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A New Bimetallic Complex Containing Ce and Al: η^8-Cyclooctatetraenylcerium-di-μ-isopropoxydiethylaluminum*

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The reduction of $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot B$, where $B = i\text{-}C_3H_7OH$ or pyridine, by $(C_2H_5)_3Al$ in the presence of cyclooctatetraene yields a new crystalline complex, $(\eta^8\text{-}C_8H_8)Ce(O\text{-}i\text{-}C_3H_7)_2Al(C_2H_5)_2$ (I) which can coordinate one mol of acetonitrile forming a crystalline adduct (II). The base can be easily removed under reduced pressure from (II) which converts into (I). The structure of complexes (I) and (II) has been investigated through mass spectrometry, alcoholysis, deuterolysis, IR and ^1H NMR. Both (I) and (II) are paramagnetic and show in the presence of polar molecules, e.g. pyridine or acetonitrile, NMR spectra noticeably dependent on the temperature. The experimental results have been interpreted on the basis of an asymmetric bridge between Ce and Al formed at $T > 45$ °C.

Introduction

Organometallic complexes of cerium containing the cyclooctatetraene (COT) ligand have been recently described. Some of them contain only the π-bonded COT ligand, *e.g.* $[(\eta^8\text{-}C_8H_8)CeCl\cdot 2THF$ [1] or $[(diglyme)K]^+ [\eta^8\text{-}C_8H_8)_2Ce]^-$ [2], but also a Ce derivative containing two types of π-ligands, *e.g.* $(\eta^8\text{-}C_8H_8)Ce(\eta^5\text{-}C_5H_5)$, is known [3].

However, we have shown previously [4] that COT is easily introduced as a ligand into Ce complexes when Ce^{IV} alcoholates are reacted with $(C_2H_5)_3Al$ in the presence of an excess of COT. This reaction was early reported by Wilke [5], but it had not been used before for the synthesis of lanthanide derivatives. In fact, we succeeded in obtaining $(\eta^8\text{-}C_8H_8)_2Ce$, $(C_8H_8)_3Ce_2$, $[K(monoglyme)]^+ [(\eta^8\text{-}C_8H_8)_2Ce]^-$ and $[K(monoglyme)]_2^+[(\eta^8\text{-}C_8H_8)Ce]^{2-}$ in good yields [4].

Pursuing our investigations along this line, we have obtained a new bimetallic complex, *i.e.* η^8-cyclooctatetraenylcerium-di-μ-isopropoxy-diethylaluminum which is the subject of this paper. Bimetallic complexes involving Al, transition metals, *e.g.* Ti or V, and organic ligands as bridging groups have been postulated to be present in homogeneous Ziegler–Natta catalytic systems on the basis of chemical and spectroscopic evidence [6, 7]. However, these complexes can be isolated with difficulty since they are rather labile [8, 9] and their characterisation was only partially successful. At the best of our knowledge, the product described in this paper represents the first example of a well characterised bimetallic complex, which involves a lanthanide, Al and an olefinic ligand.

Results and Discussion

The reaction of $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH$ with $(C_2H_5)_3Al$ (Al/Ce = 4) in toluene and in the presence of an excess of COT occurs slowly at about 100 °C:

$$Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH + 4(C_2H_5)_3Al \xrightarrow[\text{toluene}]{\text{COT}}$$
$$\underset{\text{(I)}}{(C_8H_8)Ce(O\text{-}i\text{-}C_3H_7)_2Al(C_2H_5)_2}\cdot 1/4\ C_7H_8 + $$
$$+ C_2H_6 + 3C_2H_5 \qquad (1)$$

The yield of complex (I) was 30% in 24 h. Better yields (85%) can be obtained starting from $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot Py$ rather than $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH$.

(I) separates from the reaction mixture as a yellow crystalline solid containing some toluene, which could not be removed *in vacuo* at room temperature. The lattice solvent was determined by VPC analysis on the alcoholysis products.

Complex (I) is very sensitive to air and moisture, sparingly soluble in aromatic hydrocarbons and diethyl ether, but it dissolves easily in them when low amounts of aprotic polar molecules, *e.g.* pyridine or acetonitrile, are present. On heating (I) decomposes at 170–180 °C without melting.

When (I) is dissolved at room temperature in acetonitrile and the solution is cooled to –30 °C, a new product (II) containing CH_3CN can be obtained as yellow needles (eqn. 2):

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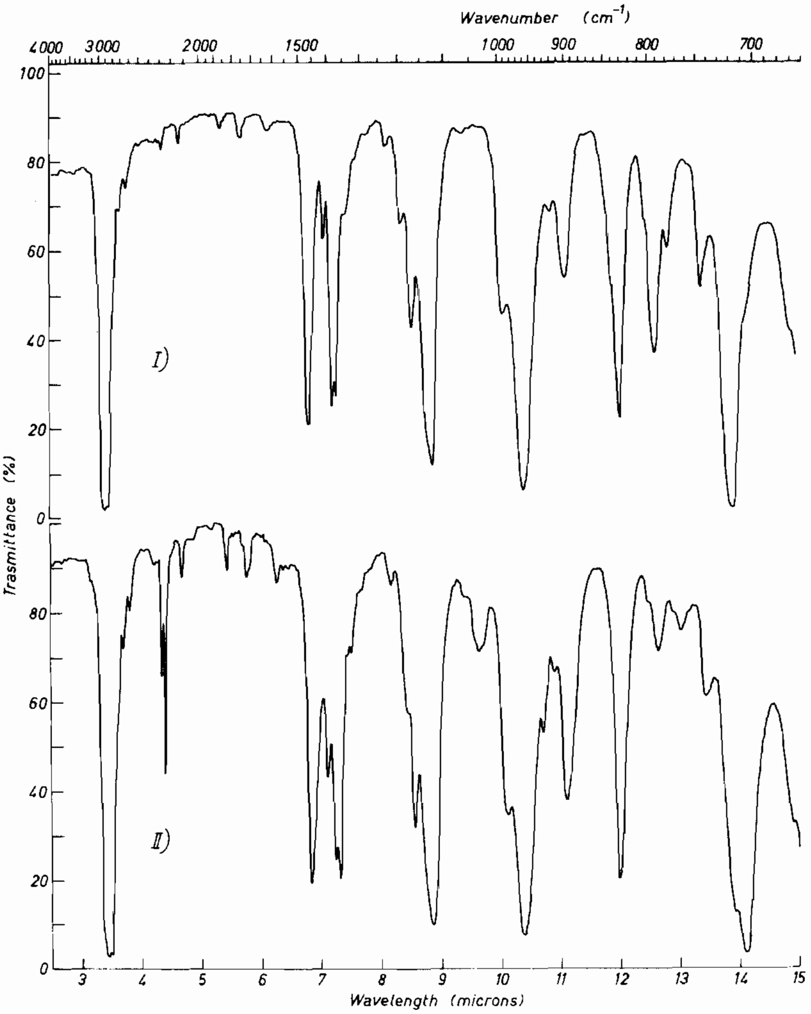

Figure 1. IR spectra (nujol) of complexes (I) and (II).

$$\text{(I)} + CH_3CN \xrightarrow{-1/4\, C_7H_8} \underset{\text{(II)}}{(C_8H_8)Ce(O\text{-}i\text{-}C_3H_7)_2\text{-}Al(C_2H_5)_2 \cdot CH_3CN} \quad (2)$$

Under reduced pressure complex (II) loses CH_3CN, already at temperatures below 0 °C, and pure (I) can be obtained (eqn. 3):

$$\text{(II)} \overset{vac.}{\rightleftharpoons} CH_3CN + \text{Pure (I)} \quad (3)$$

Both products (I) and (II) have been characterised by elemental analysis, mass spectrometry, alcoholysis, deuterolysis and by IR and NMR spectroscopy. X-ray investigations were frustrated by the difficulty to grow single crystals of suitable size for roentgenographic measurements.

Mass Spectrometry Investigations

Since (I) is practically insoluble in hydrocarbons and in polar media it forms adducts, it was impossible to perform cryoscopic molecular weight measurements. However, mass spectra of pure (I) showed the parent peak at m/e 447 having medium intensity and this suggests that (I) is monomeric, at least in vapour phase. Another peak of strong intensity was observed at m/e 418 $(M^* - C_2H_5)^+$. Three other intense peaks were observed at m/e 244 $(M^* - 203)^+$, $156(M^* - 291)^+$ and 104 $(COT)^+$. We are prone to believe that the molecular ion $(CeO)^+$ originates the peak at m/e 156. It is worth noting the high tendency of Ce to link an oxygen atom during the fragmentation process. In fact, we did not observe any peak at m/e 140 $(Ce)^+$ in the case of (I), whereas this molecular ion was found in the fragmentation of $(C_8H_8)_2Ce$ and $(C_8H_8)_3Ce_2$ [4]. The peak at m/e 244 was already observed in the mass spectra of $(C_8H_8)_2Ce$ and is due certainly to the molecular ion $[(C_8H_8)Ce]^+$.

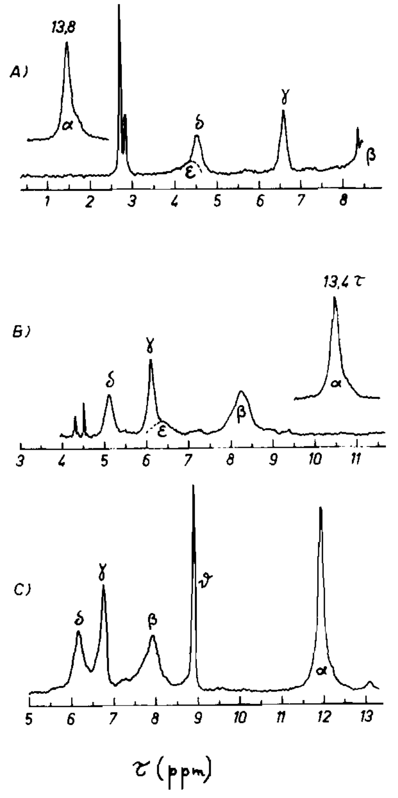

Figure 2. ^{1}H NMR spectra of (I) in benzene-d_6–acetonitrile (A), benzene-d_6–pyridine-d_5 (B) and of (II) in toluene-d_8–pyridine-d_5 (C). Temperature 80 °C; solvent mixture 1:1 by volume; reference to C_6H_6.

Alcoholysis and Deuterolysis Investigations

The alcoholysis of (I) with isopropanol yielded mainly cyclooctatrienes, *i.e.* 1,3,5- and 1,3,6-isomers, and COT according to a molar ratio $C_8H_{10}:C_8H_8 = 3$, as observed in the case of $(C_8H_8)_2Ce$ and $(C_8H_8)_3Ce_2$. White needles having paramagnetic properties can be collected from the reaction solution of (I) with anhydrous isopropanol. This product is believed to be a mixed alkoxide of Ce(III) and Al since it contains only $-OCH(CH_3)_2$ groups. Mixed alkoxides having general formula $Me[Al(O\text{-}i\text{-}C_3H_7)_4]_2$ (where Me = Mg, Ca) are known [10].

When complex (I) was subjected to deuterolysis (D_2O dissolved in diglyme) two mol of gas were evolved. VPC–mass spectrometry analysis confirmed that the gas was C_2H_5D. Neither HD nor $C_2H_4D_2$ were present. These results ruled out the possible presence of an hydride or a $-CH_2-CH_2-$ group bridging the two metals of the complex.

VPC–MS analysis of the liquid obtained by deuterolysis of (I) confirmed the results obtained by alcoholysis since $C_8H_8D_2$ (two isomers) and C_8H_8 were obtained in similar relative amounts and overall yields.

IR Investigations

Fig. 1 compares the IR spectra of complexes (I) and (II). A strong absorption band is present at 720 cm^{-1} in the spectrum of (I) and is assignable, as other weak bands at 1410, 1600, 1735 and 1840 cm^{-1}, to the homoaromatic ring of COT dianion [1, 4]. Two other strong absorptions appear at 960 and 1125 cm^{-1} which can be assigned to the isopropoxy group, since they are also present, although slightly shifted, in $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$. On the other hand, polymeric $Al(O\text{-}i\text{-}C_3H_7)_3$ freshly prepared [11] does not show this absorption pattern, but four intense bands at 953, 1035, 1125 and 1175 cm^{-1}. Therefore, isopropoxy groups of (I) should be considered, on the basis of IR spectra, as bonded to Ce or in a bridge position between the two metals, rather than bonded to Al.

A band of medium intensity at 1370 cm^{-1}, was attributed to the methyls of isopropoxy groups [12].

The spectrum of (II) is fundamentally similar to that of (I), the main differences arising from the presence of two bands at 2265 and 2297 cm^{-1} due to $-CN$ group of coordinated CH_3CN. They are shifted, respectively, by 40 and 2 cm^{-1} with respect to the absorption of the free ligand [13]. Moreover, the most intense absorption of (II), due to COT and appearing at 705 cm^{-1}, is also shifted by 15 cm^{-1} with respect to the corresponding absorption of (I).

NMR Investigations

Valuable information on the structure of (I) was obtained through ^{1}H NMR experiments, even though the signals of the spectra were not resolved because of the paramagnetic character of (I). Although chemical shifts of different protons were noticeably influenced by the type of polar solvents and their concentration, NMR spectra of (I) were not substantially modified by the different experimental conditions, as shown in Fig. 2. Broad signals are evident in Fig. 2, relative to C_6H_6, between 4 and 13 ppm and they have been assigned on the basis of their relative intensity. Thus, the most intense signal (α), corresponding to 12H and occurring between 10 and 13 ppm, has been assigned to the methyl protons of isopropoxy group, while the broad signal (β) observed between 7 and 10 ppm has been assigned to the protons (8H) of COT bonded to Ce. The interaction of these protons with the Ce paramagnetic center is probably responsible for the broadness of the β signal. Signals γ and δ, equivalent to 6H and 4H, respectively, and occurring downfield have been assigned to methyl and methylene protons of ethyl groups. The methine hydrogen of isopropoxy group (ϵ signal) is difficult to detect and probably is overlapped by other signals (Fig. 2/A and 2/B). Fig. 2/C shows, of course, the sharp signal (θ) occurring at 8.8 ppm (3H) due to the protons of CH_3CN present in complex(II).

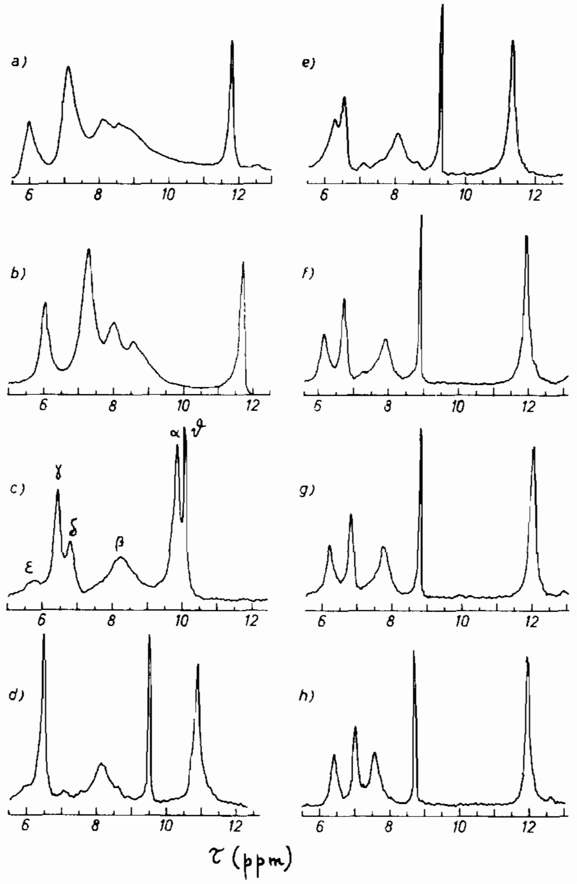

Figure 3. ^1H NMR spectra of (II) in toluene-d_8–pyridine-d_5 obtained at different temperatures. Conditions as in Fig. 2. (a) −15 °C; (b) 0 °C; (c) +25 °C; (d) +35 °C; (e) +50 °C; (f) +70 °C; (g) +90 °C; (h) +105 °C.

The most striking feature of ^1H NMR spectra of (I) and (II) is their dependence on temperature (between −15 and 105 °C) as illustrated in Fig. 3 for complex (II). When the temperature increases from 50 to 105 °C all the signals shift and become narrower but their mutual position is not modified. As a consequence of this shift, between 35 and 45 °C, γ and δ signals (due, respectively, to methyl and methylene protons of ethyl group) coalesce. Above 45 °C their mutual position is reversed with respect to that observed at $T < 35$ °C.

It is worth noting that at $T < 30$ °C the relative position of γ and δ signals is that observed in $[(C_2H_5)_3Al]_2$ [14].

We believe that an exchange of isopropoxy and ethyl ligands in the bridging position between the two metals can explain the observed phenomenon. The scheme of Fig. 4 shows the equilibria which are believed to transform the initial structure (A) of complex (II), stable at $T < 30$ °C, into the asymmetric structure (C) stable at $T > 45$ °C. Under the action of two or more molecules of base, *e.g.* acetonitrile or pyridine, the coordination of Ce increases, one of the two dative bonds of structure (A) is broken and a new intermediate situation (B) arises. A rotation along the Ce–O–Al bond allows the insertion of an ethyl group in the bridging position. In structure (C) an electron-deficient bond is associated to the dative bond in realizing an asymmetric bridge: the different electronic environment of ethyl groups accounts for the reversed position of chemical shift due to γ and δ protons.

The bridge structure (A) is relatively stable and the presence of an electron-donor as acetonitrile is unable to break the bridge of (I) or (II). This result agrees with the behaviour of $(R_2AlOR)_2$: in fact, the dative bonds of these dimeric compounds are not broken by bases [11, 15]. However, the combined action of the base and temperature succeeds in modifying substantially the NMR spectra of (II). The presence of an excess of base is necessary, according to the reaction scheme of Fig. 4, to shift the structure of complex (II) from (A) to (C) and also accounts for the noticeable increase in solubility of the complex in hydrocarbon solvents through coordination processes with the base. However, these coordination processes are reversible as demonstrated by the conversion of (II) to (I) under the action of vacuum (eq. 3). A similar behaviour was shown by $[(\eta^8\text{-}C_8H_8)CeCl]_2$, which is isoelectronic with (I) and can coordinate reversibly two mol of tetrahydrofuran [1].

(I) has a magnetic moment $\mu = 2.04$ BM which is higher than that reported for complexes $[(\eta^8\text{-}C_8H_8)CeCl\cdot 2THF]_2$ and $[K(diglyme)]^+ [(\eta^8\text{-}C_8H_8)_2Ce]^-$, *i.e.* 1.79 and 1.88 BM respectively, but is lower than the value found for $(C_5H_5)_3Ce$, *i.e.* 2.46 BM [1]. Our result indicates the existence of an unpaired electron on complex (I), in agreement with the proposed structure.

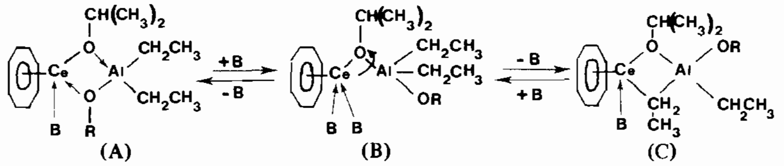

Figure 4. Reaction scheme for the rearrangement of complex (II).

Experimental

Procedure, materials, chemical analyses and physico-chemical measurements were generally described in a previous paper [4].

Al was determined colorimetrically (Perkin–Elmer mod. 303 instrument) after acid attack of products (I) or (II), complexation with *o*-oxyquinoline and extraction of the resulting complex with $CHCl_3$.

Alcoholysis and deuterolysis experiments were performed on weighed samples of (I) (0.3–0.5 g) treated, respectively, with an excess of anhydrous isopropanol or D_2O dissolved in anhydrous diglyme for 20–30 minutes at 50 °C. A gas-burette allowed us to measure the gas evolved in deuterolysis investigations. The reaction products present in the liquid phase were analyzed through VPC and determined quantitatively by making reference to synthetic mixtures.

Mass spectrometric analysis of deuterolysis products was done at low voltage by direct probe insertion (Atlas UF, mod. CH4 instrument), whereas MS analysis of (I) was performed as described previously [4].

^{1}H NMR spectra were obtained at different temperatures from mixtures of solvents, *i.e.* benzene-d_6–acetonitrile, benzene-d_6–pyridine-d_5 or toluene-d_8–pyridine-d_5, which dissolve (I) and (II).

IR spectra were recorded on a Perkin–Elmer mod. 157 instrument in nujol mulls.

Magnetic susceptibility measurements were carried out at room temperature with Gouy's method and adopting the appropriate corrections due to molecular parameters. The sample was introduced in a calibrated tube (i.d. 2 mm), weighed and set on a standard Gouy balance. The value of μ was calculated by making reference to $HgCo(NCS)_4$ and according to standard method [16].

$(\eta^8\text{-}C_8H_8)Ce(\mu\text{-}O\text{-}i\text{-}C_3H_7)_2Al(C_2H_5)_2$ (I)

Two methods were adopted to synthesize (I), differing for the starting Ce compound. The first product was $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH$ but it yielded sometime $(\eta^8\text{-}C_8H_8)_2Ce$ as impurity. The second was $Ce(O\text{-}i\text{-}C_3H_7)_4$ pyridine [17] and gave higher yield of (I).

Method a)

To a solution of 1.75 g of $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot i\text{-}C_3H_7OH$ (4.0 mmol) in 15 ml of toluene were added, at room temperature, 2.1 ml of COT (19 mmol) and 1.9 ml of $(C_2H_5)_3Al$ (13.7 mmol). The reaction mixture was heated at 105 °C for 24 h while the initial light yellow colour turned to green and finally to dark yellow. After cooling slowly (one night) to room temperature, large yellow crystals separated. They were isolated, washed with dry n-hexane and dried at room temperature under reduced pressure. Yield 0.580 g (1.3 mmol of (I), 31%).

Method b)

COT (1.5 ml, 13 mmol) and $Ce(O\text{-}i\text{-}C_3H_7)_4\cdot Py$ (2.15 g, 4.7 mmol) were dissolved in a mixture of toluene (20 ml) and cycloheptatriene (7 ml) and allowed to react with $(C_2H_5)_3Al$ (2.5 ml, 18 mmol) at 110 °C for 24 h and then for further 10 h at 100 °C. When the reaction mixture was cooled to room temperature, a microcrystalline yellow product separated. It was collected, washed repeatedly with dry n-hexane and dried *in vacuo*. Yield 1.80 g (4.0 mmol of (I), 85%).

The product separated by crystallization from the reaction mixture contained an amount of toluene (25–30% by mol with respect to Ce) which could not be removed under reduced pressure. The quantity of solvent included into (I) crystals was independent of the method of synthesis, and was determined by quantitative VPC analysis on the hydrolysis products of (I).

Pure (I) was obtained by dissolving in acetonitrile at room temperature the crystals collected from the reaction mixture. Upon cooling down to −25 °C the acetonitrile solution (I) separated as yellow needles in the form of adduct with one mol of solvent (below). After drying at room temperature under reduced pressure, pure (I) was recovered as confirmed by elemental analysis. Found: C, 48.9; H, 7.2; Ce, 31.5; Al, 5.6. $C_{18}H_{32}O_2CeAl$ calcd.: C, 48.4; H, 7.2; Ce, 31.3, Al, 6.0%. The IR spectrum of (I) is reported in Fig. 1.

$(\eta^8\text{-}C_8H_8)Ce(\mu\text{-}O\text{-}i\text{-}C_3H_7)_2Al(C_2H_5)_2\cdot CH_3CN$ (II)

The recrystallization of (I) at −30 °C from CH_3CN solution and evaporation of the excess of solvent at −10 °C under reduced pressure for short times (*ca.* 15 minutes) yielded yellow needles of pure (II). *Anal.* Found: C, 49.2; H, 7.2; N, 2.7; Ce, 29.5. $C_{20}H_{35}O_2NCeAl$ calcd.: C, 49.2; H 7.2; N, 2.9; Ce, 28.7%. The IR spectrum of (II) is reported in Fig. 1.

Deuterolysis and Alcoholysis of (I)

0.50 g of pure (I) (1.19 mmol) was dissolved in dry diglyme (3 ml) and slowly decomposed by 0.4 ml of D_2O (22.2 mmol) dissolved in 2.4 ml of diglyme. The latter solution was added dropwise to the former one and both were maintained in a closed equipment connected to a gas burette. In 10 minutes were collected 50.2 ml of gas (at 0 °C and 760 mm Hg) equivalent to 2.24 mmol (yield = 95% with respect to (I)). Mass spectrometry analysis evidenced only the presence of C_2H_5D (m/e 31); neither $C_2H_4D_2$ nor HD were detected within the limits of sensitivity (5%) of the measurement.

VPC–MS analysis of the liquid phase of reaction showed only the presence of COT (m/e 104) and D_2-

COT (m/e 108) according to the molar ratio 20/80 (overall yield 90%).

Very similar results to the previous ones were obtained through alcoholysis of (I) with anhydrous isopropanol. In this case VPC–MS analysis evidenced only COT and H_2COT (m/e 104 and 106, respectively), their yields being the same as in deuterolysis experiments.

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