

## Organometallic compounds of the lanthanides

### XXXIX \*. Cyclopentadienylytterbium(II) chlorides, $C_5R_5YbCl(L)$

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#### Abstract

$C_5H_5YbCl(THF)_2$ ,  $C_5H_5YbCl(dme)$  and the corresponding pentamethylcyclopentadienyl derivatives are prepared by the reaction of  $YbCl_2$  with  $NaC_5H_5$  or  $NaC_5Me_5$  in tetrahydrofuran or dimethoxyethane. The compounds are characterized by NMR and mass spectroscopy.

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#### Introduction

In recent years, interest in the use of various divalent lanthanide compounds in organic synthesis has increased considerably [2-7]. This coupled with the reports of Bercaw and co-workers [8] on the tendency of the pentamethylcyclopentadienyl ligand to confer stability, solubility and crystallinity to different organometallic compounds, led to active investigations in the field of divalent lanthanide organometallics, resulting in the preparation of a number of organometallic derivatives of Eu, Yb and Sm, which have readily accessible divalent states under normal solution conditions. Almost all of these compounds have the general formula  $Cp_2Ln(B)_n$  with Cp = cyclopentadienyl [9,10], mono-substituted cyclopentadienyl [11,12] or pentamethylcyclopentadienyl [13-16] and B a coordinating ligand like THF [9,13],  $Et_2O$  [14], pyridine [15],  $Me_2PCH_2PMe_2$  [17] or DME [18].

Very little attention has been paid to prepare the  $Ln^{II}$ -analogues of very important  $Ln^{III}$  complexes, the dicyclopentadienyllanthanide chlorides, which are

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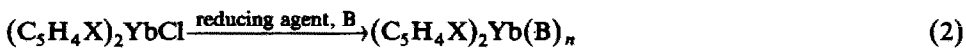
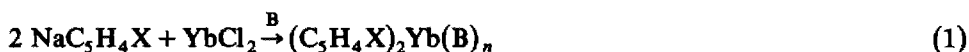
\* For part XXXVIII see ref. 1.

precursors for different lanthanide alkyls and hydrides [19–22] having useful reaction sites. Such analogues of divalent lanthanides with a reactive site for further modification of the environment around  $\text{Ln}^{\text{II}}$  by reaction with lithium alkyls or aryls can be expected to exhibit interesting chemistry. Such compounds may be subjected to hydrogenolysis to form divalent lanthanide hydrides, which are expected to have catalytic properties. Some recent attempts [23–27] demonstrate the reactivities of divalent lanthanide organometallics.

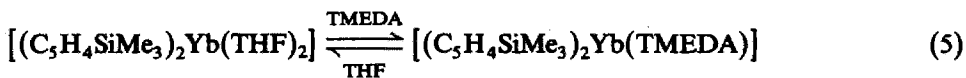
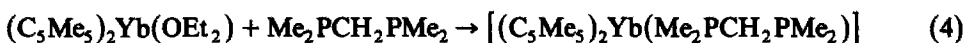
Considering these aspects we have begun attempts to synthesize cyclopentadienylytterbium(II) chloride. While this work was in progress Evans et al. [28], have reported the synthesis and X-ray structural analysis of a  $\text{Sm}^{\text{II}}$  analogue  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-I})(\text{THF})_2]_2$ . This is the first structurally characterized divalent organolanthanide compound with an active site. We report here the synthesis and characterization of a series of new  $\text{Yb}^{\text{II}}$  compounds of this type.

## Results and discussion

Organometallic compounds of  $\text{Yb}^{\text{II}}$  are larger in number compared to those of  $\text{Sm}^{\text{II}}$ . This is mainly because of the insolubility of the previously reported two  $\text{Sm}^{\text{II}}$  compounds:  $[(\text{C}_5\text{H}_5)_2\text{Sm}(\text{THF})_n]_y$  [10] and  $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Sm}(\text{THF})_n]_y$  [29]. Since the analogous compounds of  $\text{Yb}^{\text{II}}$  are soluble, many of the derivatives have been prepared either by simple ionic metathesis reactions (eq. 1), or by the reduction of trivalent ytterbium complexes with different reducing agents (eq. 2):



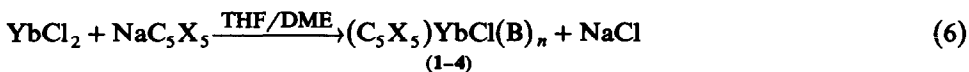
The facile coordination chemistry of  $\text{Yb}^{\text{II}}$  made it also possible to substitute one type of coordinating groups with others (eq. 3) [15], (eq. 4) [17], (eq. 5) [12]:



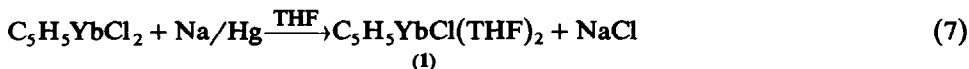
Furthermore  $\text{Yb}^{\text{II}}$  complexes are observed in non-coordinating solvents like benzene or toluene to lose coordinating solvent molecules to give unsaturated insoluble complexes [18,30].

Three properties of these compounds: the solubility of the  $\text{Yb}^{\text{II}}$  complexes, the reversible formation of coordinatively saturated and unsaturated environments and the suitable redox potential for the  $\text{Yb}^{\text{III}}\text{-Yb}^{\text{II}}$  couple ( $-1.04$  V), suggest the applicability of  $\text{Yb}^{\text{II}}$  compounds in catalysis.

The compounds described in the present communication are thus prepared by both of the ways as in eqs. 6 and 7:



(X = H, B = THF,  $n = 2$  (1); X = H, B = DME,  $n = 1$  (2);  
X = CH<sub>3</sub>, B = THF,  $n = 2$  (3); X = CH<sub>3</sub>, B = DME,  $n = 1$  (4))



The compounds 1 and 3 are soluble in THF but insoluble in toluene and alkanes. The analogous Sm<sup>II</sup> compound [(C<sub>5</sub>Me<sub>5</sub>)Sm(μ-I)(THF)<sub>2</sub>]<sub>2</sub> [28] was also reported to be insoluble in toluene. It is very interesting to notice the difference in solubilities of THF coordinated (1 and 3) and DME coordinated (2 and 4) compounds. 2 and 4 are fairly soluble in toluene and benzene. The <sup>1</sup>H NMR spectra of these two compounds are recorded in benzene-*d*<sub>6</sub> solutions. This indicates that the coordinating molecules also play an important role in solubilities of the organometallic compounds and hence their reaction chemistry. 1 was found to be more soluble in THF than the Yb<sup>III</sup> compound C<sub>5</sub>H<sub>5</sub>YbCl<sub>2</sub>(THF)<sub>3</sub>.

From the above formulations of the compounds based on elemental analyses and <sup>1</sup>H NMR spectra, the ytterbium ions may be assumed to be in a tetrahedral environment surrounded by the cyclopentadienyl group, the chloride ion and two oxygen atoms of the coordinating molecules.

From the similarity in solubility of compounds 1 and 3 with structurally characterized Sm<sup>II</sup> analogue, these two may also be assumed to possess a dimeric structure with two chloride ions bridging two units. The DME coordinated complexes 2 and 4 being soluble in aromatic solvents may be expected to have different geometry. The structure of these complexes may be similar to that of [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb(DME)] [18]. Crystals of 3 and 4 suitable for X-ray diffraction studies have been grown by diffusing pentane into THF or DME solutions. These structural studies are in progress.

### <sup>1</sup>H NMR spectral studies

The <sup>1</sup>H NMR spectral data of the complexes are given in Table 1. As expected the compounds 1, 3 and 2, 4 exhibit the ring protons and methyl protons around 5.6

Table 1

<sup>1</sup>H NMR spectral data of cyclopentadienylytterbium(II) derivatives in ppm

Compound		δ(C <sub>5</sub> H <sub>5</sub> )/(C <sub>5</sub> Me <sub>5</sub> )	δ(THF)	δ(DME)
NaC <sub>5</sub> H <sub>5</sub> <sup>a</sup>		5.51	—	—
(C <sub>5</sub> H <sub>5</sub> )YbCl(THF) <sub>2</sub> <sup>a</sup>	1	5.60	3.50, 1.63	—
(C <sub>5</sub> H <sub>5</sub> )YbCl(DME) <sup>b</sup>	2	6.29	—	3.11, 3.01
NaC <sub>5</sub> Me <sub>5</sub> <sup>a</sup>		1.91	—	—
(C <sub>5</sub> Me <sub>5</sub> )YbCl(THF) <sub>2</sub> <sup>a</sup>	3	1.80	3.58, 1.58	—
(C <sub>5</sub> Me <sub>5</sub> )YbCl(DME) <sup>b,c</sup>	4	1.77	—	1.85, 1.68

<sup>a</sup> In THF-*d*<sub>8</sub>. <sup>b</sup> In benzene-*d*<sub>6</sub>. <sup>c</sup> 270 MHz.

and 1.80 ppm, respectively. The  $\alpha$ - and  $\beta$ -proton signals of coordinated THF molecules occur at 3.5 and 1.63 ppm respectively. In **2** the methyl and methylene proton signals of the coordinated DME have not altered much while in **4** they resonate at very high field compared to free DME. The presence of coordinated DME was further confirmed from the  $^1\text{H}$  NMR spectrum of a hydrolysed  $\text{C}_6\text{D}_6$  solution of **4** with few drops of water, which exhibited the ring methyl proton signals at 1.80 ppm and free DME protons at 3.41 and 3.2 ppm as expected.

### Mass-spectral study of $(\text{C}_5\text{Me}_5)\text{YbCl}(\text{DME})$ (**4**)

Complete mass spectral investigations of only a very few organolanthanides have been reported [31–33]. In order to get an idea about the molecularity of compound **4**, the mass-spectrum has been recorded and the fragmentation of the molecules under electron impact is discussed.

The spectrum displays features characteristic of pentamethylcyclopentadienyl organometallic compounds. In the case of decamethylferrocene the base peak was found to be the molecular ion [34], but in the present example the base peak corresponds to the solvent free ion ( $M - \text{DME}$ ). This confirms the fact that the  $\text{Yb}^{\text{II}}$  compounds tend to lose the coordinated solvent molecules very easily [18,30].

TABLE 2

Mass spectral data of  $(\text{C}_5\text{Me}_5)\text{YbCl}(\text{DME})$  (**4**)

(The relative abundances of the isotopes are given in parentheses)

$m/e$	Ion	$I$	$m/e$	Ion	$I$
41	$\text{C}_3\text{H}_5$	1.2	174	$\text{Yb}(31.84)$	0.7
43	$\text{C}_3\text{H}_7$	0.8	176	$\text{Yb}(12.73)$	0.2
53	$\text{C}_4\text{H}_5$	0.5	205	$^{170}\text{Yb}^{35}\text{Cl}(2.29)$	0.4
55	$\text{C}_4\text{H}_7$	0.4	206	$^{171}\text{Yb}^{35}\text{Cl}(10.81)$	1.7
65	$\text{C}_5\text{H}_5$	0.5	207	$^{172}\text{Yb}^{35}\text{Cl}(16.48)$	2.8
77	$\text{C}_6\text{H}_5$	1.1		$^{170}\text{Yb}^{37}\text{Cl}(0.74)$	
79	$\text{C}_5\text{H}_4\text{CH}_3$	1.1	208	$^{173}\text{Yb}^{35}\text{Cl}(12.18)$	2.5
90	DME	0.3		$^{171}\text{Yb}^{37}\text{Cl}(3.5)$	
91	$\text{C}_7\text{H}_7$	2.2	209	$^{174}\text{Yb}^{35}\text{Cl}(24.05)$	4.8
93	$\text{C}_5\text{Me}_5 - 3 \text{CH}_2$	1.4		$^{172}\text{Yb}^{37}\text{Cl}(5.34)$	
103	$\text{C}_5\text{Me}_5 - 2 \text{CH}_3 - \text{H}_2$	0.3	210	$^{173}\text{Yb}^{37}\text{Cl}(3.95)$	0.6
105	$\text{C}_5\text{Me}_5 - 2 \text{CH}_3$	3.2	211	$^{176}\text{Yb}^{35}\text{Cl}(9.62)$	2.9
107	$\text{C}_5\text{Me}_5 - 2 \text{CH}_2$	0.9	213	$^{176}\text{Yb}^{37}\text{Cl}(3.12)$	0.5
115	$\text{C}_5\text{Me}_5 - \text{CH}_2 - 3 \text{H}_2$	1.0	306	$\text{C}_5\text{Me}_5^{171}\text{Yb}(12.77)$	0.6
117	$\text{C}_5\text{Me}_5 - \text{CH}_2 - 2 \text{H}_2$	0.4	307	$\text{C}_5\text{Me}_5^{172}\text{Yb}(19.47)$	0.9
119	$\text{C}_5\text{Me}_5 - \text{CH}_2 - \text{H}_2$	3.6	308	$\text{C}_5\text{Me}_5^{173}\text{Yb}(14.39)$	0.7
120	$\text{C}_5\text{Me}_5 - \text{CH}_3$	1.0	309	$\text{C}_5\text{Me}_5^{174}\text{Yb}(28.41)$	1.1
121	$\text{C}_5\text{Me}_5 - \text{CH}_2$	2.6	311	$\text{C}_5\text{Me}_5^{176}\text{Yb}(11.36)$	0.4
133	$\text{C}_5\text{Me}_5 - \text{H}_2$	0.5	340	$\text{C}_5\text{Me}_5^{170}\text{Yb}^{35}\text{Cl}(2.04)$	1.8
134	$\text{C}_5\text{Me}_5 - \text{H}$	0.9	341	$\text{C}_5\text{Me}_5^{171}\text{Yb}^{35}\text{Cl}(9.65)$	3.4
135	$\text{C}_5\text{Me}_5$	2.6	342	$\text{C}_5\text{Me}_5^{172}\text{Yb}^{35}\text{Cl}(14.71)$	3.5
136	$\text{C}_5\text{Me}_5 + \text{H}$	1.8	343	$\text{C}_5\text{Me}_5^{173}\text{Yb}^{35}\text{Cl}(10.88)$	5.8
170	$\text{Yb}(3.03)$	0.1	344	$\text{C}_5\text{Me}_5^{174}\text{Yb}^{35}\text{Cl}(21.47)$	2.2
171	$\text{Yb}(14.31)$	0.3	345	$\text{C}_5\text{Me}_5^{173}\text{Yb}^{37}\text{Cl}(3.52)$	3.6
172	$\text{Yb}(21.82)$	0.4	346	$\text{C}_5\text{Me}_5^{176}\text{Yb}^{35}\text{Cl}(8.58)$	0.9
173	$\text{Yb}(16.13)$	0.3		$\text{C}_5\text{Me}_5^{174}\text{Yb}^{37}\text{Cl}(6.96)$	

Among the ions corresponding to the ligand  $C_5Me_5$ , the spectrum contains  $L^+$ ,  $(L-H)^+$ ,  $(L-2H)^+$  and other ions resulting from elimination of one to four  $CH_2$  groups. The ion of  $m/e = 91$  is one of the most intense hydrocarbon ions, and is assigned to  $C_7H_7^+$ . The ions corresponding to different isotopes of ytterbium along with relative abundance values are given in Table 2. The peaks in the region of  $m/e = 205-213$  are assigned to the ions  ${}^xYb{}^yCl$  ( $x$  and  $y$  are the mass numbers of Yb and Cl isotopes, respectively). Similarly the ions in the regions of  $m/e = 306-311$  and  $340-346$  correspond to  $C_5Me_5Yb^+$  and  $C_5Me_5YbCl^+$  respectively. The isotopic distribution data indicate the existence of other ions formed by the combination of the different isotopes of Yb and  ${}^{35}Cl$ ,  ${}^{37}Cl$ ,  ${}^{12}C$ ,  ${}^{13}C$ ,  ${}^1H$  and  ${}^2H$ , but their relative abundance values are less than 0.1.

In addition to the main peaks given in the table, peaks of very low intensity are also observed around  $m/e = 478$  and  $443$ . The former corresponds to  $(C_5Me_5)_2Yb^{III}Cl^+$  and the latter to  $[(C_5Me_5)_2Yb^{III/II}]^+$ . Zhou et al. [32] have also observed ions corresponding to  $[(C_5H_5)_3Nd(phen) + 1]^+$  and  $[(C_5H_5)_3Nd + 1]^+$  in the mass spectrum of  $[(C_5H_5)_2NdCl(phen)]$ . They have stated that these ions have resulted from tricyclopentadienyl impurities. The  ${}^1H$  NMR spectra of none of the four compounds **1** to **4** have shown any indication of paramagnetic impurities. Therefore, we believe that these ions are formed under electron impact as shown in equation 8.



From the absence of the ion  $m/e = 686$   $[(C_5Me_5YbCl)_2]$  or its fragments, it may be assumed that **4** exists as a monomer in the gas phase.

## Experimental

The complexes described here are extremely air and moisture sensitive. Therefore, both the synthesis and subsequent manipulations of these compounds are performed by using Schlenk tubes and vacuum lines in an atmosphere of dried, oxygen-free argon. Tetrahydrofuran (THF), dimethoxyethane (DME) and pentane were dried and freed of oxygen by distilling under argon from blue sodium benzophenone ketyl immediately prior to use. THF- $d_8$  and benzene- $d_6$  were dried by refluxing over Na for several hours. Anhydrous  $YbCl_3$  was prepared from the pure oxide (Auer-Remy, West-Germany) by reaction with  $NH_4Cl$  [35]. Anhydrous  $YbCl_2$  was prepared by the reaction between stoichiometric amounts of ytterbium metal powder (Auer-Remy, West-Germany) and  $NH_4Cl$  in liquid  $NH_3$  and subsequent removal of ammonia of crystallization under vacuum [36]. Sodium pentamethylcyclopentadienide was prepared as reported earlier [22]. Elemental analyses were performed on a Perkin-Elmer CHN-Analyser 240C. Metal analyses were carried out by complexometric titration against dithizone [37], chlorine by titration with 0.1  $N$   $AgNO_3$  solution. Infrared spectra were recorded as paraffin mulls between CsI plates, using a Perkin-Elmer 560 B ( $200-4000\text{ cm}^{-1}$ ) spectrometer.  ${}^1H$  NMR spectra were obtained in sealed 5 mm tubes on Bruker WP 80 SI and Bruker WH 270 instruments. The mass spectrum was recorded on a Varian MAT 311A spectrometer.

$(C_5H_5)YbCl \cdot 2\text{ THF}$  (**1**). (a) From  $YbCl_2$  and  $NaC_5H_5$ :  $YbCl_2$  (1.2 g, 4.9 mmol) was suspended in 40 ml of dry THF in a 100 ml Schlenk flask equipped with

a pressure-equalizing dropping funnel. The magnetically stirred suspension was treated dropwise over 40 min with 4.9 mmol of  $\text{NaC}_5\text{H}_5$  (6.1 ml of 0.8 M solution in THF) at room temperature. During the addition the amount of solid decreased and a cloudy violet solution was obtained. After all of the  $\text{NaC}_5\text{H}_5$  was added, the mixture was stirred for another 3 h at room temperature. Subsequently the reaction mixture was allowed to settle while cooling to 10 °C. The cold solution was filtered through a fine frit. The filtrate volume was slowly reduced under vacuum to 10–15 ml and filtered while still cold. The resulting solid was rinsed twice with pentane yielding **1** as violet microcrystalline product (1.4 g, 68%). Anal.: Found: C, 36.91; H, 5.12; Cl, 8.02, Yb, 40.86.  $\text{C}_{13}\text{H}_{21}\text{ClYbO}_2$  calcd.: C, 37.36; H, 5.03; Cl, 8.50; Yb, 41.44%. IR (Nujol/poly(chlorotrifluoroethylene) oil;  $\text{cm}^{-1}$ ) 3560, 3050, 2715, 1735, 1430, 1350, 1290, 1030, 1005, 920, 890, 730, 695.

(b) From  $(\text{C}_5\text{H}_5)\text{YbCl}_2$ : The orange solution of  $(\text{C}_5\text{H}_5)\text{YbCl}_2$  in THF was prepared from 1.36 g (4.9 mmol) of  $\text{YbCl}_3$  and 4.9 mmol of  $\text{NaC}_5\text{H}_5$  in THF as described by Dubeck et al. [38]. To this solution a slight excess of Na/Hg was added at 0 °C and stirred for about 4 h, while allowing it to warm up to room temperature. Gradually color of the solution changed to violet and off-white solids (NaCl) formed. The solution was filtered and worked up as above. Yield: 1.1 g (50%) of **1**. Elemental analysis, IR and NMR spectra of this compound were identical with those of **1** prepared from  $\text{YbCl}_2$  and  $\text{NaC}_5\text{H}_5$ .

$(\text{C}_5\text{H}_5)\text{YbCl}(\text{DME})$  (**2**).  $\text{NaC}_5\text{H}_5$  (0.43 g, 4.9 mmol) free from THF was added to a suspension of  $\text{YbCl}_2$  (1.2 g, 4.9 mmol) in 60 ml DME. The reaction proceeded slowly and a green solution formed with a white precipitate of NaCl. Further working up as above yielded 1.2 g (67%) of **2**. Anal.: Found: C, 28.95; H, 3.92.  $\text{C}_9\text{H}_{15}\text{ClYbO}_2$  calcd.: C, 29.71; H, 4.13%.

$(\text{C}_5\text{Me}_5)\text{YbCl}(\text{THF})_2$  (**3**). This compound was prepared from 1.2 g (4.9 mmol) of  $\text{YbCl}_2$  in 40 ml THF and 4.9 mmol (8.1 ml of a 0.6 M solution in THF) of  $\text{NaC}_5\text{Me}_5$  by using the method described under 1a. Yield: 1.8 g (75%). Anal.: Found: C, 44.74; H, 6.18; Cl, 7.58.  $\text{C}_{18}\text{H}_{31}\text{YbClO}_2$  calcd.: C, 44.31; H, 6.36; Cl, 7.28%. IR (Nujol,  $\text{cm}^{-1}$ ): 3670, 2710, 1660, 1340, 1250, 1150, 1100, 1035, 940, 910, 890, 800, 720.

$(\text{C}_5\text{Me}_5)\text{YbCl}(\text{DME})$  (**4**). 0.77 g (4.9 mmol) of  $\text{NaC}_5\text{Me}_5$  (free from THF) and 1.2 g (4.9 mmol) of  $\text{YbCl}_2$  in 60 ml DME gave a violet solution on stirring for about 6 h at room temperature. Filtering the solution and subsequent workup yielded 1.6 g (75%) of **4**. Anal.: Found: C, 38.12; H, 5.46; Yb, 39.11.  $\text{C}_{14}\text{H}_{25}\text{YbClO}_2$  calcd.: C, 38.75; H, 5.77; Yb, 39.91%. IR (Nujol,  $\text{cm}^{-1}$ ): 3400, 2710, 1650, 1620, 1355, 1245, 1195, 1130, 1090, 1030, 985, 865, 800, 720.

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