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TRICARBONYLCHROMIUMPHENYLBORIC ACID

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Summary

Tricarbonylchromiumphenylboric acid has been obtained in 80% yield, from the reaction of phenylboric acid with triaminechromium tricarbonyl in boiling dioxane. Physical and chemical properties of the title compound have been studied, as well as its reactions with alcohols, corrosive mercuric chloride, halogens and some metallic salts.

Introduction

The literature on arene complexes describes extensively the chemistry of transition metal cyclopentadienyl compounds, especially ferrocene. However, only a limited number of investigations concerning arenemetal tricarbonyl compounds, which contain hetero-organic substituents in π -bonded benzene rings are reported. Seyferth et al. [1] have reported the formation and investigation of trimethylsilyl-, trimethylgermyl- and trimethylstannyl-benzenechromium tricarbonyls. Arenechromium tricarbonyl compounds of tin have been obtained analogously and comprehensively characterized [2]. Recently, the possibility of obtaining a large number of arenechromium tricarbonyl derivatives of mercury has been described [3—6]. Bis(phenylchromium tricarbonyl) mercury when treated with boron diphenyl bromide gives the boron organic compound $(C_6H_5)_2BC_6H_5Cr(CO)_3$ [7]. Taking into account the characteristic properties of this compound, as well as the great progress achieved in the investigation of metallocenylboric acid, we have tried to obtain tricarbonylchromium phenylboric acid and to study its properties.

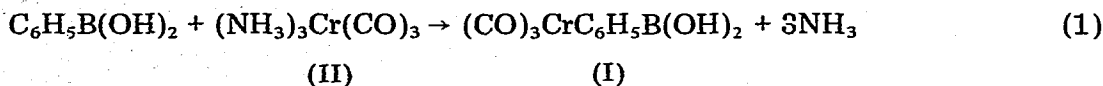
Results and discussion

Analogous to the reaction of triphenylboron with chromium hexacarbonyl in dibutyl ether [7], the reaction of phenylboric acid with $Cr(CO)_6$ in a boiling diglyme/octane mixture results in formation of a mixture containing consider-

able amounts of benzenechromium tricarbonyl, tricarbonylchromium phenylboric acid (I), its anhydride and unidentified chromium-containing compounds.

The reported use of triaminechromium tricarbonyl, $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ (II), to obtain a number of organochromium complexes [8], makes it likely that reaction of II with phenylboric acid may turn out to be a suitable route for the production of I. Therefore, we have first worked out a simple method for the synthesis of I under atmospheric pressure, which is far more convenient for laboratory use than conventional methods [9,10] which employ the same reaction in bombs under pressure.

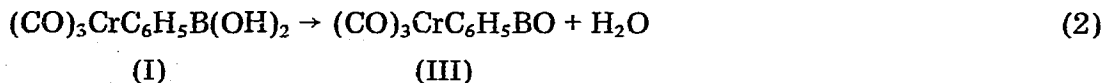
It has been found that II reacts with phenylboric acid in boiling dioxane to form arenechromium tricarbonyl which, after treatment with a 10% solution of hydrochloric acid, gives pure tricarbonylchromium phenylboric acid (I) in an 80–85% yield (eq. 1).



I is a yellow crystalline substance, relatively stable in air but quite readily oxidizable in solutions.

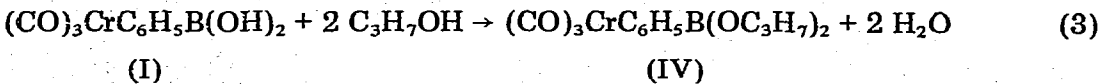
The IR spectrum of I has strong absorption bands at 1920 and 2070 cm^{-1} , corresponding to valent oscillation of the C—O bond and bands due to Cr—CO deformation oscillation at 658, 622 and 533 cm^{-1} . In the range of ligand oscillations the spectra of I and phenylboric acid are very similar. The spectrum of I displays valent C—C oscillations of a bonded ligand at 1530 and 1522 cm^{-1} , it retains bands in the range of 1350 cm^{-1} characteristic for a B—O bond and a wide absorption band at 3150 cm^{-1} attributable to valent oscillations of the O—H bond.

On heating in vacuo, I loses water readily and is converted to the anhydride III (eq. 2). The latter is a yellow crystalline substance which decomposes in a



sealed capillary at 155°C. The IR spectrum of III displays all the bands characteristic of the initial compound I, except for the band at 3150 cm^{-1} which corresponds to valent oscillations of the O—H group. Equation 2 is reversible, therefore I may be recovered on treating III with water.

I and III on heating with n-propanol under conditions of azeotropic sublimation of water with benzene, esterify readily to form tricarbonylchromium phenylboric n-propyl ether (IV) (eq. 3). IV is a yellow substance which sublimates



in vacuo at 80–90°C, m.p. 71–73°C. The properties of IV are identical with those of the product obtained directly from phenylboric n-propyl ether and chromium hexacarbonyl. Compound IV is very sensitive even to traces of moisture, it reacts with water to give I, which presents a severe problem in the investigation of its physical and chemical properties.

reflux condenser and a burette to measure gas evolution. After refluxing for 6 h 75% of the calculated quantity of ammonia had been evolved. The reaction mixture was filtered through a 4-filter and the solvent was distilled in vacuo. Hydrochloric acid solution (60 ml, 10%) was added to the dry yellow residue and heated for 5 min. After filtering the hot reaction mixture a bright-yellow precipitate was obtained, washed several times with hot water and dried in vacuo over P_2O_5 . The weight of the residue was 5.3 g (83%). Recrystallization from water resulted in pure tricarbonylchromium phenylboric acid. (Found: C, 41.23; H, 2.67; Cr, 20.49. $C_9H_7BCrO_5$ calcd.: C, 41.55; H, 2.73; Cr, 20.15%.)

Tricarbonylchromium phenylboric n-propyl ether

I (1.0 g, 0.004 mol), dry n-propanol (15 ml) and pure benzene (20 ml) were loaded into a 100 ml flask connected to a dephlegmator provided with a head to control reflux sampling. The mixture was heated for 3 h and the azeotropic mixture as well as excess n-propanol were refluxed in the temperature range 76–93°C. The residue was dried in vacuo, recrystallized from hexane and sublimed in vacuo at 90°C/0.1 mmHg. A yellow crystalline substance was obtained (0.85 g, 63%).

$Cr(CO)_6$ (6.6 g, 0.03 mol), $C_6H_5B(OC_3H_7)_2$ (6 ml), diglyme (20 ml) and octane (50 ml) were loaded into an apparatus provided with an automatic device [4] to return refluxed $Cr(CO)_6$ and a burette to measure gas evolution. The contents were heated for 6 h over a bath at 150°C. After cooling, the reaction mixture was filtered, the solvent sublimated, the mixture washed with hexane and the bright-yellow residue sublimed in vacuo at 80°C.

Reaction of I with mercury(II) chloride

$HgCl_2$ (0.272 g, 0.001 mol) in aqueous ethanol (5 ml) was added to a hot mixture of I (0.258 g, 0.001 mol) in 10 ml of the same solvent. A fine yellow precipitate appeared which was filtered after heating for a short time, washed with hot water and dried in vacuo over P_2O_5 . After chromatography on an Al_2O_3 column, phenylchromium tricarbonylmercury(II) chloride (0.373 g, 83%) was obtained. (Found: Cl, 7.46; Cr, 11.12. $C_9H_5ClCrHgO_3$ calcd.: Cl, 7.79; Cr, 11.58%.)

Reaction of I with copper(II) bromide

$CuBr_2$ (0.400 g, 0.002 mol) in aqueous dimethoxyethane (10 ml) was added to a solution of I (0.258 g, 0.001 mol) in 15 ml of the same solvent at 0°C. When the addition of copper(II) bromide was complete, the reaction mixture was stirred for 30 min and filtered into a separating funnel containing benzene at room temperature. The benzene layer was washed several times with distilled water, dried over anhydrous Na_2SO_4 and the solvent distilled in vacuo. The yellow crystalline residue was sublimed at 60°C/ 1×10^{-2} mmHg. Benzenechromium tricarbonyl (0.050 g, 23%) was obtained (m.p. 160–161°C).

Reaction of I with copper(II) chloride

$CuCl_2 \cdot 2H_2O$ (0.500 g, 0.001 mol) in $C_2H_4(OCH_3)_2$ (10 ml) was added to a solution of I (0.258 g, 0.001 mol) in the same solvent. The reaction procedure was the same as the afore-mentioned; benzenechromium tricarbonyl was isolated in a small yield.

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