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## Synthesis and reactivity of naphthalene complexes of ytterbium

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### Abstract

The complexes formulated as  $C_{10}H_8Yb_x(THF)_y$  ( $x = 1-2$ ,  $y = 2-4$ ) have been obtained as black pyrophoric powders by reactions of anhydrous ytterbium diiodide with a lithium naphthalide in THF. The reactions of samarium and europium iodides, with  $C_{10}H_8Li$ ,  $YbI_2$  with lithium  $\beta$ -methylnaphthalide, as well as  $YbCl_3$  with  $C_{10}H_8Na$  and sodium anthracide give similar complexes. The properties of these highly reactive products suggest that they are arene  $\pi$ -complexes of zerovalent lanthanoids. The reactions of these complexes with  $O_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$ , amides, cyclopentadiene, olefines, benzophenone, benzaldehyde and ethylene oxide have been carried out.

Interaction of ytterbium and europium with naphthalene in liquid  $NH_3$ -THF gives the green solutions of the metal naphthalides.

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### Introduction

We recently found that cyclopentadienides and anhydrous halides of rare earth elements react with dinitrogen under ambient conditions in the presence of sodium or lithium naphthalides [1,2]. Hydrolysis of the mixture liberates ammonia. In order to ascertain the nature of the particles or complexes which are directly responsible for the dinitrogen fixation we investigated the products formed by reactions of ytterbium halides, samarium and europium iodides, with  $C_{10}H_8Li$  and related compounds in the absence of dinitrogen. These conditions are similar to those for the preparation of "active metals" as described by Rieke and coworkers [3–5]. They have shown [3] that reduction of  $d$ -metal halides by lithium in presence of a small amount of naphthalene gives finely divided, extremely reactive, black metal powders containing substantial amounts of carbon, hydrogen,  $LiOH$  and other admixtures. Reduction of  $UCl_4$  and  $ThCl_4$  by  $C_{10}H_8^{2-}[Li(TMED)]_2$  (TMED = tetramethylethylenediamine) in hydrocarbon solvents gives slurries of "active" actinoids [5]. Bromides of Sm, Eu and Yb when treated with  $C_{10}H_8Na$  in THF also give finely

dispersed powders of these metals [6]. The formation of a black highly reactive slurry of praseodymium takes place by  $\text{PrCl}_3$  and potassium in THF under reflux [7].

In contrast to these data we have found [8] that interaction of lanthanoid halides with alkali metal naphthalides leads to formation of the organometallic complexes. They do not react with dinitrogen under ambient conditions but show very high reactivity in many other processes.

## Results and discussion

### Synthesis

It has been established that during 15–30 min after the addition of  $\text{YbI}_2$  to two moles of lithium naphthalide in THF, the signal from the radical-anion  $\text{C}_{10}\text{H}_8^{\cdot-}$  in the ESR spectrum of reaction mixture disappears and a black finely dispersed precipitate is formed. After extraction with THF and drying in vacuo at  $20^\circ\text{C}$  the complex was formulated as  $\text{C}_{10}\text{H}_8\text{Yb}(\text{THF})_3$  (I). The product contains traces ( $\sim 0.1\%$ ) of iodine, obviously as  $\text{LiI}$ . In some cases the ytterbium content in the complex is enhanced and the ratio  $\text{Yb}/\text{C}_{10}\text{H}_8$  can be as high as 2. The reason for this remains unclear. Variation in the composition of the complexes is dependent on differences in the quality of the reagents and the solvents used. The THF content in the complex varies between 2.5–3.5 moles depending on the conditions used to dry the complex. The yield of I is usually in excess of 80%. The black powder formed in the reaction of  $\text{YbCl}_3$  with three moles of sodium naphthalide, contains naphthalene, ytterbium and THF and in addition, about three moles of  $\text{NaCl}$  owing to the poor solubility of this salt in THF. The presence of  $\text{NaCl}$  was confirmed by X-ray phase analysis. The ratio of ytterbium/naphthalene in this case is nearly 2. The THF content was determined only qualitatively by IR spectroscopy.

Lithium  $\beta$ -methyl-naphthalide reacts with  $\text{YbI}_2$  to give the complexes  $\beta\text{-MeC}_{10}\text{H}_7\text{Yb}_x \cdot (\text{THF})_y$  ( $x = 1-2$ ,  $y = 2-3$ ), properties of which are similar to those of the  $\text{C}_{10}\text{H}_8$ -analogues.

Some differences are observed in the reaction of  $\text{YbI}_2$  with lithium biphenylide or lithium anthracide. The change in colour of the reaction mixture (indicates that the reaction is taking place) was observed immediately after the reagents were mixed, but the signal from the  $\text{C}_{14}\text{H}_{10}^{\cdot-}$  remains in the ESR spectrum of the reaction mixture even after 24 h. No precipitates are formed. Lithium anthracide and  $\text{YbCl}_3$  give a black precipitate formulated as  $\text{C}_{14}\text{H}_{10}\text{Yb}_x(\text{THF})_y(\text{LiCl})_2$  ( $x = 1-2$ ,  $y = 2-3$ ) in 30% yield. The signal from the  $\text{C}_{14}\text{H}_{10}^{\cdot-}$  radical-anion in solution does not disappear although its intensity significantly decreases. Higher yields of the black anthracene product (65%) were obtained in the reaction of  $\text{YbCl}_3$  with  $\text{C}_{14}\text{H}_{10}\text{Na}$ . From the amounts of anthracene, metal, salt and THF present in it, a stoichiometry of  $\text{C}_{14}\text{H}_{10}\text{Yb}_x(\text{THF})_y(\text{NaCl})_3$  ( $x = 1-2$ ,  $y = 1-2$ ) was deduced. Reaction of the samarium and europium iodides with  $\text{C}_{10}\text{H}_8\text{Li}$  gives the complexes  $\text{C}_{10}\text{H}_8\text{Ln}_x(\text{THF})_y$  ( $\text{Ln} = \text{Sm}, \text{Eu}$ ;  $x = 1-1.5$ ;  $y = 3-4$ ). Their properties are similar to ytterbium compound I. Naphthaleneeuropium was isolated in 80% yield whereas the solid Sm derivative was obtained in  $< 10\%$  yield because the latter does not precipitate even after prolonged centrifugation of the reaction mixture.

The variation in the composition of the complexes slightly influences their physical properties and reactivity. At the same time the presence in the reaction

mixture of even trace amounts of oxygen and moisture or oxyhalide admixture in the starting salt, dramatically decreases the reactivity of the products.

A different type of compound was obtained from the direct reaction of ytterbium with naphthalene. These reagents do not react in the THF medium (nor does Yb with anthracene). But such a reaction proceeds readily when a solution of  $C_{10}H_8$  in THF is added to the blue solution of ytterbium in liquid  $NH_3$  at  $-78^\circ C$ . The reaction mixture turns green and the ESR spectrum shows the characteristic signal of  $C_{10}H_8^{\cdot -}$  ( $A(H(1))$  4.98 G,  $A(H(2))$  1.88 G; quintet of quintets) instead of the singlet from the solvated electron. Removal of ammonia by evaporation in vacuo at  $-78^\circ C$  leaves ytterbium naphthalide (containing coordinated  $NH_3$ ) in the THF solution. If this solution is warmed to  $-35^\circ C$  or stored at  $-78^\circ C$ , ammonolysis of the complex takes place with formation of  $Yb(NH_2)_2$ , dihydronaphthalene, and naphthalene. Hydrolysis of the same solution at  $-78^\circ C$  gives  $C_{10}H_8$ ,  $C_{10}H_{10}$  and  $Yb(OH)_3$ . Similar results were obtained with europium.

#### *Properties and reactivity*

Naphthalene complexes of samarium, europium and ytterbium are isolated as black pyrophoric powders. These powders are insoluble in THF, and in DME, but dissolve readily in liquid ammonia to give dark green solutions, ESR spectra which reveal the presence of the radical-anion  $C_{10}H_8^{\cdot -}$ . The room-temperature magnetic moments for these complexes (Sm,  $\mu_{eff}$  3.5 BM; Eu,  $\mu_{eff}$  8.2 BM; Yb, diamagnetic) are near to magnetic moments proposed for the corresponding Ln(0). Full data on the magnetic properties of the naphthalene complexes of Sm, Eu, Yb and the other lanthanoids will be published elsewhere. The complexes lose some naphthalene on heating in vacuo to give dark-brown water- and HCl-insoluble materials which do not contain free metal. Slow decomposition of the complexes is observed at room temperature, thus freshly prepared complexes were used in reactions.

The chemical properties of arenelanthanoid complexes are illustrated by the reactions summarized in Table 1. All reactions were carried out in THF at room temperature. In order to maintain reaction stoichiometry and to calculate the product yields, the lanthanoid content of each starting complex was determined before use.

Hydrolysis of naphthalene and anthracene complexes gives hydrogen, the lanthanoid hydroxides, and a mixture of the isomers of dihydronaphthalene or dihydroanthracene in high yield. The reactions with cyclopentadiene gives unhydrogenated  $Cp_2Ln$  and arene, whereas reaction with amines gives a mixture of hydrogenated and unhydrogenated arenes and the associated amides. These reactions are an attractive new route to cyclopentadienides and amides of lanthanoids.

Oxidation of the complexes in THF by dry oxygen leads to the abstraction of naphthalene (or anthracene). Interaction of naphthalenytterbium with carbon dioxide gives a pale-yellow precipitate, hydrolysis of which gives a mixture of the isomers of dihydronaphthalenedicarboxylic acid. It should be noted that when the reaction occurs in the presence of free naphthalene it does not lead to an increase in the yield of  $C_{10}H_8(COOH)_2$  i.e. the carboxylation of naphthalene is not catalytic in this case. In the reaction of  $CO_2$  with anthracene complex anthracene-2-carboxylic acid was obtained unexpectedly instead of dihydroanthracenedicarboxylic acid. The reason for such a remarkable difference in the reaction route of the naphthalene and anthracene complexes is unclear. Only naphthalene and dihydronaphthalenedi-

Table 1

## Reactions of the arene complexes of lanthanoids

Complex ( $x = 1-2$ ; $y = 2-4$ )	Reagent	Reaction time (h)	Products (yield(%))
$C_{10}H_8Yb_x(THF)_y$	$H_2O$	20 <sup>a</sup>	$Yb(OH)_3$ (98), $C_{10}H_{10}$ (82), THF (112), $H_2$
	$Ph_2CO (H^+)$	24	$(Ph_2COH)_2$ (67)
	$PhHCO (H^+)$	24	$(PhHCOH)_2$ (70)
	$CH_2CH_2O (H^+)$	0.1	$HOCH_2(CH_2)_2CH_2OH$ (100), $C_{10}H_8$ (83)
$C_{10}H_8Yb_x(THF)_y(NaCl)_3$	$O_2$	18	$Yb_2O_3$ (96), $C_{10}H_8$ (98)
	$CO_2 (H^+)$	5	$C_{10}H_8(COOH)_2$ (85)
	$CO (H^+)$	20	$C_{10}H_8(COOH)_2$ (56)
	$(Me_3Si)_2NH$	4	$[(Me_3Si)_2N]_2Yb$ (88), $C_{10}H_8$ (53), $C_{10}H_{10}$ (47), $H_2$
	$Et_2NH$	8	$(Et_2N)_2Yb(THF)_{0.5}$ (52), $C_{10}H_8$ (52), $C_{10}H_{10}$ (48), $H_2$
$\beta-MeC_{10}H_7Yb_x(THF)_y$	$CpH$	6	$Cp_2Yb$ (50), $C_{10}H_8$ (93), $H_2$
	$H_2O$	0.1	$Yb(OH)_3$ (95), $\beta-MeC_{10}H_9$ (97), $H_2$
$C_{14}H_{10}Yb_x(THF)_y(NaCl)_3$	$CpH$	4	$Cp_2Yb$ (93), $\beta-MeC_{10}H_7$ (93), $H_2$
	$H_2O$	0.1	$Yb(OH)_3$ (97), $C_{14}H_{12}$ (97), NaCl (99), $H_2$
	$O_2$	7	$Yb_2O_3$ (99), $C_{14}H_{10}$ (95)
	$(Me_3Si)_2NH$	4	$[(Me_3Si)_2N]_2Yb$ (57), $C_{14}H_{10}$ (32), $C_{14}H_{12}$ (34), $H_2$
	$CpH$	4	$Cp_2Yb$ (62), $C_{14}H_{10}$ (73), $H_2$
$C_{10}H_8Sm_x(THF)_y$	$CO_2 (H^+)$	3	$\beta-C_{14}H_9COOH$ (54)
	$H_2O$	0.1	$Sm(OH)_3$ (97), $C_{10}H_{10}$ (25), $C_{10}H_8$ (75)
$C_{10}H_8Eu_x(THF)_y$	$CpH$	8	$Cp_2Sm$ (10), $Cp_3Sm$ (12), $C_{10}H_8$ (90)
	$H_2O$	0.5	$Eu(OH)_3$ (100), $C_{10}H_{10}$ (100)
	$CpH$	1.5	$Cp_2Eu$ (89), $C_{10}H_8$ (91)

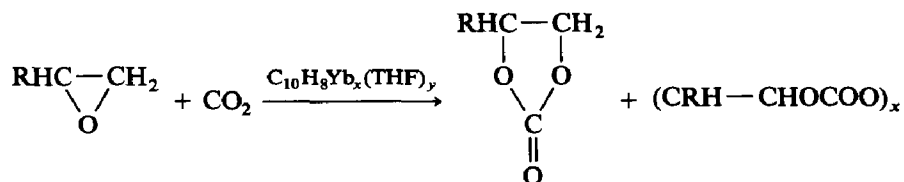
<sup>a</sup> In toluene.

carboxylic acid were identified after hydrolysis of the mixture formed in the reaction of naphthalene complex with carbon monoxide.

When benzophenone is added to a slurry of I in THF the precipitate dissolves gradually and the mixture becomes dark blue, the ESR spectrum of which reveals the presence of the benzophenone radical-anion ( $A(H(o, p))$  2.1 G;  $A(H(m))$  0.7 G). After 15 min at room temperature the solution had turned dark red, and the  $Ph_2CO^{\cdot-}$  signal in the ESR spectrum had disappeared. This stage of the reaction probably corresponds to the formation of ytterbium pinacolate because hydrolysis of the red solution gives benzopinacol. The formation of the C-C bond also takes place in reactions with benzaldehyde and ethylene oxide, to give 1,2-diphenylethylene glycol after hydrolysis, and the 1,4-butanediol, respectively.

A catalytic amount of naphthalenyttterbium causes ethylene oxide to polymerize. Conversion of ethylene oxide attains 100% after 20 h at 20°C (7% of I was used). Anthracene complex also catalyzes the polymerization of  $C_2H_4O$ , but its activity is less. The reaction of epoxides with  $CO_2$  in the presence of catalytic amounts of  $C_{10}H_8Yb_x(THF)_y$  (1 atm, 20°C) leads to the formation of alkylencarbonates in

80% yield together with a small amount of polycarbonate.



R = H, CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>Me-*p*

The dicarbonate *p*-(CH<sub>2</sub>CO<sub>2</sub>CHCH<sub>2</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> was obtained from diglycidyl ether of hydroquinone under the same conditions.

The complex C<sub>10</sub>H<sub>8</sub>Yb<sub>x</sub>(THF)<sub>y</sub> (1–5%) catalyzes the polymerization of styrene, methylmethacrylate, ethylacrylate, isoprene and piperilene at room temperature. Piperilene gives more than 80% of the *trans*-polymer under these conditions whereas polyisoprene is produced in approximately equal amounts of the *cis*- and the *trans*-forms. The same ytterbium complex catalyzes the copolymerization of ethylene oxide with styrene and piperilene.

## Conclusion

The data presented here do not permit definite conclusions to be drawn on the nature of the complexes formed in the reactions of the alkali metal naphthalides with anhydrous rare earth element halides in THF medium. We can only say that these complexes are not radical-ion salts (on the basis of the ESR spectroscopy data and the magnetic properties). There are three possible structures: (a) the simple physical adsorption of naphthalene on to the surface of the finely divided metal, (b) the existence of a covalent or ionic bond between arene and the lanthanoid cation, and (c) the existence of a  $\pi$ -bond between the arene ligand and the metal. We think that (c) is the most plausible. These products should obviously be regarded as complexes of zerovalent lanthanoids with the arene, which acts as an  $\eta^4$ -ligand like the dienes. The  $\eta^6$ -coordination of the arene in these compounds is also possible but we think it is less probable because the properties of the naphthalene complexes obtained differ greatly from those of the recently synthesized, novel bis-arene complexes of lanthanoids, the molecular structures of which have been determined by X-ray diffraction [9]. At the same time the properties of naphthalenelanthanoids are similar to those of alkene and alkyne lanthanoids complexes synthesized by metal vapor technique [10].

## Experimental

All manipulations during the synthesis and isolation of the products were carried out in vacuo by use of standard Schlenk techniques. Solvents were dried over molecular sieves and deoxygenated before use. THF was distilled from ketyl benzophenone solution. Quantitative analyses of rare earth elements and halogenides were performed by a complexometric method [11,12] and by gravimetric analysis. The C and H analyses of some of the arenelanthanoids gave scattered results therefore the composition of the arene ligands and THF in the complexes was quantitatively determined by gravimetric and GLC analysis after hydrolysis of each sample. In some cases THF content in the products was determined by mass losses

undergone by the sample. The IR spectra were recorded on a Perkin–Elmer 577 spectrometer; ESR spectra were recorded on a Bruker ER-200 D SCR spectrometer. Chromatographic analyses of volatile products were carried out by use of a Tsvet-104 instrument, non-volatile organic products were analysed on the liquid chromatograph Tsvet-304.

The anhydrous  $\text{YbCl}_3$  was prepared by chlorination of  $\text{Yb}_2\text{O}_3$  by a published procedure [13]. The iodides  $\text{LnI}_2$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ ) were prepared by reaction of the corresponding lanthanoid with an excess of  $\text{MeI}$  in THF [14]. The samarium iodide obtained under these conditions contains 76% of  $\text{SmI}_3$  and 24% of  $\text{SmI}_2$ . Individual  $\text{SmI}_2$  was prepared by reaction of  $\text{Sm}$  with  $\text{CH}_2\text{I}_2$ , but this salt gives poor results in the reaction with lithium naphthalide.

#### *Preparation of $\text{C}_{10}\text{H}_8\text{Yb}(\text{THF})_3$ (I)*

In a typical reaction,  $\text{YbI}_2$  (1.76 g, 4.12 mmol) was added to 25 ml of THF solution of lithium naphthalide (from 1.05 g (8.20 mmol) of  $\text{C}_{10}\text{H}_8$  and 0.058 g (8.28 mmol) of  $\text{Li}$ ), the mixture was stirred for 0.5 h. The mixture turned black. The mixture was centrifuged and solution was decanted from the precipitate. The latter was then washed with THF ( $3 \times 20$  ml) and dried for 1 h under vacuum at room temperature to give I as a black powder in yield 1.68 g (79%). Anal. Found: C, 49.69; H, 6.42; Yb, 33.82.  $\text{C}_{22}\text{H}_{32}\text{O}_3\text{Yb}$  calcd.: C, 51.08; H, 6.18; Yb, 33.44%. IR (Nujol): 1500, 1395 s, 1180 s, 1130, 1060, 1035 s, 970 s, 915, 880, 780, 740, 705 s,  $450\text{ cm}^{-1}$ .

The other complexes were prepared similarly:  $\text{C}_{10}\text{H}_8\text{Yb}_2(\text{THF})_3(\text{NaCl})_3$  in 95% yield,  $\beta\text{-MeC}_{10}\text{H}_7\text{Yb}_x \cdot (\text{THF})_y$  in ca. 45% yield,  $\text{C}_{14}\text{H}_{10}\text{Yb}_x(\text{THF})_y(\text{NaCl})_3$  in ca. 65% yield,  $\text{C}_{10}\text{H}_8\text{Sm}(\text{THF})_3$  in 9%, and  $\text{C}_{10}\text{H}_8\text{Eu}(\text{THF})_3$  in 80% yield.

#### *Hydrolysis of I*

To a suspension of I (0.64 g, 1.23 mmol) in 5 ml of toluene was added 0.1 ml of water. Evolution of hydrogen was observed and the precipitate became colourless. After 20 h the mixture was centrifuged, the toluene solution was decanted from the precipitate of  $\text{Yb}(\text{OH})_3$  (identified as  $\text{Yb}_2\text{O}_3$ ; 0.23 g, 98%) and the  $\text{Yb}(\text{OH})_3$  was washed with toluene ( $3 \times 5$  ml). The toluene solution and extract contained dihydronaphthalene (0.13 g, 82%) and THF (0.3 g, 112%), as detected by GLC.

#### *Oxidation of $\text{C}_{10}\text{H}_8\text{Yb}_2(\text{THF})_3(\text{NaCl})_3$*

A suspension of  $\text{C}_{10}\text{H}_8\text{Yb}_2(\text{THF})_3(\text{NaCl})_3$  (1.47 g, 1.69 mmol) in 10 ml of THF was stirred for 18 h under dry air, and became colourless. It was separated from solution by centrifugation and washed with benzene ( $2 \times 5$  ml) and water ( $3 \times 5$  ml), to leave the insoluble  $\text{Yb}_2\text{O}_3$  (0.64 g, 98%). Naphthalene (0.21 g, 98% in benzene-THF solution) was detected by GLC. The aqueous solution contained 0.29 g (96%) of  $\text{NaCl}$ .

#### *Reaction of $\text{C}_{10}\text{H}_8\text{Yb}_2(\text{THF})_3(\text{NaCl})_3$ with $\text{CO}_2$*

A suspension of  $\text{C}_{10}\text{H}_8\text{Yb}_2(\text{THF})_3(\text{NaCl})_3$  (1.62 g, 1.87 mmol) in 10 ml of THF was stirred under  $\text{CO}_2$  at atmospheric pressure for 5 h, during which 157 ml (7 mmol) of  $\text{CO}_2$  had been absorbed and the initial black colour of the mixture had turned light-brown. The mixture was treated with water (5 ml) and 20%  $\text{HCl}$  (10 ml), and 66 ml (42%) of carbon dioxide was evolved. The mixture was extracted with

ether ( $3 \times 5$  ml) and benzene ( $3 \times 5$  ml). The solvents were evaporated from extract, the residue was dried in vacuum and crystallized by hexane from ether solution to give 0.34 g (85%) of  $C_{10}H_8(COOH)_2$  as 3 isomers (by GLC). The aqueous layer was treated with 30% NaOH and the  $Yb(OH)_3$  precipitate was washed with water and calcinated to give 0.71 g (97%) of  $Yb_2O_3$ .

*Reaction of  $C_{10}H_8Eu_x(THF)_y$ , with cyclopentadiene*

A solution of cyclopentadiene (0.72 g, 11 mmol) in 2 ml of THF was added to a suspension of 0.484 g of  $C_{10}H_8Eu_x(THF)_y$  (Eu content 34.7%) in 10 ml of THF. The reaction was accompanied by vigorous hydrogen evolution and a change in the colour of the mixture from black to yellow. The mixture was stirred for 2 h at room temperature and centrifuged. The yellow precipitate was washed with THF ( $2 \times 5$  ml) and dried in vacuo at  $160^\circ C$  for 2 h to give  $Cp_2Eu \cdot (THF)_{0.5}$  in 0.31 g (89%) yield (by IR spectroscopy and elemental analysis). GLC and LSC analysis revealed the presence of  $C_{10}H_8$  and the absence of dihydronaphthalene in THF solution.

*Reaction of  $C_{10}H_8Yb_2(THF)_3(NaCl)_3$  with  $Et_2NH$*

To a suspension of 1.96 g (2.26 mmol) of  $C_{10}H_8Yb_2(THF)_3(NaCl)_3$  in 15 ml of THF was added a solution of  $Et_2NH$  (1.61 g, 22.05 mmol) in 5 ml of THF on cooling. The reaction was accompanied by hydrogen evolution, partial dissolution of the precipitate and a change in the colour of the solution from black to a dark cherry-red. The mixture was stirred for 8 h, centrifuged, and the solution was separated from precipitate by decanting. THF was removed in vacuo and the residue was recrystallized from pentane at  $-78^\circ C$  to give dark cherry-red crystals of  $(Et_2N)_2Yb \cdot (THF)_{0.5}$  (0.83 g, 52%); m.p.  $126^\circ C$ . Anal. Found: C, 33.97; H, 6.91; N, 7.64; Yb, 49.02.  $C_{10}H_{24}N_2O_{0.5}Yb$  calcd.: C, 34.01; H, 6.79; N, 7.92; Yb, 48.99%. IR: 1440, 1370, 1320, 1130, 1050, 720,  $370\text{ cm}^{-1}$ . In the mother liquor 0.15 g (52%) of  $C_{10}H_8$  and 0.14 g (48%) of  $C_{10}H_{10}$  was detected by GLC.

*Reaction of I with benzophenone*

A solution of  $Ph_2CO$  (0.6 g, 3.3 mmol) in 10 ml THF was added to 0.85 g (1.6 mmol) of complex I. The mixture immediately became blue and the precipitate dissolved. After 2–3 min the blue colour of solution turned dark-red. Hydrolysis of the solution gives a precipitate of  $Yb(OH)_3$  (0.36 g, 100%) and benzopinacol (0.4 g, 67%) which was detected in THF solution by LSC.

*Reaction of I with ethylene oxide*

Complex I (1.2 g, 2.3 mmol) was added to a solution of 0.23 g (5.2 mmol) of ethylene oxide in 10 ml THF. The mixture was shaken for 10 min at room temperature. The precipitate of I did not dissolve but its initial black colour turned light-grey. The mixture was centrifuged and the solution was decanted from precipitate. The solution contained 0.24 g (83%) of naphthalene. The precipitate was hydrolyzed in THF medium to give 0.23 g (100%) of 1,4-butanediol (detected by GLC in the organic layer) and a precipitate,  $Yb(OH)_3$  (0.39 g, 75%).

*Reaction of  $CO_2$  with cresylglycidyl ether in the presence of I*

A mixture of 1.67 g (10 mmol) of cresylglycidyl ether, 10 ml of THF and 0.1 g (0.19 mmol) of I was stirred under  $CO_2$  at room temperature. During 30 min 220 ml

(0.98 mmol) of CO<sub>2</sub> was absorbed. The mixture was stirred for 24 h under these conditions. The precipitate was separated after centrifugation and THF was evaporated from solution. Recrystallization of the residue from THF/hexane (1 : 1) gave 2 g (96%) of *p*-cresylpropylenecarbonate, m.p. 102°C. Anal. Found: C, 62.84; H, 5.57. C<sub>11</sub>H<sub>12</sub>O<sub>4</sub> calcd.: C, 63.45; H, 5.80.

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