

## STUDIES ON DICYCLOHEPTATRIENYLCEERIUM(IV) DICHLORIDE

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### SUMMARY

The interaction of cycloheptatriene with dipyridiniumcerium(IV) hexachloride<sup>1</sup> in benzene yields dicycloheptatrienylcerium(IV) dichloride, in which cycloheptatriene is present as the cycloheptatrienyl anion and may be  $\pi$ -bonded. The preparation, properties and IR spectra of this compound are described.

### INTRODUCTION

Much work has been done on organometallic compounds containing tropyliene or substituted tropylienes complexed with the Group VIB elements, iron and vanadium<sup>2-7</sup>. Recently it has been shown that the direct interaction of cycloheptatriene with metal chlorides of Group IVB and VB and metal oxide chlorides of Group VIB elements gives substitution complexes of dicycloheptatrienylmetal chlorides or metal oxide chlorides with evolution of hydrogen chloride<sup>8</sup>. Although  $\text{CeCl}_4$  is unstable, its dipyridinium complex is sufficiently stable to be dried at  $120^\circ$  *in vacuo*. Cerium(IV) alkoxides<sup>9</sup>, tetracyclopentadienyl- and tetraindenylcerium<sup>10</sup>, have been prepared from this complex.

We describe below the preparation of dicycloheptatrienylcerium(IV) dichloride by treatment of dipyridinium cerium(IV) hexachloride with cycloheptatriene in benzene. The dark brown crystalline compound thus obtained is quite stable at ordinary temperature. It is soluble in common organic solvents and melts with decomposition at  $88^\circ$ .

### EXPERIMENTAL

All operations were carried out in dry nitrogen under anhydrous conditions. Dipyridinium cerium(IV) hexachloride was prepared by the method used by Bradley *et al.*<sup>1</sup>. All the solvents used were purified and dried by conventional methods. IR spectrum (in KBr) was taken on Perkin-Elmer Model-137 Spectrophotometer. Cerium was determined as 8-hydroxyquinolate, carbon and hydrogen were estimated by the usual microanalytical methods, and chloride was estimated as silver chloride.

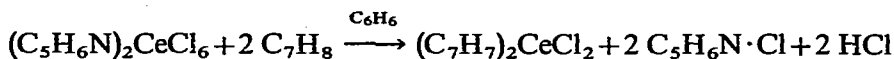
### Preparation of dicycloheptatrienylcerium(IV) dichloride

To 3.1 g (0.006 mole) of dipyridinium cerium(IV) hexachloride in 150 ml of dry benzene was added 1.2 g (0.013 mole) of cycloheptatriene. The mixture was refluxed until no more hydrogen chloride was evolved. The cooled contents were filtered through G-4 sintered glass disc and the residue was washed with dry benzene. The filtrate and the washings were evaporated under reduced pressure (30–35 mm). The thick brown paste on repeated crystallization from petroleum ether (60–80°) gave dark brown crystals of  $(C_7H_7)_2CeCl_2$ . (Found: C, 42.60; H, 3.5; Ce, 35.8; Cl, 18.1.  $C_{14}H_{14}CeCl_2$  calcd.: C, 42.75; H, 3.59; Ce, 35.62; Cl, 18.02%). Yield 50–52%, melts at 88° with decomposition. It is fairly soluble in acetone, dioxane, dimethylformamide, benzene, toluene, chloroform, dichloromethane, carbon disulphide, tetrahydrofuran, giving brown solutions, and partially soluble in carbon tetrachloride, acetic acid, and methanol, and is insoluble in xylene and higher alcohols. It is unaffected by cold or hot water or cold dilute acid, but decomposes in hot dilute alkalis and dissolves in hot nitric, sulphuric and hydrochloric acids. Its IR spectrum taken in KBr shows the following absorption peaks: 3000 vs, 1700 vw, 1670 w, 1650 w, 1625 (sh), 1600 (sh), 1570 w, 1560 m, 1550 m, 1530 m, 1510 m, 1460 s, 1425 (sh), 1370 s, 1160 w, 1020 vw, 720 vw.

### DISCUSSION

Dicycloheptatrienylcerium(IV) dichloride prepared by the interaction of dipyridinium cerium(IV) hexachloride and cycloheptatriene in benzene is quite stable. Dilute acids and alkalis do not react with it in the cold, indicating that the compound possesses characteristics analogous to  $(C_5H_5)_4Ce^{10}$ .

The preparation of dicycloheptatrienylcerium(IV) dichloride may be regarded as analogous to the preparation of dicycloheptatrienyl chlorides of Groups IVB, VB and metal oxide chlorides of Group VIB elements<sup>8</sup>.



Even in presence of excess cycloheptatriene not more than two chlorine atoms are replaced.

The IR spectrum of dicycloheptatrienylcerium(IV) dichloride shows absorption frequencies at  $3000\text{ cm}^{-1}$  (C–H stretching),  $1460\text{ cm}^{-1}$  (C–C stretching), at  $1160, 1020\text{ cm}^{-1}$  (C–H deformation) at  $1650, 1670\text{ cm}^{-1}$  (possibly C=C stretching) which indicate the probable presence of  $\pi$ -bonded  $C_7H_7^-$  groups analogous to  $\pi$ -cyclopentadienyl rings in  $(C_5H_5)_4Ce^{10}$  and other  $\pi$ -cyclopentadienyl transition metal complexes<sup>11–13</sup>.

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