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BOROHYDRIDE DERIVATIVES OF DICYCLOPENTADIENYL THALLIUM(III) AND DIINDENYLTHALLIUM(III)

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SUMMARY

Dicyclopentadienylthallium(III) chloride and diindenylthallium(III) chloride react with sodium borohydride in tetrahydrofuran to yield dicyclopentadienylthallium(III) borohydride and diindenylthallium(III) borohydride respectively. The IR spectra, thermal stabilities and some physical properties of the products are described.

INTRODUCTION

Thallium(I) borohydride[1,2] and chlorothallium(III) diborohydride[3] are known but there is no reference in the literature to the cyclopentadienyl compounds of thallium(III) containing borohydride groups. The present paper deals with the characterization of dicyclopentadienylthallium(III) borohydride and diindenylthallium(III) borohydride prepared by the reaction of dicyclopentadienylthallium(III) chloride and diindenylthallium(III) chloride with sodium borohydride in tetrahydrofuran.

$$(C_5H_5)_2TlCl + NaBH_4 \rightarrow (C_5H_5)_2TlBH_4 + NaCl$$
$$(C_9H_7)_2TlCl + NaBH_4 \rightarrow (C_9H_7)_2TlBH_4 + NaCl$$

Infrared studies reveal metal-to-boron bonding through hydrogen atoms of the BH_4^- radical.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Good quality tetrahydrofuran was further purified by distillation from lithium aluminium hydride. Infrared spectra (in KBr) were recorded on a Perkin–Elmer Model-137 spectrophotometer. Thallium was estimated as thallic oxide, and carbon and hydrogen by microanalytical methods, while the presence of cyclopentadienyl, indenyl and borohydride groups was inferred from infrared spectra.

Preparation of dicyclopentadienylthallium(III) borohydride

Sodium borohydride (0.15 g, 0.004 mol) was added to dicyclopentadienylthallium(III) chloride (1.48 g, 0.004 mole) in tetrahydrofuran (100 ml). The reaction mixture was stirred for 2–3 h and then refluxed for 8–10 h at 80–85°. The solution was filtered through a G-4 sintered glass disc and the residue was washed with tetrahydrofuran. The combined filtrate and washings, upon evaporation under reduced pressure (20 mmHg), yielded a dirty yellow paste which on further recrystallization from petroleum ether (60–80°) and subsequent drying under reduced pressure gave orange-yellow $(C_5H_5)_2TlBH_4$, yield 58%. (Found: C, 34.0; H, 3.9; Tl, 57.9; $C_{10}H_{14}BTl$ calcd.: C, 34.37; H, 4.04; Tl, 58.5%.)

The product is thermally stable up to 104° and is unaffected by water and alkali. It is soluble in methanol, ethanol, acetone, tetrahydrofuran and carbon disulphide but insoluble in benzene, toluene, CCl_4, $CHCl_3$, and CH_2Cl_2. Its IR spectrum shows the following frequencies: 3125 s, 2260 s, 2120 w, 1910 w, 1705 m, 1630 m, 1580 m, 1470 m, 1400 w, 1185 s, 1065 w, 1040 m, 1000 s, 910 w, 885 s, 745 m cm^{-1}.

Preparation of diindenylthallium(III) borohydride

Diindenylthallium(III) borohydride was prepared similarly, except that the reaction was carried out at 100–105° for 10–12 h until the reaction mixture became dark yellow. The orange-red product, $(C_9H_7)_2TlBH_4$, was obtained in 55% yield. (Found: C, 47.9; H, 3.84; Tl, 45.0; $C_{18}H_{18}TlB$ calcd.: C, 48.09; H, 4.04; Tl, 45.47%.)

The compound is thermally stable up to 195° and is unaffected by water and alkali. It is fairly soluble in $CHCl_3$, CH_2Cl_2, CS_2, DMF and THF and sparingly soluble in CCl_4 and alcohols but insoluble in benzene, toluene and xylene. Its IR spectrum shows the following frequencies: 3000 s, 2280 s, 2095 w, 1700 m, 1650 w, 1590 m, 1540 w, 1450 s, 1375 s, 1175 s, 1045 w, 970 w, 880 m, 765 w, 720 m, cm^{-1}.

DISCUSSION

The cyclopentadienyl group is characterised by a C–H stretching absorption at 3125 cm^{-1}, a C–C stretching band at 1470 cm^{-1}, C–H in-plane bending at 1065, 1045 cm^{-1} and C–H out-of-plane bending at 885 cm^{-1}. The indenyl group is indicated by the usual peaks of $C_5H_5^-$ group[4] as discussed above but additionally shows the peaks due to the phenyl part at 1375 cm^{-1} (C–H stretching), 1590 cm^{-1} (C–C stretching), at 765 cm^{-1} (C–H out of plane bending) and 720 cm^{-1} (methylene rocking vibration). Indene[5] itself shows an absorption band at ≈ 700 cm^{-1}.

The presence of the BH_4^- group is indicated by the strong absorption at ≈ 2300 cm^{-1} and ≈ 1175 cm^{-1} which may be due to B–H stretching (asymmetric) and BH_2 deformation respectively[6–9], while the bands at ≈ 2100 cm^{-1} and ≈ 1375 cm^{-1} may be due to vibrations of bridging hydrogen atoms[9,10]. Some of the absorptions in the region 1500–1100 cm^{-1} arising from the borohydride group may be obscured due to overlap with bands from cyclopentadienyl or indenyl group and therefore, in general, the band in the region ≈ 2100 cm^{-1} remains the most sensitive test for the presence of a hydrogen bridge between the metal and boron atom. The infrared spectra of dicyclopentadienylthallium(III) borohydride and diindenylthallium(III) borohydride clearly indicates the bond formation between the metal and boron atom through hydrogen analogous to the structure assigned to di-π-cyclopentadienylmetal mono- or di-borohydride derivatives of Group IV metals on the basis of infrared assignments as well as of nuclear magnetic resonance[9,10]. From the data it seems that the similar metal–hydrogen–boron bond formation may be involved in the compounds, dicyclopentadienylthallium(III) borohydride and diindenylthallium(III) borohydride, wherein the cyclopentadienyl as well as the indenyl radical retains delocalized π-bonds character.

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