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THE SYNTHESIS AND PROPERTIES OF BIS(PHENYLTRICARBONYLCHROMIUM)MERCURY

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SUMMARY

The reaction of diphenylmercury with chromium hexacarbonyl in a boiling diglyme/octane mixture results in the formation of bis(phenyltricarbonylchromium)-mercury in 70% yield. This compound reacts with mercuric chloride, iodine, hydrochloric acid and $LiAlH_4$ producing (phenyltricarbonylchromium)mercury chloride, iodobenzene chromium tricarbonyl and benzene chromium tricarbonyl, respectively, all in high yield.

INTRODUCTION

Of π-bonded aromatic systems of transition metals, arenemetal tricarbonyls of the Group VIB elements are of particular interest in that almost any benzene derivative may serve as a ligand. In spite of the large number of arenetricarbonyl complexes known at present, practically no reports have appeared of the synthesis and properties of compounds with organometallic substituents of the type: $(CO)_3M$-$C_6H_5M'R_{n-1}$ (where M = Cr, Mo and W; M' = non-transition metal; n = metal valency; R = organic radical, halogen, etc.).

Only one report[1] has appeared regarding the preparation of (trimethylsilyl-, trimethylgermyl- and trimethylstannyl)benzenechromium tricarbonyls by the direct reaction of $(CH_3)_3M'C_6H_5$ (M' = Si, Ge or Sn) with chromium hexacarbonyl. As organomercury compounds generally exhibit a high reactivity, the preparation of benzenechromium tricarbonylmercury derivatives is of considerable interest since these compounds may be suitable for use as intermediates in syntheses.

RESULTS AND DISCUSSION

When diphenylmercury was refluxed with excess $Cr(CO)_6$ in diglyme/octane solution evolution of carbon monoxide occurred and yellow crystals were formed which were stable in air, decomposing without melting at 235–240°.

$$(C_6H_5)_2Hg + 2\,Cr(CO)_6 \rightarrow [(CO)_3CrC_6H_5]_2Hg + 6\,CO$$

Elemental analysis, IR and NMR spectra suggested a structure for the π-complex in which the aromatic rings of diphenylmercury are bonded with two chromium tricarbonyl fragments.

Subsequent to this particular work, information on the synthesis of $[(CO)_3CrC_6H_5]_2Hg$ has appeared[2].

The structure of bis(phenyltricarbonylchromium)mercury (I) has been completely established by a study of the subsequent reactions of the compound. The desymmetrizing reaction of (I) with mercuric chloride results in the formation of (phenyltricarbonylchromium)mercury chloride (II) in 80% yield.

$$[(CO)_3CrC_6H_5]_2Hg + HgCl_2 \rightarrow 2\,(CO)_3CrC_6H_5HgCl$$

Reaction of C_6H_5HgCl with chromium hexacarbonyl did not result in the formation of this compound. (Phenyltricarbonylchromium)mercury chloride is a crystalline yellow compound relatively stable in air in the solid state but decomposing readily in solution. On heating it decomposes without melting at 130°.

The interaction of (I) with iodine in dimethoxyethane at −30° resulted in the formation of iodobenzenechromium tricarbonyl (III) in 85% yield.

$$[(CO)_3CrC_6H_5]_2Hg + 2I_2 \rightarrow 2(CO)_3CrC_6H_5I + HgI_2$$

Increasing the reaction temperature to room temperature resulted in the partial evolution of carbon monoxide and reduced the yield of (III) to 50–55%. Direct reaction of iodobenzene with chromium hexacarbonyl does not result in the formation of iodobenzenechromium tricarbonyl, although this compound has been obtained in low yield (12.5%) by Ofele[3] through use of the following reaction:

$$C_6H_5I + (\gamma\text{-picoline})_3Cr(CO)_3 + 3\,BF_3 \rightarrow IC_6H_5Cr(CO)_3 + BF_3\cdot\gamma\text{-picoline}$$

Compound (I) reacts slowly at room temperature with 2 moles of hydrogen chloride in 75% dimethoxyethane to yield benzenechromium tricarbonyl. Using a tenfold excess of HCl and increasing the temperature to 75° increases the yield to 90%.

$$[(CO)_3CrC_6H_5]_2Hg + 2\,HCl \rightarrow 2(CO)_3CrC_6H_6 + HgCl_2$$

Under mild conditions, through the use of reducing agents, such as lithium tetrahydroaluminate, it is possible to induce the evolution of the corresponding arene from an aromatic mercury compound[4]. The addition of $LiAH_4$ to a suspension of (I) in ether results in the rapid precipitation of metallic mercury from the system and $C_6H_6Cr(CO)_3$ was isolated from the reaction mixture in 86% yield.

These reactions show that benzenechromium tricarbonyl derivatives of mercury are relatively stable and undergo typical reactions of organomercury compounds with the retention of the arenechromium tricarbonyl structure. This suggests the possibility of obtaining organochromium complexes with various substituents in the benzene ring by the use of appropriate reagents.

EXPERIMENTAL

All processes were carried out under a dry, oxygen-free, nitrogen atmosphere. The solvents used were previously dried and out-gassed with nitrogen.

Bis(phenyltricarbonylchromium)mercury

Synthesis of this compound was achieved by the method described by Strohmeier[5]. $Cr(CO)_6$ (6.60 g, 30 mmoles), 5.33 g (15 mmoles) of diphenylmercury, 70 ml of diglyme and 70 ml of octane were placed in the reaction flask. The mixture was refluxed for 8–10 h during which time complete evolution of the calculated quantity of carbon monoxide occurred. On cooling, yellow crystals precipitated from the solution, and the solution together with precipitate was placed on to a glass filter and washed with acetone until the crystals were completely dissolved. The product thus obtained was purified by elution from an alumina column. Initially chloroform was used as an eluant to remove any unreacted diphenylmercury, and during this process a small quantity of an unidentified yellow arenechromium tricarbonyl product (0.20 g) was also isolated. The yellow band at the top of the column was washed out with acetone, and the solution evaporated to dryness when 6.62 g of $[(CO)_3CrC_6H_5]_2Hg$ was obtained (yield 70%). (Found: C, 35.33; H, 2.09; Cr, 16.35; Hg, 31.70. $C_{18}H_{10}Cr_2HgO_6$ calcd.: C, 34.50; H, 1.59; Cr, 16.61; Hg, 31.95%.)

Reaction of bis(phenyltricarbonylchromium)mercury with mercuric chloride

(I) (1.03 g, 1.5 mmoles), 0.90 g (3 mmoles) of mercuric chloride and 120 ml n-butanol were placed in a 200 ml glass tube, the contents frozen in liquid nitrogen, and the tube evacuated and sealed, and placed in a thermostat at 85° for 10 h. After this time, the tube was removed and opened, and the hot reaction mixture filtered to remove a fine white precipitate. Excess n-butanol was then removed by evaporation *in vacuo* until the volume of the mixture had been reduced to 1/4 of its initial value. At this stage a bright yellow precipitate was formed, which was filtered off on to a glass filter and washed with hexane when 1.25 g of $(CO)_3CrC_6H_5HgCl$ was obtained (yield 80%). The substance was further purified by recrystallization from n-butanol. (Found: C, 24.49; H, 1.16; Cr, 11.58; $C_9H_5ClCrHgO_3$ calcd.: C, 24.05; H, 1.11; Cr, 11.58%.)

Reaction of bis(phenylchromiumtricarbonyl)mercury with iodine

(I) (0.63 g, 1 mmole) and 100 ml of dimethoxyethane were placed in a three-necked 200 ml flask equipped with stirrer, dropping funnel and connected to a gas burette. Iodine (0.51 g, 2 mmoles) in 30 ml of dimethoxyethane was added slowly to the flask while the latter was thoroughly stirred and cooled to −30°. After addition of all the iodine to the system, the mixture was further stirred for 30 min. The solvent was then removed *in vacuo* and iodobenzenechromium tricarbonyl was separated from mercury iodide by elution on an alumina column using benzene as an eluant. Removal of the benzene resulted in the formation of a yellow crystalline residue which sublimed *in vacuo* at 60°. Yield 0.58 g of $IC_6H_5Cr(CO)_3$ corresponding to 85%.

Reaction of bis(phenyltricarbonylchromium)mercury with hydrogen chloride

(I) (1.25 g, 2 mmoles), 40 ml of 1 *N* HCl and 100 ml of dimethoxyethane were placed in a 200 ml tube which was then sealed *in vacuo*, placed in a thermostat at 75° and held there for 10 h. After this time the tube was removed from the thermostat, opened, and the contents placed in a separating funnel together with 50 ml of benzene. The benzene layer was washed with water several times, dried with anhydrous $CaCl_2$, the solvent was removed and the residue sublimed *in vacuo* at 65°. Benzenechromium tricarbonyl was obtained in a yield of 0.77 g (90%).

Reaction of bis(phenyltricarbonylchromium)mercury with lithium tetrahydroaluminate

(I) (2.09 g, 3.3 mmoles) and 200 ml of ether were placed into a three-necked 500 ml flask equipped with reflux condenser, stirrer and dropping funnel and the suspension obtained was treated with an excess of $LiAlH_4$. Metallic mercury precipitated immediately. The mixture was then heated under reflux for 30 min, cooled and filtered and the resulting solution treated with dilute sulphuric acid. The ether layer was washed several times and dried with anhydrous $CaCl_2$. Ether was then removed and the resulting yellow crystal precipitate sublimed *in vacuo* at 65°. A yield of 1.22 g (86%) of benzenechromium tricarbonyl was obtained.

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