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METAL TETRAHYDRIDOBORATES AND TETRAHYDRIDOBORATOMETALLATES

XIII *. NEW AND CONVENIENT SYNTHESES OF DICYCLOPENTADIENYLZIRCONIUM TETRAHYDRIDOBORATE

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Summary

Dicyclopentadienylzirconium bis(tetrahydridoborate) is obtained in high yield from dicyclopentadienylzirconium dihydride and diborane or catecholborane in tetrahydrofuran.

Introduction

Transition metal tetrahydridoborates are generally synthesized by metathesis of the corresponding halides with $LiBH_4$, $NaBH_4$ or $Al(BH_4)_3$ [2–5]. The search for a convenient route to tetrahydridoborates from B_2H_6 or $H_3B \cdot D$ ($D = THF$, NR_3) and a metal hydride has been focused on the metal hydrides of Main Group elements [6]. It was expected that this efficient method would also work with transition metal hydrides provided that they contain hydridic hydrogen. This report describes results obtained with dicyclopentadienylzirconium dihydride.

Experimental

All manipulations were carried out under rigorously dry conditions under dinitrogen using standard Schlenk tube and high vacuum techniques. Solvents were distilled from sodium/benzophenone ketyl and stored under dinitrogen. Commercially available catechol was sublimed in vacuo prior to use. Dicyclopentadienylzirconium dihydride [7], catecholborane and $BH_3 \cdot THF$ [8] were prepared according to literature procedures.

Nujol–Hostaflon mulls were used in recording IR spectra on a Perkin–Elmer 325 instrument, and NMR data were obtained using a VARIAN FT 80 or JEOL FX 90

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* For part XII see ref. 1.

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spectrometer. Chemical shifts are given relative to TMS (^1H, ^{13}C) and $BF_3 \cdot O(C_2H_5)_2$ (^{11}B).

Dicyclopentadienylzirconium bis(tetrahydridoborate)

(a) 4.4 ml of a 1.7 *M* solution of BH_3 in tetrahydrofuran (THF) was added dropwise to a stirred suspension of 670 mg Cp_2ZrH_2 (3 mmol) in 20 ml THF. All the material rapidly went into solution. After 1 h, only the ^{11}B NMR signals of the BH_4^- and the excess $BH_3 \cdot THF$ were observed, indicating quantitative formation of $Cp_2Zr(BH_4)_2$. The solvent was then removed in vacuo and the residue sublimed to give 505 mg $Cp_2Zr(BH_4)_2$ (67%) at 110°C/10^{-3} Torr.

(b) A well stirred slurry of 670 mg Cp_2ZrH_2 (3 mmol) in 5 ml THF (or toluene) was cooled to -60°C and 4.7 ml of a 0.77 *M* solution of catecholborane in THF was added. The mixture was then allowed to warm to room temperature. After stirring for an additional hour the insoluble material was filtered off and washed with 15 ml THF. After 3 h drying in vacuo a yield of 476 mg (75%) of dicyclopentadienylzirconium catecholate, dec.p. 344–346°C, was obtained. The combined filtrates were freed from solvent and excess catecholborane. Sublimation of the solid residue at 110°C/10^{-3} Torr gave 221 mg $Cp_2Zr(BH_4)_2$ (88%).

IR, ^1H and ^{11}B NMR data for $Cp_2Zr(BH_4)_2$ agreed precisely with literature values [9,10,11]; $\delta(^{13}C)$ 114.1 ppm (in C_6D_6). Analysis: Found: C, 58.03; H, 3.82; Zr, 27.61. $C_{16}H_{14}O_2Zr$ (329.51) calcd.: C, 58.62; H, 4.28; Zr, 27.68%. Mass spectrum: $m/e = 656$ $(M_2)^+$, 4%; 591 $(M_2 - C_5H_5)^+$, 34%; 328 $(M)^+$, 100%; 263 $(M - C_5H_5)^+$, 87%. Recorded and simulated spectra are in excellent agreement.

Dicyclopentadienylzirconium catecholate

A solution of 330 mg catechol in 15 ml benzene was added dropwise to a stirred suspension of 670 mg Cp_2ZrH_2 (3 mmol) in 15 ml benzene. Gas was evolved, and 136 ml (101%) (s.c.) were collected. After the hydrogen evolution ceased the suspension was stirred for 2 h more and the solid was filtered off. After washing with benzene and drying, 892 mg (93%) of $Cp_2ZrO_2C_6H_4$, dec.p. 344–346°C, was obtained. The IR and mass spectra were identical with those of the product described above.

Discussion

Dicyclopentadienylzirconium dihydride rapidly reacts with the borane-tetrahydrofuran complex. Dicyclopentadienylzirconium bis(tetrahydridoborate) I is produced quantitatively and can thus be isolated in high yield. The reaction proceeds according to eq. 1. Attempts to detect the expected intermediate, $Cp_2Zr(H)BH_4$, by monitoring the reaction by ^{11}B NMR spectroscopy failed,

$$Cp_2ZrH_2 + 2\,H_3B{\cdot}THF \longrightarrow \underset{(I)}{Cp_2Zr(BH_4)_2} + 2\,THF \qquad (1)$$

(2)

(3)

Compound I was also readily obtained from Cp_2ZrH_2 and catecholborane according to eq. 2. No dicyclopentadienylzirconium bis(dihydridocatecholborate) was observed, implying that this primary product disproportionates into the compounds shown by eq. 2 more rapidly than it is formed. The IR, ^1H and ^{11}B NMR data for I corresponded very well with literature values [9–11]. As expected, only a single ^{13}C resonance signal was found.

Dicyclopentadienylzirconium catecholate(II) has been reported to be a monomeric, unstable compound [12]. This is in strong contrast with the properties of compound II obtained by either eq. 2 or 3. Compound II is virtually insoluble in all common organic solvents, and so we could not record its NMR spectra. It is not attacked by dilute hydrochloric acid; this and its solubility characteristics argue strongly against a mononuclear formulation for II. We therefore, suggest a dimeric or polymeric structure, with the catecholate moiety acting as a bridging group between two Cp_2Zr units. This is in accord with the rather high decomposition temperature and with the mass spectrum (190 ° C, 70 eV), in which the dimer and its degradation products are clearly seen. Although higher oligomers were not observed, a polymeric structure for the solid cannot be ruled out.

Compound II reacts sluggishly with diborane in THF due to its insolubility, and gives I. At temperatures $< 0\,°C$ virtually no reaction was observed.

The present study suggests that transition metal tetrahydridoborates can be conveniently synthesized from the hydride components. The reaction may provide a test of the hydridic nature of specific transition metal hydrogen bonds.

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