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Synthesis of a new asymmetric cyclopentadienyl ligand: application to the preparation of a trivalent samarium complex

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Abstract

A short synthesis of a new asymmetric cyclopentadienyl ligand 2 (Cp'H) substituted by a benzyl ether group in the β position on the side chain of the ring is described. Reaction of its potassium salt with samarium triiodide leads to the isolation of a trivalent samarium complex Cp'_2SmI.

Key words: Samarium; Cyclopentadienyl; Chirality

1. Introduction

The interest in lanthanide cyclopentadienyl complexes in catalysis has increased greatly during recent years. Marks *et al.* [1] showed that pentamethylcyclopentadienyl lanthanide compounds were among the most active catalysts for hydrogenation reactions or ethylene polymerization and later extended the scope of these compounds to catalysis of cycloamination, hydroboration and hydrophosphorylation of olefins [2–4]. Hydrosilylation reaction of olefins as well as dehydrogenative coupling of silanes were also reported [5,6]. Catalytic activity of pentamethylcyclopentadienyl yttrium complexes for hydrogenation and cyclization of dienes was investigated by Molander *et al.* [7,8]. More recently, the first results of asymmetric catalysis by lanthanide compounds were obtained by the use of asymmetric cyclopentadienyl ligands, for hydrogenation and cycloamination reactions [9,10].

Most of the cyclopentadienyl lanthanide complexes that show catalytic activity are coordinated by substituted cyclopentadienyl ligands as these ligands increase the stability and the solubility of the compounds compared to the unsubstituted cyclopentadienyl ligand. In our previous work, we studied the preparation of alkyl samarium complexes starting from divalent bis cyclopentadienyl samarium and found that only bis cyclopentadienyl benzyl complexes were stable in THF at room temperature [11,12]. We did not obtain catalytic activity for hydrogenation reactions using bis cyclopentadienyl samarium complexes [13]. We have now synthesized a new asymmetric cyclopentadienyl ligand and applied it to the preparation of a trivalent samarium complex.

2. Experimental details

The reactions for the preparation of potassium anion and samarium complexes and the preparation of samples for analyses were carried out under an argon atmosphere using Schlenk, vacuum line or glovebox techniques. All solvents used for the preparation of samarium complexes and for NMR studies (THF-d_8 and toluene-d_8) were distilled on sodium benzophenone ketyl and degassed immediately prior to use. SmI_2 was prepared according to the published method [14]. SmI_3 was obtained by reacting SmI_2 and I_2 in THF in the molar ratio 1:0.5 at room temperature.

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Bruker AM 200 and AM 250 NMR spectrometers operating at 200 and 250 MHz for ^1H and 50.4 and 63 MHz for ^{13}C were used for determining spectra. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$, relative to C_7D_7H, 2.09, for spectra in toluene-d_8 or relative to C_4D_7HO, 1.72, for spectra in THF-d_8. Infrared spectra were recorded as Nujol mulls using CsI plates on a Perkin-Elmer 883 spectrometer and are reported in cm^{-1}. GC analyses were performed with a 25-m BP 1 capillary column connected to a computing integrator. Mass spectra (MS) (70 eV) data were determined on a Ribermag R-10 gas chromatograph/mass spectrometer. The FTICR mass spectra were obtained by laser desorption (LD), with an Extrel FTMS 2001-DT instrument equipped with a 3.0 T superconducting magnet and interfaced to a Spectra-Physics Quanta-Ray GCR-11 pulsed Nd : YAG laser operating at the fundamental wavelength (1064 nm) with an estimated output of 20–50 mJ/pulse following a published technique [15]. Carbon and hydrogen analyses were performed on a Perkin-Elmer automatic analyser.

2.1. Preparation of (S)-ethyl-2-benzyloxypropanoate (3)

At room temperature, to a mixture of (*S*)-(−)-ethyl lactate (11.32 ml, 100 mmol) and benzyl-2,2,2-trichloroacetimidate (30.30 g, 120 mmol) in 150 ml of cyclohexane/methylene chloride (2:1), was added a catalytic amount of trifluoromethane sulfonic acid (1.8 ml, 2 mmol). After 2.5 h, the reaction mixture was filtered and the white precipitate of 2,2,2-trichloroacetimide was washed with cyclohexane. The filtrate was washed twice with a saturated solution of $NaHCO_3$ and with a solution of NaCl. The crude product was purified by flash chromatography. A colourless oil was obtained (14.56 g, 70% yield, b.p. = 95°C/0.04 Torr)).

^1H NMR ($CDCl_3$): δ 1.30 (t, 3H, $J = 7.5$ Hz); 1.45 (d, 3H, $J = 7.5$ Hz); 4.05 (q, 1H, $J = 7.5$ Hz); 4.30 (q, 2H, $J = 7.5$ Hz); 4.45–4.70 (dd, 2H); 7.35 (m, 5H) ppm. $[\alpha]^{20} = -80.90°$ (C = 7.15 AcOEt). MS: *m/e* 135 (1.88), 107 (1.98), 102 (28.10), 91 (100.00).

Compound **4** was prepared by the described procedure and has a specific rotation $[\alpha]^{20} = +42.50°$ (C = 5.185, $CHCl_3$), which corresponds to ee = 93% [16].

2.2. Preparation of (S)-2-benzyloxypropyl p-toluenesulfonate (5)

To a solution of alcohol **4** (4.70 g, 28.6 mmol) in 40 ml pyridine was added tosyl chloride (10.90 g, 57.20 mmol) at 0°C. After stirring overnight at room temperature, the reaction mixture was extracted with ether, washed with water and sodium hydroxide. The crude product was obtained as an orange oil (8.33 g, 91% yield).

^1H NMR ($CDCl_3$): δ 1.15 (d, 3H, $J = 6$ Hz); 2.40 (s, 3H); 3.65 (m, 1H); 4.00 (d, 2H, $J = 7$ Hz); 4.50 (m, 2H); 7.20–7.40 and 7.70 (m, 9H) ppm. $[\alpha]^{20} = -2.80°$ (C = 4.425 MeOH). M/S: *m/e* 279 (1.12), 179 (8.63), 155 (8.02), 107 (35.38), 91 (100.00), 65 (11.65). HRMS: *m/e* M^+ Calc: 320.1082 a.m.u. Found: 320.1061 amu.

2.3. Preparation of the mixture of 1-(S)-(2-benzyloxypropyl) cyclopentadiene and 2-(S)-(2-benzyloxy-propyl) cyclopentadiene (2)

A 0.4 M solution of NaCp (55 ml, 21.7 mmol) in THF was added dropwise to a solution of tosylate **5** (5.8 g, 18 mmol) in 50 ml THF at 0°C under argon. The reaction mixture was stirred overnight at room temperature. After extraction by Et_2O and flash chromatography, **2** was obtained as a yellow oil (3.23 g, 84% yield). b.p. = 170°C/0.01 Torr.

^1H NMR ($CDCl_3$): δ 1.15 (d, 3H, $J = 6$ Hz); 2.55–2.70 (m, 2H); 2.95 (d, 2H, $J = 6$ Hz); 3.55–3.70 (m, 1H); 4.47 (d, 2H, $J = 7$ Hz); 6.00–6.40 (m, 3H); 7.20–7.40 (m, 5H) ppm.

^1H NMR (C_6D_6): δ [1.10 (d, $J = 6$ Hz), 1.20 (d, $J = 6$ Hz), 3H]; 2.40–2.70 (m, 2H); 2.80 (s, 2H); [3.50 (q, $J = 6$ Hz), 3.60 (q, $J = 6$ Hz), 1H]; 4.30–4.45 (m, 2H); 6.00–6.55 (m, 3H); 7.05–7.45 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 20.00 ($2 \times CH_3$); 36.90 (CH_2 isomer 1); 37.70 (CH_2 isomer 2); 41.30 (CH_2 of C_5 ring isomer 1); 44.00 (CH_2 of C_5 ring, isomer 2); 70.00 ($2 \times CH_2$); 74.60 (CH–O, isomer 1); 75.00 (CH–O, isomer 2); 127.3, 127.5, 128.50 and 128.85 (Ph); 131.16, 132.32, 133.51 and 135.08 ($2 \times$ CH of C_5 ring) ppm. $[\alpha]^{20} = +25.85°$ (C = 3.27 MeOH). MS: *m/e* 214 (M^+, 2.10), 172 (1.61), 171 (1.94), 170 (2.26), 169 (0.97), 108 (18.23), 91 (100), 79 (88.71), 65 (17.42). HRMS: Calc. 214.136. Found: 214.143. IR: 3064, 3032, 2971, 2866, 1604, 1495, 1452, 1373, 1342, 1306, 1241, 1205, 1129, 1069, 1027, 949, 898, 809, 735, 696, 676, 585, 456, 374 cm^{-1}. Anal: Found: C 84.13; H 8.42%. $C_{15}H_{18}O$ calc.: C 84.07; H 8.46%.

2.4. Preparation of (S)-(2-benzyloxypropyl) cyclopentadienyl potassium (7)

A solution of **2** (0.462 g, 2.37 mmol) in 20 ml THF was added to a suspension of KH (0.095 g, 2.37 mmol) in 10 ml THF at −20°C. After 0.5 h, the mixture was warmed to room temperature, filtrated and THF was removed under reduced pressure to give a brown oil. After addition of hexane, a pale yellow powder was obtained (0.385 g, 70% yield).

^1H NMR (THF-d_8): δ 1.20 (d, 3H, $J = 7$ Hz); 2.50–2.80 (m, 2H); 3.51 (m, 1H); 4.50 (m, 2H); 5.40 (m, 4H), 7.25 (m, 5H); ppm. ^{13}C NMR (THF-d_8): δ 20.45 (CH_3); 36.81 (CH_2–Cp); 63.19 (CH_2–Ph); 77.51 (CH–O); 104.13 and 105.74 (C_5H_4); 115.40 (C_5H_4); 127.55,

127.85 and 128.77 (Ph) ppm. IR: 1193, 1145, 1048, 940, 794, 760, 737, 700, 570, 490, 440, 315 cm^{-1}. MS: LD m/z 291.01 (M + K, 8.67). Anal: Found: C 69.97, H 7.16 $C_{15}H_{17}OK$ calc.: C 71.43; H. 6.75%.

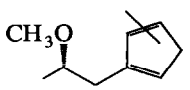
2.5. Synthesis of bis [(S)-(2-benzyloxypropyl) cyclopentadienyl] samarium iodide (6)

To a suspension of $SmI_3(THF)$ (0.337 g, 0.5 mmol) in 10 ml THF was added a solution of Cp'K (0.252 g, 1 mmol) in 5 ml THF. At the end of the addition the solution had turned yellow with a white precipitate of KI which was filtrated (0.136 g). The solution was concentrated under vacuum, and the orange oil extracted with toluene. After filtration and evaporation of toluene, the oil was precipitated by addition of hexane to give a pale yellow powder (0.228 g, 65% yield).

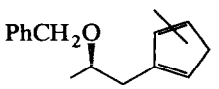
^1H NMR (toluene-d_8 25°C): δ 0.61 (br s, 3H, CH_3); 1.71 (d, 1H, $J = 17$ Hz); 2.11 (d, 1H, $J = 17$ Hz); 3.89 (m, 1H); 6.12 (m, 2H); 6.24 (br s, 1H); 7.01–7.08 (m, 5H); 7.76 (br s, 1H); 10.11 (br s, 1H); 13.11 (br s, 1H). (35°C): 0.64 (br s, 3H, CH_3); 1.83 (d, 1H, $J = 16$ Hz); 2.06 (d, 1H, $J = 16$ Hz); 3.86 (m, 1H); 6.15 (2H); 6.66 (s, 1H, C_5H_4); 6.86–7.15 (m, 5H, Ph); 8.06 (s, 1H, C_5H_4); 10.33 (s, 1H, C_5H_4); 13.36 (s, 1H, C_5H_4) ppm. IR: 1204; 1035; 1020; 917; 840; 792; 772; 742; 697; 625; 452; 380; 333 cm^{-1}. MS (FW for Sm 154): LD/positive m/z 580 (56.0) Cp'_2Sm; 494 (21.9) Cp'SmI; 489 (19.3) Cp'(Cp'–CH_2Ph)Sm; 367 (11.0) Cp'Sm; 281 (37.3) SmI. LD/negative m/z 616 (92.0) Cp'(Cp'–CH_2Ph)SmI; 525 (26.7) (Cp'–CH_2Ph)$_2$SmI; 398 (46.3) (Cp'–CH_2Ph)$_2$Sm. Anal: Found: C 52.73, H. 5.09 $C_{30}H_{34}O_2SmI$ calc.: C 51.2; H 4.84.

3. Results

With the aim of preparing asymmetric samarium complexes, we were interested in the chiral cyclopentadiene **1** with a pendant ether group described by Quian [17]. This ligand could allow us to study the influence of the coordinating group on the stability of the complexes and to prepare asymmetric complexes with the asymmetric centre close to the metal if intramolecular coordination occurs. We first tried to prepare the compound **1**, following the reported procedure, which gave poor yields in our hands due to a very low yield in the methylation step. We then planned to synthesize the analogous cyclopentadiene **2** in which a benzyl group replaces the methyl group.



(1)



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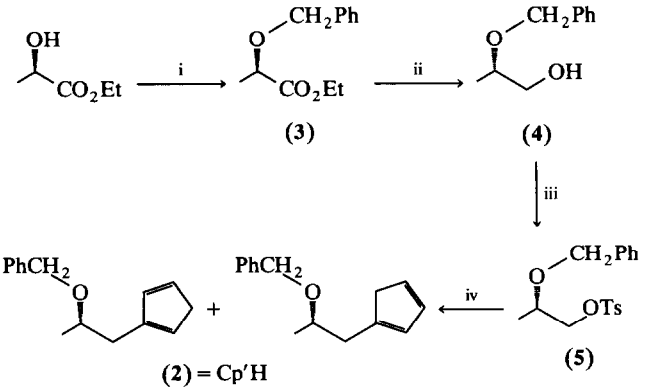

Scheme 1. (i) Benzyl trichloroacetimidate, CF_3SO_3H cat, C_6H_{12} / CH_2Cl_2 (2:1), 70% yield, 97% ee; (ii) $LiAlH_4$, Et_2O, 0°C to room temperature, 84% yield, 93% ee; (iii) TsCl, pyridine, 0°C, 91% yield; (iv) NaCp, THF, 84% yield.

The new asymmetric cyclopentadiene **2** was synthesized in four steps starting from (*S*)-(−) ethyl lactate following Scheme 1. Several methods were tried for the benzylation of ethyl lactate and the use of benzyl trichloroacetimidate was found to give the best yield of **3** (70%) [18]. A NMR study with $Eu(fod)_3$ indicated that no racemization occurred during formation of **3**. The following reactions are the same as for the preparation of compound **1**: reduction of ester **3** by $LiAlH_4$ in alcohol **4**, which was transformed in the tosylate **5**. Compound **5** reacted with sodium cyclopentadienyl yielding the substituted cyclopentadiene **2**. The specific rotation of **4**, compared to that given in the literature indicates 93% enantiomeric purity for this alcohol [16]. Tosylate **5** could not be crystallized and its enantiomeric purity could not be measured by NMR or spectrometric methods. The cyclopentadiene **2** was obtained as an equimolar mixture of the two isomers with the substituent on the double bond, as shown by ^1H and ^{13}C NMR spectra; this compares with results previously described for other substituted cyclopentadienes [19]. We have not yet evaluated the enantiomeric purity of **2**, by chiral HPLC or GC analysis, the problem being complicated by the presence of two isomers. Nevertheless, the two last steps of the preparation are supposed to occur without racemization. The new asymmetric cyclopentadiene Cp'H **2** was synthesized in 45% overall yield.

We intended first to prepare a divalent samarium compound Cp'_2Sm by an exchange reaction of an alkali-metal salt of the cyclopentadiene **2** and SmI_2, following the same procedure described for $Cp_2Sm(THF)_2$ or $Cp^*_2Sm(THF)_2$ (Cp^* = pentamethylcyclopentadienyl) [20,21]. A solution of Cp'H in THF was added to an equimolar amount of NaH at room temperature. A beige solution was obtained, which was then added to a solution of SmI_2 in THF in the

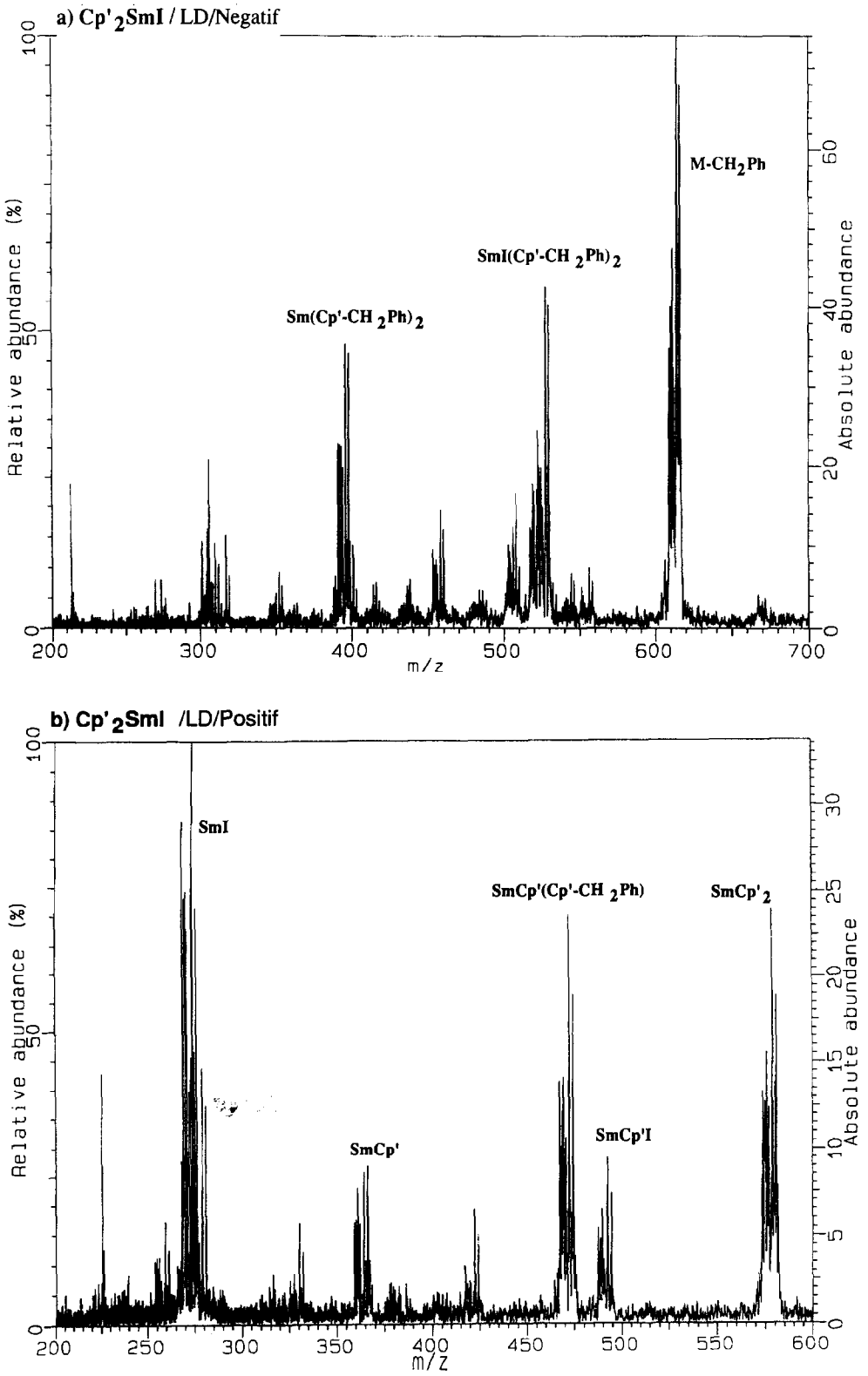
a) Cp'2SmI / LD/Negatif
Relative abundance (%)
Absolute abundance
m/z
M-CH2Ph
SmI(Cp'-CH 2Ph)2
Sm(Cp'-CH 2Ph)2
b) Cp'2SmI /LD/Positif
SmI
SmCp'(Cp'-CH 2Ph)
SmCp'2
SmCp'
SmCp'I

Fig. 1.

assumed stoichiometry 2:1. The solution turned from blue to green-blue. After evaporation of the solution, extraction of the residue by toluene and precipitation with hexane, a small amount of a light yellow powder could be isolated. This product was identified by various analyses (^{1}H NMR, FTICR/MS spectra, elemental analysis) as the trivalent compound **6** of formula Cp'_2SmI and not as the expected divalent samarium compound. An oxidative addition process by Cp'H, present due to the formation of Cp'Na in low yield can explain the presence of the trivalent compound, as well as redistribution reactions of ligands.

In order to confirm the structure of **6** and to be able to isolate this compound in good yield, we studied the reaction of the potassium anion of the ligand **2** with SmI_3. The potassium salt **7** was prepared by reacting **2** with potassium hydride in THF, and after evaporation of the THF and treatment with hexane, was isolated as a brown yellow powder in 70% yield and identified by NMR and FTICR/MS. When a THF solution of **7** was added to a suspension of SmI_3 in THF, in the ratio 2:1, the solution turned light brown and the yellow precipitate was replaced by a white precipitate. After filtration, evaporation of THF, extraction with toluene and treatment with hexane, a light yellow powder was obtained, identified as Cp'_2SmI by its FTICR/MS and its ^{1}H NMR spectra.

$$Cp'H + KH \xrightarrow{THF} Cp'K + 1/2\ H_2$$
(7)

$$2\ Cp'K + SmI_3 \xrightarrow{THF} Cp'_2SmI + 2\ KI$$
(6)

Positive and negative ion LD/FTICR mass spectra were obtained for compound **6** and are presented in Fig. 1. Different degrees of fragmentation are observed and the patterns are in agreement with the elemental composition of the complex. Although there is no molecular peak, the fragments $M-CH_2Ph$ and $SmI(Cp'-CH_2Ph)_2$ in the negative ion LD mass spectrum (Fig. 1(a)) confirm the presence of two Cp' ligands and an iodine around the samarium atom. The positive ion LD mass spectrum (Fig. 1(b)) shows the loss of one iodine and different degrees of fragmentation of the Cp' ligand; a very intense peak corresponding to a samarium-iodine fragment indicates the presence of iodine in the complex. There is no evidence of the formation of a dimeric species as no peak of mass superior to that of the monomer is observed.

The ^{1}H NMR spectrum in toluene-d_8 at room temperature presents broad lines which indicates a fluxional behaviour in solution. When the temperature is increased, four signals of equal intensity, corresponding to the protons of the cyclopentadienyl rings, appear at low field, one doublet for the methyl groups and one signal for the CH_2 protons of the benzyl group. Two signals are observed for the two protons of the CH_2 groups adjacent to the chiral group as they are non-equivalent. The ^{1}H NMR pattern at high temperature indicates that the two cyclopentadienyl ligands are magnetically equivalent. Only one diastereomer is observed, either the minor isomer is in too small amount, or it has been separated during the precipitation of the complex, or the two isomers have the same ^{1}H NMR spectrum.

Various lanthanide compounds with amino or ether groups in the β position on the lateral chain of cyclopentadienyl groups have been prepared [22–27]. In the complex $(Me_2NCH_2CH_2C_5H_4)_2NdCl$ the two nitrogen atoms are coordinated to the neodymium and for other divalent and trivalent derivatives with two ether cyclopentadienyl ligands, ($MeOCH_2CH_2C_5H_4$ = Cp''H), X-ray structures also indicate that the two oxygen atoms are coordinated to the lanthanide atoms. X-Ray crystallographic analyses for complexes Cp''_2LnI (Ln = Yb, Sm) showed that the metal is five-coordinated by two cyclopentadienyl rings, two oxygen and the halogen displaying a trigonal bipyramidal geometry [26].

The dynamic process observed in solution for **6** has not been mentioned so far for lanthanide complexes coordinated by ether or amino cyclopentadienyl ligands. If we assume that compound **6** presents a solid state structure analogous to that of Cp''_2SmI (represented in Fig. 2), the dynamic process displayed by **6** can be explained either by a rapid exchange between coordinated and uncoordinated oxygen on the samarium, or by a rapid interconversion of five-coordinated structures (*e. g.* trigonal bipyramidal and square pyramidal) on the NMR time scale. Equilibrium between a monomeric and a dimeric form cannot be discarded; the X-ray structure of Cp''_2LaCl indicates a dimer but Cp''_2YbI and Cp''_2SmI are monomeric as well as $(C_5Me_5)_2SmI(THF)$ [23,26,28]. We are currently trying to obtain single crystals of **6** suitable for X-ray crystallographic analysis to confirm the structure.

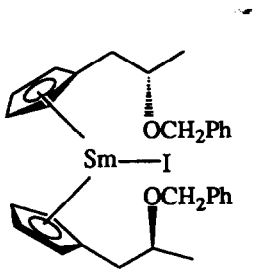

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Fig. 2.

A short and easy synthesis of a new asymmetric cyclopentadienyl ligand Cp'H and of its potassium salt has been realized. A trivalent asymmetric samarium complex Cp'_2SmI has been isolated in good yield from SmI_3 and characterized. The mechanism of formation of this compound from SmI_2 is under investigation. We intend to examine the activity of Cp'_2SmI in various reactions catalysed by lanthanides [29–32].

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