized half-sandwich complexes of Yb^{II} are of essential practical interest since they might serve as suitable precursors for the synthesis of mixed-ligand derivatives. Up to now, only very few compounds of this type such as [$Cp^*YbI(THF)_2$][14] and [$(1,2$-$Me_2NCH_2CH_2)_2$-C_5H_3]$YbI(THF)_2$ [15] are known, probably due to the pronounced tendency of heteroleptic Ln^{II} compounds to equilibrate in solution to the corresponding symmetric derivatives.[16] Since half-sandwich indenyllanthanide(II) halide complexes are still unknown, we tried to synthesize the mixed indenyl iodide complex of divalent ytterbium.

Results and Discussion

Naphthalene complexes of ytterbium[17,18] proved to be suitable precursors for the preparation of various Yb^{II} and Yb^{III} derivatives. In particular, these complexes readily react with CH and EH acidic compounds affording the corresponding derivatives of divalent ytterbium in good yields.[17] Thus, the reaction of (μ-$C_{10}H_8$)[$YbI(DME)_2$]$_2$ (**1**) with indene was proposed as a convenient method for the preparation of indenylytterbium(II) iodide. In contrast to a metathetical pathway, the formation of an alkali halide, which very often hampers the synthesis of organolanthanide complexes, is avoided.

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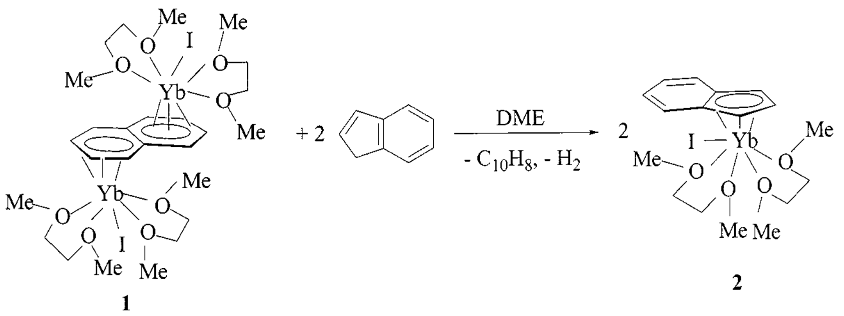

Scheme 1

The reaction of (μ-$C_{10}H_8$)[YbI(DME)$_2$]$_2$ (**1**) with indene in DME occurs at room temperature with progressive dissolution of **1**, evolution of hydrogen and formation of free naphthalene, and is complete within ca. 4 hours. Ruby-red diamagnetic crystals of [C_9H_7YbI(DME)$_2$] (**2**) separate at 0 °C from the filtered and concentrated reddish-brown DME solution with yields of 76% (Scheme 1).

Complex **2** has been characterized by elemental analysis, IR spectroscopy, magnetic measurements and by single crystal X-ray diffraction. It dissolves in DME, THF and pyridine, but is stable only in DME solution. A ligand rearrangement occurs in THF or pyridine yielding equimolar amounts of the symmetric compounds [(C_9H_7)$_2$Yb(THF)$_2$] and YbI$_2$(THF)$_4$ [Equation (1)].

$$2\,(C_9H_7)YbI(DME)_2\,(\mathbf{2}) \rightarrow (C_9H_7)_2Yb(THF)_2 + YbI_2(THF)_2 \qquad (1)$$

Complex **2** is diamagnetic corresponding to the Yb^{2+} oxidation state.[19] The ^{1}H and ^{13}C NMR spectra recorded in [D$_8$]THF or [D$_5$]pyridine show a complex pattern of signals due to simultaneous or exclusive presence of the ligand exchange products.

The single crystal X-ray diffraction study of complex **2** – the crystal and structure refinement data are listed in Table 1 – shows monomeric molecules (Figure 1) with the ytterbium atom coordinated in a distorted octahedral fashion to one iodine atom, the five-membered ring part of the indenyl ligand, and the four oxygen atoms of the two DME molecules. The fact that the distances of the ytterbium atom to three of the carbon atoms [C(1), C(2), and C(3)] forming the coordinating cyclopentadienyl part of the indenyl ligand are shorter than the remaining two Yb–C(4) and Yb–C(9) distances, indicate a certain transition from an η^5- to an η^3-bonding mode. This is also consistent with a ring slippage of 0.27 Å. In contrast to **2**, the bis(indenyl) complexes [(C_9H_7)$_2$Yb(DME)][9] and [(C_9H_7)$_2$Yb(THF)$_2$][10] show a distorted tetrahedral ligand arrangement with slightly shorter Yb–ring centroid and Yb–O distances (Yb–C_g: 2.43/2.45 Å; Yb–O: 2.41/2.38 Å).

To examine the utility of complex **2** for the synthesis of mixed ligand complexes of divalent ytterbium, we reacted **2** in DME with equimolar amounts of sodium cyclopentadienide, which did not result in the formation of the expected [(C_5H_5)Yb(C_9H_7)], but instead gave a mixture of the two ligand-exchanged products [(C_5H_5)$_2$Yb(DME)] and [(C_9H_7)$_2$Yb(DME)]. This result corresponds to that reported by Roesky et al.,[21] who isolated [Li(THF)$_3${μ^2–η^8–C_8H_8)}Sm(C_8H_8)] after the reaction of [(C_8H_8)SmI(THF)$_2$] with (1,4-$R_2C_8H_6$)Li$_2$ [R = 2-(dimethylsilyl)-*N*,*N*-dimethylaniline], formed by ligand rearrangement, instead of a heteroleptic complex. Both examples demonstrate a facile transfer of multi-η-bonded anionic carbocyclic ligands from one lanthanide centre to another, a chemical behaviour which already has been observed with cyclopentadienyl complexes of the lanthanides [Equation (2)].[22–24]

$$2\,(C_9H_7)YbI(DME)_2\,(\mathbf{2}) + 2\,C_5H_5Na \rightarrow (C_9H_7)_2Yb(DME) + (C_5H_5)_2Yb(DME) + 2\,NaI \qquad (2)$$

Table 1. Crystal data and structure refinement for **2**

Empirical formula	$C_{17}H_{27}IO_4Yb$
M$_r$ [g mol^{-1}]	595.33
Crystal system	orthorhombic
Space group	*Pca*2$_1$ (No. 29)
Unit cell dimensions	
a [Å]	14.1633(3)
b [Å]	10.0847(3)
c [Å]	14.1803(3)
$\alpha = \beta = \gamma$ [°]	90
V [Å^3]	2025.41(9)
Z	4
$\rho_{calcd.}$ [g/cm^3]	1.952
μ (Mo-K_α) [mm^{-1}]	6.156
F(000)	1136
Crystal dimensions [mm^3]	0.38 × 0.30 × 0.24
Data collection θ range [°]	2.02–27.50
h	–17/18
k	–13/8
l	–18/18
Collected/unique reflections	14717/4573
R_{int}	0.0637
Reflections with $I > 2\sigma(I)$	3772
Max./min. transmission	0.3631/0.1218
Goodness-of-fit on F^2	1.023
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0363$, $wR_2 = 0.0645$
R indices (all data)	$R_1 = 0.0531$, $wR_2 = 0.0695$
Absolute structure parameter	0.017(11)
Larg. Diff. peak and hole [e/Å^3]	1.040/–1.443

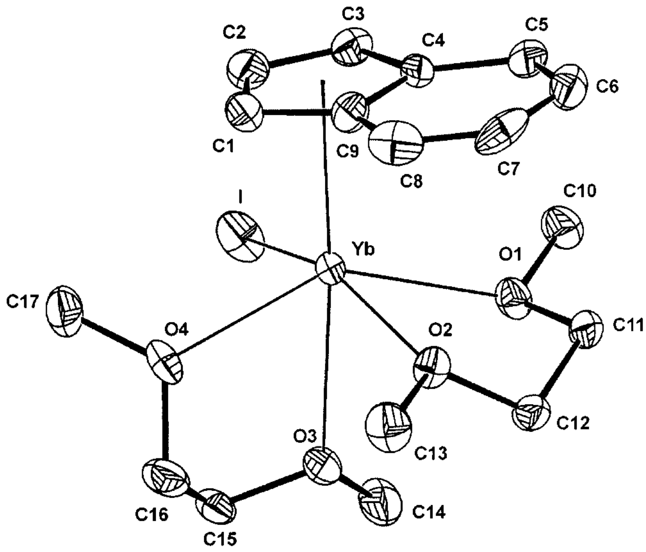

Figure 1. ORTEP drawing[20] and numbering scheme of the molecular structure of **2** (50% probability thermal ellipsoids); all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°) [Cg is defined by the ring atoms C(1), C(2), C(3), C(4), C(9)]: Yb(1)−Cg 2.533(3), Yb−C(1) 2.789(8), Yb−C(2) 2.689(8), Yb−C(3) 2.734(7), Yb−C(4) 2.889(7), Yb−C(9) 2.914(8), Yb−I 3.1423(7), Yb−O(1) 2.431(5), Yb−O(2) 2.437(5), Yb−O(3) 2.573(5), Yb−O(4) 2.472(4); Cg−Yb−I 105.37(9), Cg−Yb−O(1) 107.15(16), Cg−Yb−O(2) 100.66(14), Cg−Yb−O(3) 172.29(16), Cg−Yb−O(4) 105.7(2), O(1)−Yb−O(2) 66.92(17), O(1)−Yb−O(3) 78.48(17), O(1)−Yb−O(4) 143.4(2), O(2)−Yb−O(3) 76.48(17), O(2)−Yb−O(4) 91.54(17), O(3)−Yb−O(4) 67.5(2), O(1)−Yb−I 96.38(14), O(2)−Yb−I 152.41(11), O(3)−Yb−I 78.76(13), O(4)−Yb−I 90.08(12); ring slippage (Å): Cg 0.274

Experimental Section

All experiments were performed in evacuated tubes using standard Schlenk techniques, thus excluding traces of air and water. THF, DME, and toluene were purified by distillation from sodium/benzophenone ketyl. [D_5]pyridine was dried with CaH_2 and condensed in vacuum prior to use. Commercially available indene (Dalhim Ltd.) was used after drying with CaH_2 and subsequent distillation. Compound **1** was prepared from $YbI_2(THF)_2$, $C_{10}H_8$ and Li according to literature methods.[18] IR spectra were recorded as Nujol mulls on a Specord M80 spectrophotometer. NMR spectra were recorded in [D_8]THF or [D_5]pyridine at 298 K using a Bruker DPX 200 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane.

[$(C_9H_7)YbI(DME)_2$] (2): A solution of indene (1.91 g, 16.44 mmol) in DME (10 mL) was slowly added to a suspension of **1** (8.92 g, 8.19 mmol) in DME (50 mL) at room temperature with vigorous stirring. The suspended **1** disappeared within 4 h. The resulting solution was filtered and slowly concentrated in vacuum at room temperature until crystallization started. The concentrate was then cooled to 0 °C and left overnight. The mother liquor was decanted from ruby-red crystals of **2**, which were washed with cold DME and dried in vacuum. Yield: 3.70 g (76%). − IR (Nujol): $\tilde{\nu}$ = 3060 (w), 1340 (s), 1320 (m), 1250 (m), 1200 (m), 1125 (s), 980 (m), 870 (s), 750 (s), 720 (s), 700 cm^{-1} (s). − $C_{17}H_{27}IO_4Yb$ (595.34): calcd. C 34.30, H 4.57, I 21.33, Yb 29.07; found C 33.84, H 4.11, I 20.95, Yb 29.50.

Ligand Exchange of 2 in THF: Compound **2** (0.78 g, 1.31 mmol) was dissolved in THF (15 mL) at room temperature. Within 1 h a pale yellow precipitate formed. The precipitate was separated by filtration, washed with cold THF and dried in vacuo yielding $YbI_2(THF)_2$ (0.33 g, 88%). Hexane (5 mL) was then slowly added to the mother liquor, and the resulting solution was cooled to 0 °C and left overnight. Ruby-red crystals of [$(C_9H_7)_2Yb(THF)_2$] (0.30 g, 83%) were isolated after filtration. − ^1H NMR (200 MHz, [D_8]THF): δ = 5.74 [d, ^3J(H,H) = 3.2 Hz, 2 H, aryl-H^1,H^3], 6.20 [t, ^3J(H,H) = 3.2 Hz, 1 H, aryl-H^2], 6.62−6.67 (m, 2 H, aryl-H^5, H^6), 7.29−7.34 (m, 2 H, aryl-H^7, H^8). − ^{13}C NMR (50.3 MHz, [D_8]THF) δ = 94.0 (aryl-C^1, C^3), 116.6 (aryl-C^2 and aryl-C^5,C^6), 120.4 (aryl-C^4,C^7), 127.1 (aryl-C^8,C^9).

Reaction of 2 with NaCp: A solution of NaC_5H_5 (0.33 g, 3.75 mmol) in DME (15 mL) was slowly added to a solution of **2** (2.26 g, 3.79 mmol) in DME (30 mL) precooled to 0 °C with vigorous stirring. The reaction mixture was allowed to warm up to room temperature, was then stirred for 12 h and filtered. The resulting brown solution was concentrated in vacuum until the growth of green crystals started and was then cooled to 0 °C. 0.4 g (54%) of [$(C_5H_5)_2Yb(DME)$] was isolated. The IR and ^1H NMR spectra as well as the microanalytical data were in agreement with those given previously.[25] Long term cooling or condensation of hexane into the solution decanted from the precipitated [$(C_5H_5)_2Yb(DME)$] resulted in the simultaneous growth of both green and ruby-red crystals. Parts of the red crystals were separated manually and found to be [$(C_9H_7)_2Yb(DME)$]. − ^1H NMR (200 MHz, [D_8]THF): δ = 3.26 (s, 6 H, OCH_3, DME), 3.49 (s, 4 H, CH_2O, DME), 5.73 [d, ^3J(H,H) = 3.3 Hz, 2 H, aryl-H^1,H^3], 6.19 [t, ^3J(H,H) = 3.2 Hz, 1 H, aryl-H^2], 6.62−6.68 (m, 2 H, aryl-H^5,H^6), 7.30−7.35 (m, 2 H, aryl-H^4,H^7). − ^{13}C NMR (50.3 MHz, [D_8]THF): δ = 59.3 (OCH_3, DME), 72.8 (CH_2O, DME), 94.0 (aryl-C^1, C^3), 116.6 (aryl-C^2 and aryl-C^5,C^6), 120.4 (aryl-C^4,C^7), 127.1 (aryl-C^8,C^9).

Crystal Structure Determination: Data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å) with area-detector by use of ω scans at 173 K. The structure was solved by direct methods using SHELXS-97[26] and refined on F^2, using all reflections, with SHELXL-97.[27] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The idealized methyl groups were allowed to rotate about their X−C bond. The absolute structure parameter was determined according to Flack[28] with SHELX-97. SADABS[29] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors are summarized in Table 1. The PLATON program[30] was used for the geometric analysis of the structure.
Crystallographic Data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-164375 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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