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ALKOXY DERIVATIVES OF CERIUM(IV)

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SUMMARY

Tricyclopentadienylcerium(IV) chloride (I) and tetracyclopentadienylcerium(IV) (II) react with primary and secondary alcohols ROH (R = Me, Et, Pr, i-Pr, Bu, i-Bu, i-C_5H_{11}) in benzene to give (π-C_5H_5)$_3$Ce(OR) compounds. Infrared and some physical characteristics of all products are reported.

INTRODUCTION

Alkoxy derivatives of π-cyclopentadienyltitanium[1,2],-zirconium[3], -uranium and -thorium[4], -molybdenum[5,6] and -tungsten[7,8,9] complexes are known. Tetraalkoxycerium(IV)[10] and its chloroderivatives[11] have already been reported but there is no reference in the literature to cyclopentadienyl compounds of cerium(IV) containing alkoxy groups. This paper deals with the preparation and properties of such complexes of general formula $(C_5H_5)_3Ce(OR)$ obtained from reactions of tricyclopentadienylcerium(IV) chloride (I) and tetracyclopentadienylcerium(IV), with various primary and secondary alcohols in benzene as shown in the following equations:

$$(C_5H_5)_3CeCl + ROH \rightarrow (C_5H_5)_3Ce(OR) + HCl$$

$$(C_5H_5)_4Ce + ROH \rightarrow (C_5H_5)_3Ce(OR) + C_5H_6$$

(R = Me, Et, Pr, i-Pr, Bu, i-Bu, i-C_5H_{11})

EXPERIMENTAL

All reactions were carried out under anhydrous conditions. Dry alcohols were further purified by azeotropic distillation in presence of benzene. Benzene, dried over and distilled initially from sodium and then from phosphorus pentoxide, was also purified by azeotropic distillation. Depolymerised cyclopentadiene obtained from its dimer was used to prepare sodium cyclopentadienide[12]. Tetracyclopentadienylcerium(IV) and tricyclopentadienylcerium(IV) chloride[13,14] were prepared by treating dipyridinium cerium(IV) hexachloride with sodium cyclopentadienide. Tricyclopentadienylcerium(IV) chloride was also prepared by treating dipyridinium cerium(IV) hexachloride with tetracyclopentadienylcerium(IV) in tetrahydrofuran.

Cerium was estimated as its 8-hydroxyquinolinate, the alkoxy groups (OMe, OEt and O–i-Pr in the products were determined by the chromic acid method[15,16].

Preparation of tricyclopentadienylalkoxycerium(IV) compounds

A mixture of 1.86 g (0.005 mole) of tricyclopentadienylcerium(IV) chloride, dry methanol (30 ml) and dry benzene (50 ml) was stirred for 1–2 h and the refluxed at 75° for 5–6 h. The solution was filtered through a G-4 sintered glass disc and the residue was washed with benzene. The filtrate together with the washings were evaporated to dryness under reduced pressure (20–25 mm) leaving a dark brown paste which on repeated washing with petroleum ether (60–80°) and subsequent drying under reduced pressure gave a brown compound of formula $(C_5H_5)_3CeOMe$.

Properties and analytical data for higher alkoxy derivatives of tricyclopentadienylcerium(IV) chloride, prepared analogously from the appropriate alcohol under similar conditions but at higher temperatures, are given in Table 1.

Preparation of tricyclopentadienylalkoxycerium(IV) compounds

Tetracyclopentadienylcerium(IV), 2 g (0.005 mole) in benzene (40 ml), was added to dry ethanol (25 ml). The mixture was refluxed for 8–9 h at 80–85° and the volatile constituents were distilled out azeotropically, leaving a dark brown pasty mass which on repeated washing with hot petroleum ether and subsequent drying under reduced pressure gave a chocolate brown product of formula $(C_5H_5)_3CeOEt$.

Methoxy and higher alkoxy derivatives of tetracyclopentadienylcerium(IV) were prepared by from the appropriate alcohols under similar conditions and their characteristics and analytical data are given, in Table 1.

TABLE 1

ANALYTICAL DATA AND CHARACTERISTICS OF $(C_5H_5)_3Ce(OR)$

Compound colour	*Yield*	*Time of reaction (h)*	*Analysis, found (calcd)*	
			Cerium	*OR*
$(C_5H_5)_3Ce(OCH_3)$ brown	40	6	38.0 (38 24)	8 3 (8 47)
$(C_5H_5)_3Ce(OC_2H_5)$ chocolate brown	50	8–9	36 6 (36 83)	11 7 (11 93)
$(C_5H_5)_3Ce(O\text{-}nC_3H_7)$ brownish black	55	9	35 25 (35.52)	
$(C_5H_5)_3Ce(O\text{-}i\text{-}C_3H_7)$ brown	45	12–13	35 3 (35 52)	14 7 (14 97)
$(C_5H_5)_3Ce(O\text{-}n\text{-}C_4H_9)$ brown	50	12	34 15 (34 30)	
$(C_5H_5)_3Ce(O\text{-}i\text{-}C_4H_9)$ dark brown	40	9	34 1 (34 30)	
$(C_5H_5)_3Ce(O\text{-}i\text{-}C_5H_{11})$ coffee brown	50	7	33 0 (33 16)	

RESULTS AND DISCUSSION

The infrared spectra of the above compounds were recorded using KBr pellets, nujol mull or in thin layer on a Perkin–Elmer Model 137 Spectrophotometer at 4000–670 cm^{-1}. The cyclopentadienyl group exhibited characteristic C–H stretching at ≈3010 cm^{-1}, C–C stretching bands at 1480–1420 cm^{-1}, C–H in-plane bending at ≈1035 cm^{-1} and C–H out-of-plane bending at ≈840 cm^{-1}. The vibrational bands, at about 1190 cm^{-1} are attributable to methoxy, at 1170 cm^{-1} to ethoxy and at 1110 and 1150 cm^{-1} to isopropoxy groups while the bands at 1100 and 1150–1170 cm^{-1} are characteristic of butoxy groups and those at 1100 and 1050 cm^{-1} of the isopentyloxy groups[17,18]. The bands at 1610–1660 cm^{-1} are probably associated with the C–O linkage of the alkoxy groups.

The products are generally brown, extremely sensitive to moisture, but stable in a dry inert atmosphere. They are soluble in tetrahydrofuran, dioxane and halogenated solvents but insoluble in water, being readily hydrolysed on heating or treatment with dilute acids and alkalies. They are non-volatile and do not sublime *in vacuo*. The methoxy, ethoxy and isopropoxy derivatives turn chromic acid solution (12% H_2SO_4, 1 N $K_2Cr_2O_7$) green.

Infrared spectra, physical properties and elemental analysis are compatible with the formulae $(C_5H_5)_3Ce(OR)$ for these compounds where R is Me to n-C_5H_{11}. The infrared spectra of compounds also suggest that the linkage between the cyclopentadienyl rings and the metal atom retains the character of delocalized π-bonds while the alkoxy groups are probably attached to the metal atom by σ bonds.

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