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TETRACYCLOPENTADIENYL AND TETRAINDENYL COMPOUNDS OF CERIUM(IV)

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SUMMARY

Interaction of $(C_5H_6N)_2CeCl_6$ with the sodium salt of cyclopentadiene or indene in tetrahydrofuran gives tetracyclopentadienylcerium or tetraindenylcerium. The IR spectra and other properties indicate that the hydrocarbon ligands are covalently bonded in these compounds.

INTRODUCTION

Though studies of tricyclopentadienylcerium(III)[2] and of dicyclopentadienylcerium(III) chloride and its derivatives[3] have been reported, no cyclopentadienyl and indenyl compounds of cerium(IV) have been described. This may be because cerium(IV) compounds are not stable, but while $CeCl_4$ is unstable its dipyridinum complex[1] is stable and Bradley *et al.*[4] have prepared cerium(IV) alkoxides from it.

We describe below the preparation of tetracyclopentadienylcerium and tetraindenylcerium by treatment of dipyridinium cerium hexachloride[1] with sodium cyclopentadienide or sodium indenide in tetrahydrofuran.

EXPERIMENTAL

Operations were carried out under anhydrous conditions and at reduced pressure. Solvents were dried and purified before use. A good grade of tetrahydrofuran was further purified by distallation in presence of $LiAlH_4$. $(C_5H_6N)_2CeCl_6$ was prepared as previously described[1]. Freshly depolymerized cyclopentadiene and indene were used for the preparation of their sodium salts. Infrared spectra were recorded on a Perkin–Elmer Model 137 spectrophotometer in KBr or chloroform. Cerium was determined as 8-hydroxyquinolate, while carbon and hydrogen were estimated by the usual microanalytical methods.

Preparation of tetracyclopentadienylcerium

To $(C_5H_6N)_2CeCl_6$, (2.6 g, 0.005 mole) in tetrahydrofuran (120 ml) was added sodium cyclopentadienide (0.025 mole) in tetrahydrofuran (75 ml). The mixture was refluxed at 100–110° with vigorous stirring for 10–12 h until reddish brown product formed. The cooled mixture was filtered through G-4 sintered glass disc and the residue washed with tetrahydrofuran. The filtrate and the washings were evaporated almost to dryness under reduced pressure (5–10 mm) to leave a thick brown paste, which on crystallization from light petroleum (b.p. 60–80°) yielded a red-orange crystalline compound which corresponded to $(C_5H_5)_4Ce$ (65%). (Found: C, 59.80; H, 5.10; Ce, 34.50. $C_{20}H_{20}Ce$ calcd.: C, 59.97; H, 5.03; Ce, 34.98%.)

The product is quite stable, thermally and chemically but melts with decomposition at 225–226°. It is soluble in THF, dioxane, DMF, CH_2Cl_2, $CHCl_3$, CS_2, methanol, ethanol and acetic acid, less soluble in benzene, and CCl_4 and insoluble in toluene xylene, butanol and higher alcohols. The compound is unaffected by water and dilute acids, but is decomposed by concentrated HCl, H_2SO_4 and by dilute hot alkalies. It dissolves in concentrated nitric acid. Its IR spectrum shows the following frequencies: 3070 m, 2980 s, 1710 m, 1620 w, 1440 s, 1370 m, 1160 m, 1050 m, 905 w, 860 m, 740 m, 690 m cm^{-1}.

Preparation of tetraindenylcerium

Tetraindenylcerium was prepared analogously, except that the reaction was carried out at 120–125° for 8–9 h, until production of a deep brown solid seemed complete. The red-brown compound was shown to be $(C_9H_7)_4Ce$ (40%). (Found: C, 71.8; H, 4.7; Ce, 23.2. $C_{36}H_{28}Ce$ calcd.: C, 71.97; H, 4.69; Ce, 23.32%.)

The product is quite stable thermally and chemically, but melts with decomposition at 136° (sharp). It is fairly soluble in acetone, dioxane, alcohol, DMF, benzene, CCl_4, $CHCl_3$, CH_2Cl_2, CS_2 and THF and less soluble in toluene, acetic acid and higher alcohols. It is unaffected by hot or cold water, and by dilute acids, but is decomposed by hot dilute alkalies and by concentrated hydrochloric acid. It dissolves in hot nitric acid. Its IR spectrum shows the following frequencies: 2980 m, 1770 s, 1620 m, 1460 m, 1380 w, 1220 w, 1150 w, 1050–1000 sh, 840 m, 750 s, 710 m cm^{-1} (where m = medium, w = weak, s = strong, sh = shoulder).

DISCUSSION

The cyclopentadienylcerium prepared by the interaction of dipyridinium cerium(IV) hexachloride with sodium cyclopentadienide is thermally and chemically relatively stable, but decomposes at 225°. Dilute acids and alkalies do not destroy it, which suggests that it has characteristics similar to those of tetracyclopentadienyl compounds of transition metals[6-9]. Tetraindenylcerium has very similar properties, and resembles tetraindenyl compounds of other transition metals[10-11].

The formation of tetracyclopentadienyl- and tetraindenylcerium may be regarded as analogous to the formation of tetraalkoxides of cerium or tetracyclopentadienyl or tetraindenyl compounds of various transition metal atoms[5-9,10-11], and represented as follows:

$$(C_5H_6N)_2CeCl_6 + 4\ NaR \rightarrow Ce(R)_4 + NaCl + 2\ C_5H_5N \cdot HCl$$

$R = C_5H_5$ or C_9H_7

The IR spectrum of tetracyclopentadienylcerium shows the characteristic absorption peaks of the C_5H_5-group[12], *viz.* the frequencies at 3070, 2980 cm^{-1} (C–H stretching), 1440 cm^{-1} (C–C stretching) at 1160, 1050 cm^{-1} (C–H deformation) at 860 cm^{-1} (C–H out-of-plane deformation).

The IR spectrum of tetraindenylcerium shows the various absorption peaks due to phenyl group in addition to the usual C_5H_5 group frequencies[12], at 1380 cm^{-1} (C–H stretching), 1620 cm^{-1} (C–C stretching), and also at 710 cm^{-1}. (Indene itselfs shows[13] absorption band at 700 cm^{-1}.)

The IR spectrum of $(C_5H_5)_4Ce$ contains a band at 2980 cm^{-1}, in addition to the usual C–H stretching of C_5H_5 group at 3070 cm^{-1}, which indicates that the C_5H_5 rings may be covalently bonded[12] to the cerium atom. Further evidence for covalent character is that the complex reacts with dry HCl to give cyclopentadienylcerium trichloride; the properties are consistent with those reported for tetracyclopentadienyl compounds of Ti, Zr, Nb and tricyclopentadienyl compounds of Ti and V[6–8], and differ from those of tricyclopentadienylcerium[2] or tetracyclopentadienyluranium or -thorium[14], which are ionic in nature.

The bonding between the cerium atom and the idenyl groups in tetraindenylcerium can be regarded as analogous to that in $(C_5H_5)_4Ce$ (described above) or in triindenyl derivative of samarium(III)[15].

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