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NEW π-CYCLOOCTATETRAENYL AND π-CYCLOPENTADIENYL COMPLEXES OF CERIUM

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Summary

The reduction of $Ce(O\text{-}i\text{-}C_3H_7)_4$ by $(C_2H_5)_3Al$ in the presence of cyclooctatetraene (COT) yielded $(C_8H_8)_2Ce$ (I) or $(C_8H_8)_3Ce_2$ (II). An excess of COT was conducive to the formation of I, whereas controlled amounts of reagents were necessary to obtain II which was easily converted into I by an excess of COT. X-ray investigations, carried out on a single crystal of I, showed it to be isomorphous with $(C_8H_8)_2Me$, where Me = U or Th. I oxidized metallic K in monoglyme yielding the complexes $[K(monoglyme)]^+[(C_8H_8)_2Ce]^-$ (III) and $([K(monoglyme)]^+)_2[(C_8H_8)_2Ce]^{2-}$ (IV) in high yield. The reaction between $Ce(O\text{-}i\text{-}C_3H_7)_4$ and $(C_5H_5)_2Mg$ gave $(C_5H_5)_3Ce(O\text{-}i\text{-}C_3H_7)$ (V) in low yield; it was isolated by sublimation.

Introduction

Some complexes of cerium containing the cyclooctatetraene (COT) ligand have been described recently, for instance, $(K \cdot 2THF)^+[(\eta^8\text{-}C_8H_8)_2Ce]^-$ was obtained from the reaction of $CeCl_3$ with $K_2(C_8H_8)$ (molar ratio 1 : 2) in tetrahydrofurane (THF) [1]; when the reagents were in the ratio 1 : 1 the complex $[(\eta^8\text{-}C_8H_8)CeCl \cdot 2THF]_2$ resulted [2]. However, the ether in the ionic complex can be replaced by other donor molecules of suitable basicity applied in the necessary concentration. In the presence of diglyme the complex $[K(diglyme)]^+[(\eta^8\text{-}C_8H_8)_2Ce]^-$ has been isolated [3] and both its structure and that of $(\eta^8\text{-}C_8H_8)CeCl \cdot 2THF$ [4] have been elucidated by X-ray investigations. According to these studies the complexes contain the COT molecule as a planar ligand centered on the metal. In particular, in the complex $[K(diglyme)]^+[(\eta^8\text{-}C_8H_8)_2Ce]^-$ the potassium cation is coordinated both to the oxygen atoms of diglyme and to one of the COT molecules, while the anion is a sandwich complex of Ce with the two eight-membered rings in a staggered arrangement (D_{8d} symmetry).

More recently the complex $(C_5H_5)Ce(C_8H_8)$, containing one cyclopentadienyl and one cyclooctatetraenyl ligand has been synthesized, but structural data have not yet been published [5]. Very likely it has a sandwich structure, similar to that postulated for $(C_5H_5)Ln(C_8H_8)$ (where Ln = Yb, Sm, Ho) [6] which implies complete filling of the 4*f* orbital and the presence of 5 electrons in the 5*d* orbital; it would then be likely to form labile adducts with Lewis bases.

In this paper we report the synthesis and characterization of new complexes of Ce containing the COT ligand. They were obtained by treating $Ce(OR)_4$ [7] and $(C_2H_5)_3Al$ in the presence of COT, according to the procedure described by Wilke [8] for $(C_8H_8)_3Ti_2$ and other transition metal complexes containing COT ligands.

In principle we thought it feasible to attempt the synthesis of Ce complexes containing the COT (and also the cyclopentadienyl ligand) in such numbers as to give a range of electronic situations at the Ce atom, from incomplete 4*f* and 5*d* orbitals (e.g., the complex $(C_5H_5)Ce(C_8H_8)$) to complete saturation (e.g., the dianion $[(C_8H_8)_2Ce]^{2-}$, not yet described).

Results and discussion

When a solution of $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ [7] in pure COT was allowed to react with an excess of $(C_2H_5)_3Al$ at 140°C for 1 h, black needles of $(C_8H_8)_2Ce$ (I) separated on cooling (eq. 1). The product I is sparingly soluble in aromatic hydrocarbons, chlorinated aromatic hydrocarbons and ethers (THF, mono- and diglyme) giving red-brown solutions. In the presence of oxygen I reacts immediately (pyrophoric), but it is relatively stable in deaerated water (slow decomposition). As is shown in Fig. 1, the IR spectrum of I has two strong absorption bands at 692 and 902 cm^{-1} and weak absorptions at 1325, 1640 and 1790 cm^{-1}. These bands are typical of the COT ligands when they have aromatic character (i.e., π-bonded C_8H_8 rings) as occurs in the series of $KLn(C_8H_8)_2$ complexes [9]. The same conclusion is drawn from the ^1H NMR spectrum of I which consists of a single sharp signal at δ 5.6 ppm. Hence all the protons of I are in the same electronic situation.

$$Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH + 5(C_2H_5)_3Al \xrightarrow[\text{65\% yield}]{C_8H_8,\ \text{excess}}$$

$$\underset{\text{(I)}}{(C_8H_5)_2Ce} + 5(C_2H_5)_2Al(O\text{-}i\text{-}C_3H_7) + C_2H_6 + 4C_2H_5^{\cdot} \qquad (1)$$

I gives a clean mass spectrum with the parent peak at *m/e* 348, in agreement with a cerium atom binding two COT moieties.

Preliminary X-ray studies carried out on a single crystal of I reveal that it is isomorphous with $(\eta^8\text{-}C_8H_8)_2U$ and $(\eta^8\text{-}C_8H_8)_2Th$ [10] (see Table 1). Therefore, the structural situation found in $(C_8H_8)_2Ti$ [11], where the carbon atoms of one COT ligand are not the same distance from the metal atom, can be excluded for the molecule of I. On the basis of crystallographic and spectroscopic evidences here reported we believe that two η^8-cyclooctatetraenyl rings are coordinated by Ce in complex I. When reaction 1 is carried out at lower temperatures (110—115°C) in cycloheptatriene as solvent and at a molar ratio $C_8H_8/Ce \leqslant 5$, a green micro-

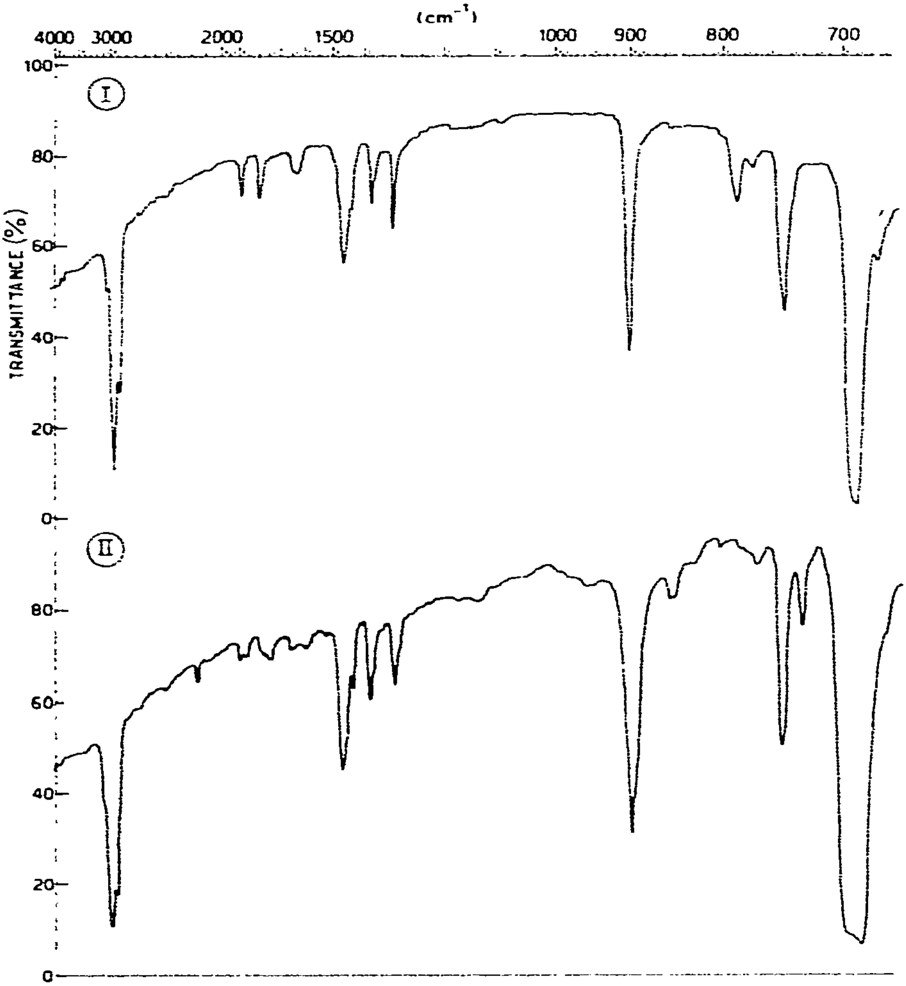

Fig. 1. IR spectra of $(C_8H_8)_2Ce$ (I) and $(C_8H_8)_3Ce_2$ (II).

crystalline powder can be recovered which corresponds to a new COT-cerium derivative (II, eq. 2).

$$2\ Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH + 10\,(C_2H_5)_3Al + 3\ C_8H_8 \xrightarrow[67\%\ \text{yield}]{30\ \text{min}}$$

$$\underset{(II)}{(C_8H_8)_3Ce_2} + 10\,(C_2H_5)_2Al(O\text{-}i\text{-}C_3H_7) + 2\ C_2H_6 + 8\ C_2H_5^{\bullet} \qquad (2)$$

It may be surprising that cycloheptatriene (CHT) does not participate in reaction 2 but evidently the coordination ability of COT is much greater than that of CHT; complex II can also be obtained in good yield by using toluene as solvent. On the other hand, CHT does not behave as an inert medium in the absence of COT since when CHT is used instead of COT in reaction 1 a black amorphous powder can be isolated. This insufficiently-characterized product

TABLE 1

COMPARISON OF STRUCTURAL DATA OF I WITH THOSE OF $(COT)_2U$ AND $(COT)_2Th$

	I [a]	$(COT)_2U$ [b]	$(COT)_2Th$ [b]
a (Å)	7.10	7.084	7.058
b (Å)	8.82	8.710	8.819
c (Å)	10.76	10.631	10.704
β (°)	97.9	98.75	98.44
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Molecules/unit cell	2	2	2

[a] Unrefined data. [b] Ref. 10. b.

contained CHT ligand and gave reproducible IR spectra with two strong bands at 715 and 810 (br) cm^{-1}. These absorptions might be attributed to η^7-C_7H_7 ligands bonded to the Ce atom [12], rather than to the homotropylium ligand [13].

Complex II is highly sensitive to oxygen and is immediately decomposed by deaerated water or alcohols; its very low solubility in organic solvents and its microcrystalline nature frustrate attempts to characterize it through ^1H NMR spectroscopy and X-ray diffraction (single crystal investigations).

The mass spectra of II indicate that elimination of the $(C_8H_8Ce)^+$ fragment occurs under the conditions employed (200—270°C, 10^{-6} Torr). The absence of ions from further degradation of $(C_8H_8Ce)^+$ might be interpreted in terms of a possible dismutation of II into I and formation of polymeric nonvolatile $[(C_8H_8)Ce]_n$.

The IR spectra of II suggests the existence of two different types of cyclooctatetraene rings in the complex. In fact, the out-of-plane bending band due to C—H (between 680 and 690 cm^{-1}) and the band due to benzenoid systems (in the region 1600—1910 cm^{-1}) are split into two components (Fig. 1). Since the IR spectra are rather simple and contain sharp bands, one can rule out the polymeric form of II. Also the rearrangement of one molecule of COT to dipentalene, which can be coordinated by transition metals [14], is excluded by the lack of any band near 800 cm^{-1}. However, the different compositions of complexes I and II are clearly confirmed by their X-ray powder spectra which are compared in Table 2.

We suggest that the structure of II may involve two external planar rings of COT centered on each atom of Ce, while the third molecule of COT is arranged between the two metal atoms, each of which receives 5 electrons from the central molecule of COT. Hence, each atom of Ce should accomodate 15 electrons in its $4f$ and $5d$ orbitals so that II would be isoelectronic with $(C_5H_5)Ce(C_8H_8)$. As further support of our conclusion, we cite the almost quantitative conversion of II to I when the former is heated in an excess of COT at 140°C and in the presence of catalytic amounts of $(C_2H_5)_3Al$.

Both I and II yield a mixture of cyclooctatrienes (1,3,6- and 1,3,5-isomers) and minor amounts of COT (overall yield ca. 85%; C_8H_{10}/C_8H_8 ca. 80/20) when treated with anhydrous isopropanol. Neither cycloheptatriene nor cycloheptadiene were detected in the alcoholysis products of II, thus confirming that cycloheptatriene (the possible solvent of reaction 2) did not participate in the formation of complex II.

TABLE 2

X-RAY POWDER DATA OF COMPLEX I AND II [a]

I	d (Å)	II	d (Å)
s	6.748	s	8.539
s	6.211	vw	7.637
s	5.451	vw	6.810
vw	4.608	vs	6.211
vw	4.353	s	5.277
ms	4.020	w	4.662
ms	3.581	w	4.356
vw	3.336	vw	4.009
w	3.238	vw	3.745
vw	3.124	w	3.562
ms	2.976	vw	3.370
w	2.812	vw	3.278
ms	2.724	ms	3.128
w	2.649	vw	3.018
w	2.553	w	2.887
ms	2.461	ms	2.795
w	2.345	w	2.665
ms	2.248	w	2.541
w	2.196	vw	2.452
w	2.073	ms	2.297
w	2.024	vw	2.208
		v	2.138
		vw	2.068

[a] Visually estimated intensities reported as: vs = very strong, s = strong, m = medium, ms = medium strong, mw = medium weak, w = weak, vw = very weak.

It is worth noting the analogous chemical behaviour of COT derivatives of Ti and Ce. In fact, these metals yield complexes with different stoichiometries, i.e. $(C_8H_8)_2Me$ and $(C_8H_8)_3Me_2$ [8,11]: all the complexes furnish the hydrogenated ligand (C_8H_{10}) after alcoholysis, but it is only the prevalent component in the case of Ce derivatives. In the alcoholysis products of $(C_8H_8)_2Ti$ the molar ratio C_8H_{10}/C_8H_8 is reversed and was found to be ca. 0.5. These results support an ionic interaction between ligand and metal, strongest in the case of the Ce complexes.

Since I needs two electrons to reach saturation of the 4*f* and 5*d* orbitals of Ce, it is able to oxidize metallic K yielding III (eq. 3), which is similar to $[K(diglyme)]^+[(C_8H_8)_2Ce]^-$ [1], when the ratio I/K is 1 : 1. The yield of III was

$$(C_8H_8)_2Ce + K \xrightarrow[\text{monoglyme}]{30^\circ C} \underset{\text{(III)}}{[K(monoglyme)]^+[(C_8H_8)_2Ce]^-} \qquad (3)$$

almost quantitative after 30 minutes: III appeared as a green crystalline product and its structure was confirmed by comparing its analytical and spectroscopic data with those of $[K(diglyme)]^+[(C_8H_8)_2Ce]^-$ [9]. In fact, in the IR spectrum of III there are absorption bands due to planar C_8H_8 ligands (680, 895, 1590, 1730, 1840 cm^{-1}) and to the ether ligand (1085, 1130, 1320 cm^{-1}).

The pathway of reaction (3) must be rather complicated since the red-brown colour of the monoglyme solution of I changes to light green when the ratio I/K is 2 : 1. A homogeneous olive green solution is also obtained when I is treated with an excess of K. After removal of the excess of K and concentration of the monoglyme solution, a new microcrystalline green complex IV is obtained in good yield (eq. 4). The IR spectrum of IV is very similar to that of III in the

$$(C_8H_8)_2Ce + 2K \xrightarrow[\text{monoglyme}]{30^\circ C} ([K(\text{monoglyme})]^+)_2[(C_8H_8)_2Ce]^{2-} \qquad (4)$$

(IV)

region of absorptions due to C_8H_8 ligands (682, 887, 1600, 1730, 1830 cm^{-1}), whereas the bands due to the monoglyme ligand (1080, 1128, 1195 cm^{-1}) are more intense in the case of IV. The lack of volatility of IV and III ruled out mass spectrometry measurements.

The dianionic nature of the dicyclooctatetraene complex in the molecular structure of IV seems likely on the basis of the experimental conditions under which the compound is obtained (i.e., with an excess of metallic K) and by taking into account the formal electron saturation of the outer orbitals of the Ce atom ($4f^{14}$, $5d^{10}$) in IV. It is interesting to observe that I can be obtained according to eq. 1 by reducing other Ce compounds, e.g. $Ce(Acac)_3$ but in this case the final product is accompanied by a greater amount of impurities. A general advantage in using $Ce(OR)_4$ compounds in organometallic syntheses stems from their high solubility in hydrocarbon solvents. Their versatility is exemplified by the synthesis of the new complex $(C_5H_5)_3CeO\text{-i-}C_3H_7$ (V) which has been accomplished according to eq. 5. V can be recovered by sublimation from

$$3\,(C_5H_5)_2Mg + 2\,Ce(O\text{-i-}C_3H_7)_4 \xrightarrow[20^\circ C]{\text{Benzene}}$$

$$2\,(C_5H_5)_3CeO\text{-i-}C_3H_7 + 3\,Mg(O\text{-i-}C_3H_7)_2 \qquad (5)$$

(V)

the reaction mixture at 170°C, but only in very low yield (<5%). Attempts to isolate pure V from the reaction mixture by extraction with aliphatic solvents were unsuccessful. V appeared as black microcrystals and was characterized through elemental analysis, mass spectrometry, IR and ^{1}H NMR spectroscopy. Absorption bands, typical of π-C_5H_5 ligands bonded to lanthanides [15] have been observed at 770, 985, 1320 cm^{-1}. The ^{1}H NMR spectra showed a sharp singlet at δ 5.68 ppm, due to the 15 protons of the cyclopentadienyl rings, a doublet at δ 1.36 ppm (J 6 Hz) due to the six protons of the methyl groups, and a septet centered at δ 6.15 ppm due to the methine of the isopropyl group. These observations are in agreement with the assigned structure.

Eq. 5 appears to afford a feasible route to other tricyclopentadienyl monoalkoxy derivatives of Ce which have not been described so far, whereas other complexes having the general formula $(C_5H_5)_3CeX$ (where X = alkyl, BH_4, CN, CNS) have been obtained recently and seem rather stable [16].

Attempts to synthesize $(C_5H_5)_4Ce$ [17] according to eq. 5 and sublimation from the reaction mixture were unsuccessful, perhaps because of the lower thermal stability of $(C_5H_5)_4Ce$ compared to that of V. Indeed the stability of $(C_5H_5)_3CeO\text{-i-}C_3H_7$ is rather peculiar if one bears in mind that dimeric $[(C_5H_5)_2LnX]_2$ (where X = phenoxy or carboxylate and Ln = Sm, Eu, Gd, Dy, Er, Yb, Lu) exhibit noticeable weakness in the Ln-X bond [18].

Experimental

Procedure and materials

All experiments were carried out under dry nitrogen. Solvents were purified by conventional methods and freed from oxygen and moisture by distillation from NaH under nitrogen. Dimethoxyethane (monoglyme, Fluka) was freshly distilled from $LiAlH_4$. Cycloheptatriene and cyclooctatetraene (both Fluka products) were used after flash-distillation. $(C_2H_5)_3Al$ (Schuchardt) was employed as received. $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ was prepared according to ref. 5, while $(C_5H_5)_2Mg$ was obtained from magnesium metal and cyclopentadiene [19]. $(C_8H_8)_2Ti$ was prepared as previously described [8].

Chemical analyses and physico-chemical measurements

Because of the instability to moisture of the complexes described in this paper, samples for C—H analysis were sealed and weighed in thin-walled capillaries under dry nitrogen. The results reported for each compound are the average of at least two determinations. Ce and K were determined, after attack of the complex with conc. H_2SO_4, by titration with 0.02 *N* $FeSO_4$ solution and by atomic absorption (Perkin—Elmer instrument, mod. 303), respectively.

Alcoholysis reactions were carried out on weighed samples of I or II (60—80 mg) placed in a flask connected with a reservoir containing an excess of anhydrous isopropanol (1 ml). The mixture was allowed to react at room temperature overnight. The reaction products were analyzed by VPC (Erba Fractovap BF instrument; column: carbowax 1500, 3 m; carrier: He, 150 ml/min; $T = 93°C$) and quantitatively determined by making reference to synthetic mixtures.

Mass spectra were measured with a LKB 9000 Mass Spectrometer by direct probe insertion at 70 eV and with a source temperature of 200—270°C. IR spectra were recorded on a Perkin—Elmer model 157 spectrometer from nujol mulls. ^1H NMR spectra were obtained from a Varian mod. HA-100 instrument (in benzene-d_6, at room temperature; reference to HMDS). A Siemens AED diffractometer, using Zr-filtered Mo-K_α radiation, was used to determine the cell dimensions of I from Weissenberg photographs obtained from a single crystal sealed in a thin-walled glass capillary. X-ray powder patterns were collected by a Debye—Scherrer camera (Cu-K_α radiation).

$(C_8H_8)_2Ce$ (I)

To a solution of 1.1 g of $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ (2.53 mmol) in 5.5 ml of COT (47.6 mmol) were added, at room temperature, 11.65 mmol of pure $(C_2H_5)_3Al$ (1.4 ml) with stirring. The mixture was then slowly heated up to 140°C and maintained at this temperature for 2 h. After cooling slowly (14 h) to room temperature, black crystals (red-violet powder) separated. The supernatant red-brown solution was decanted and the crystalline product was repeatedly washed with dry n-hexane and dried under reduced pressure at room temperature. Yield of pure I 0.58 g (0.167 mmol, 66%). (Found: C, 54.7; H, 4.9; Ce, 39.9%. $C_{16}H_{16}Ce$ calcd.: C, 55.1; H, 4.6; Ce, 40.3%.) The mass spectrum of I showed the parent ion at *m/e* 348 and peaks at *m/e* 244 $(M^+ - C_8H_8)^+$ and 140 $(M^+ - C_{16}H_{16})^+$. The IR spectrum showed the main bands at 692vs, 746m, 790w, 902s, 1325w, 1640w, 1790w, 1890w cm^{-1}.

The ^1H NMR spectrum showed a sharp singlet at δ 5.6 ppm. Crystals suitable for X-ray determinations were obtained directly by slow cooling of the reaction mixture or by recrystallization of I from COT or toluene. The X-ray powder data of I are collected in Table 2.

$(C_8H_8)_3Ce_2$ *(II)*

COT (1.7 ml, 14.75 mmol) and $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ (1.3 g, 2.98 mmol) were dissolved in 15 ml of CHT and $(C_2H_5)_3Al$ (1.9 ml, 14.0 mmol) was added with stirring. The yellow solution was slowly heated up to 110—115°C until the colour of the reaction mixture turned to green. Within 30 min a microcrystalline green product separated. The reaction products were cooled to room temperature and the green crystals were separated and washed with dry n-hexane. Pure II was dried under reduced pressure. Yield 0.570 g (0.96 mmol, 67%). (Found: C, 49.5; H, 4.3; Ce, 47.2. $C_{24}H_{24}Ce_2$ calcd.: C, 48.6; H, 4.1; Ce, 47.3%.) The mass spectrum showed ions at *m/e* 348 $(M^+ - C_8H_8Ce)^+$. The main bands in the IR spectrum were at 588sh, 592vs, 747m, 900s, 1325w, 1600w, 1660w, 1740w, 1780w, 1860w, 1910w cm^{-1}. The product II can be obtained in the yield reported above when toluene is used as solvent instead of CHT. The X-ray powder data of II are reported in Table 2.

Conversion of II into I

II (0.200 g, 0.58 mmol) and $(C_2H_5)_3Al$ (0.05 ml, 0.37 mmol) were dissolved in an excess of pure COT (4 ml, 34.8 mmol). The initially green solution was heated with stirring up to 130°C for 1 h when it turned red-brown. After cooling, black crystals separated from the reaction mixture. They were identified as I by elemental analysis (Found: C, 53.1; H, 4.6. $C_{16}H_{16}Ce$ calcd.: C, 54.7; H, 4.9%), IR spectroscopy and X-ray powder data (see Table 2).

Reaction of $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ *with CHT*

$Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ (0.710 g, 1.63 mmol) was allowed to react with an excess of CHT (8 ml, ca. 80 mmol) in the presence of $(C_2H_5)_3Al$ (1.9 ml, 14.0 mmol). The reaction mixture was heated up to 120°C and maintained at this temperature for 2 h. A light, amorphous and dark powder separated progressively. It was collected, washed with dry n-pentane and dried. The product was practically insoluble in all common solvents. Yield: 0.25 g. The elemental analysis data were reproducible (Found: C, 42.7; H, 5.0; Ce, 52.1%), but did not agree with a simple structure involving the Ce atom and the cycloheptatrienyl ligand. However, it was ascertained that the product contained the CHT ligand (a mixture of cycloheptadiene/cycloheptatriene 65 : 35 was established through VPC/MS measurements in the alcoholysis products). The IR spectrum showed main bands at 690sh, 715s, 760sh, 830m, 910s, 960m, 1125w, 1570vw and 1670vw.

Alcoholysis of I and II

Both I and II gave, by alcoholysis with anhydrous isopropanol, cyclooctatetraene and a mixture of cyclooctatrienes (1,3,5- and 1,3,6-isomers, identified by VPC and mass-spectrometry fragmentation). The overall yield from I was 87% (25% of C_8H_8 and 75% of C_8H_{10}). Similarly II gave 20% of C_8H_8 and 80%

of C_8H_{10} (overall yield 80%). Neither cycloheptadiene nor cycloheptatriene were found in the alcoholysis products of II. A sample of $(C_8H_8)_2Ti$ alcoholysed under the same conditions yielded 66% of C_8H_8 and 33% of C_8H_{10} (overall yield 85%).

$[K(monoglyme)]^+[(C_8H_8)_2Ce]^-$ (III)

I (0.35 g, 1 mmol) was dissolved in monoglyme (15 ml) and sand of potassium metal (0.048 g, 1 mg-atom) was added to the black solution. After 30 min stirring at 30° C, K dissolved completely and the reaction mixture became green. The solution was concentrated under reduced pressure to 5 ml. On adding dry n-pentane bright green microcrystals separated. Yield of pure III 0.40 g (0.84 mmol, 84%). (Found: C, 50.8; H, 5.5; K, 8.5. $C_{20}H_{26}O_2CeK$ calcd.: C, 50.3; H, 5.5; K, 8.2%.) The IR spectrum showed main bands at: 682vs, 742m, 895vs, 1085m, 1130m, 1320m, 1590w, 1730w, 1840w cm^{-1}.

$([K(monoglyme)]^+)_2[(C_8H_8)_2Ce]^{2-}$ (IV)

I (0.58 g, 1.66 mmol) dissolved in 25 ml of monoglyme was allowed to react with sand of potassium metal (0.150 g, 3.84 mg-atom) at 60° C for 1 h. The colour of the reaction mixture turned to dark green while the excess of unreacted K was removed by filtration. The recovered solution was concentrated to 10 ml and, on adding a few ml of n-pentane, an olive-green microcrystalline powder separated. After repeatedly washing with n-pentane and drying, the product was identified as pure IV: yield 0.50 g (0.83 mmol, 50%). (Found: C, 48.1; H, 6.1; Ce, 22.8; K, 12.9. $C_{24}H_{36}O_4K_2Ce$ calcd.: C, 47.5; H, 5.9; Ce, 23.1; K, 12.9%.) The IR spectrum showed main bands at 682vs, 852s, 887vs, 1030m, 1080vs, 1128s, 1195m, 1600w, 1730w, 1830w cm^{-1}.

$(C_5H_5)_3Ce(O\text{-}i\text{-}C_3H_7)$ (V)

$(C_5H_5)_2Mg$ (0.320 g, 2.1 mmol) was allowed to react with $Ce(O\text{-}i\text{-}C_3H_7)_4 \cdot i\text{-}C_3H_7OH$ (0.590 g, 1.3 mmol) in benzene (10 ml) at room temperature for 4 h. The solvent was evaporated under reduced pressure and the crude residue was sublimed in high vacuum at 150° C. V was recovered as black microcrystals (0.020 g, 0.051 mmol, 4%). (Found: C, 55.7; H, 6.0. $C_{18}H_{22}OCe$ calcd.: C, 54.8; H, 5.6%.) The mass spectrum showed the parent peak at *m/e* 394 (M^+) and ions at *m/e* 334 $(M - C_3H_7OH)^+$, 329 $(M - C_5H_6)^+$, 270 $(M - C_5H_6 - C_3H_7O)^+$, 264 $(M - C_{10}H_{10})^+$, 205 $(M - C_{10}H_{10} - C_3H_7O)^+$. The IR spectrum showed main bands at 770s, 840w, 985w, 1120w, 1130m, 1370w, 3100w cm^{-1}.

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