SYNTHESIS AND REACTIONS OF A BIS(PENTAFLUOROPHENYL)COBALT COMPLEX

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SUMMARY

The synthesis and some reactions of a bis(pentafluorophenyl)cobalt complex are described. The reaction with tri-n-butylphosphine to yield a phosphine complex, bis(pentafluorophenyl)bis(tri-n-butylphosphine)cobalt is also reported.

INTRODUCTION

The reactions of alkyl and aryl Grignard reagents with cobaltous halide for many years have been a subject of considerable interest[1]. It is generally accepted that the reaction yields an unstable* organocobalt compound whose exact nature is still unknown[1-3]. It has been shown that a pentafluorophenyl group should facilitate the formation of an organo–transition metal bond having a stability much greater than its hydrogen analog[5]. With this in mind we set out to synthesize and study some of the reactions of a bis(pentafluorophenyl)cobalt compound.

SYNTHESIS AND REACTIONS

A bis(pentafluorophenyl)cobalt complex** (I) was synthesized through the reaction between pentafluorophenylmagnesium bromide (II) and cobaltous bromide.

$$2\ C_6F_5MgBr + CoBr_2 \xrightarrow{\text{THF}} \text{``}(C_6F_5)_2Co\text{''} + MgBr_2 \tag{1}$$
$$\text{(II)} \qquad\qquad\qquad \text{(I)}$$

Dioxane was added to the reaction mixture in an attempt to separate the magnesium bromide as the dioxane complex. The results were only partially successful since after filtering the dioxane/magnesium halide complex, the filtrate still contained magnesium bromide. Removal of the solvent from the dark blue filtrate yielded a crude blue solid

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* Tsutsui and Zeiss[4] have isolated dimesitylcobalt from the reaction between mesitylmagnesium bromide and cobaltous bromide.
** A pure $(C_6F_5)_2Co$ compound has not been isolated as yet. Our attempts at isolating it in a manner similar to the isolation and characterization of $C_6F_5Cu^6$ have been unsuccessful. Undoubtedly $(C_6F_5)_2Co$ exists as a coordinate complex with the solvent and $MgBr_2$. For the sake of simplicity, the complex (I) will be represented as "$(C_6F_5)_2Co$".
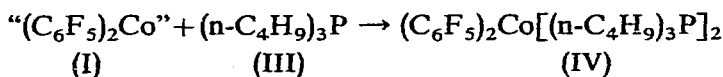
material. Soxhlet extraction of this material with hexane produced a free flowing, blue, powdery solid which appeared to decompose on exposure to air.
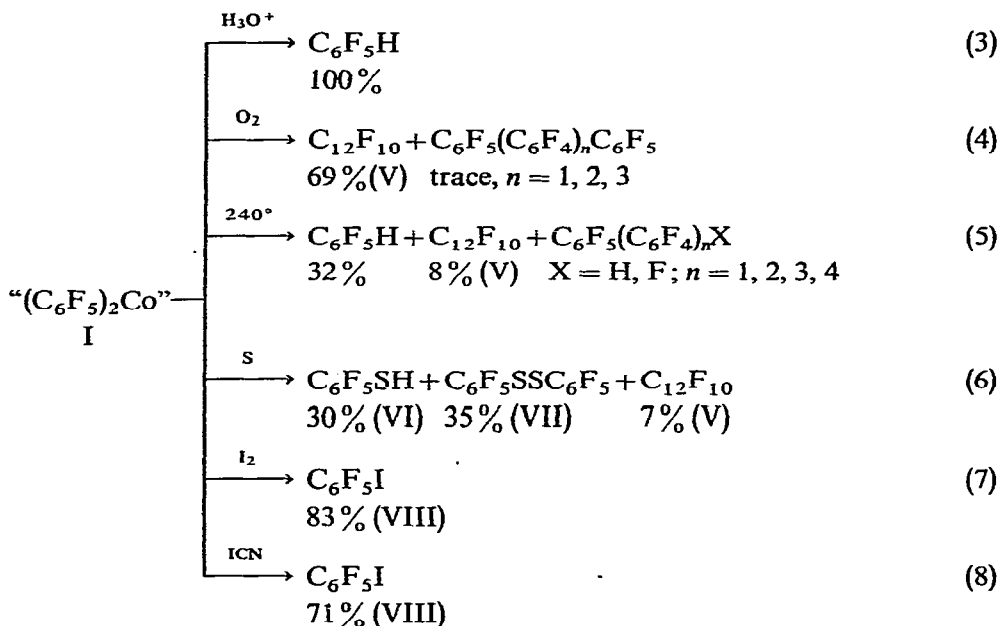
The blue solid material was soluble in anhydrous THF, and such solutions were stable for several days at room temperature.

Strong evidence for the presence of a $(C_6F_5)_2Co$ complex was provided by an experiment in which tri-n-butylphosphine (III) was added to such a THF solution. A stable phosphine complex*, bis(tri-n-butylphosphine)bis(pentafluorophenyl)cobalt (II) (IV) was isolated in 44% yield:

$$\text{``}(C_6F_5)_2Co\text{''} + (n\text{-}C_4H_9)_3P \rightarrow (C_6F_5)_2Co[(n\text{-}C_4H_9)_3P]_2$$
$$\quad (I) \qquad\qquad (III) \qquad\qquad\qquad (IV)$$

Compound (IV) could also be synthesized following the reported procedure of Phillips and co-workers[7], through the reaction between pentafluorophenylmagnesium bromide and the complex of tri-n-butylphosphine and cobalt bromide. The complex (IV) decomposes in organic solutions (e.g. C_6H_6, CCl_4, THF), when exposed to air. In refluxing dioxane or THF, (IV) decomposes rapidly to pentafluorobenzene and a gray magnetic solid, believed to be metallic cobalt.

The organocobalt complex (I), like pentafluorophenylmagnesium bromide[8],

$$
\begin{array}{ll}
\xrightarrow{\text{H}_3\text{O}^+} & C_6F_5H \\
& 100\%
\end{array} \qquad (3)
$$

$$
\begin{array}{ll}
\xrightarrow{\text{O}_2} & C_{12}F_{10} + C_6F_5(C_6F_4)_nC_6F_5 \\
& 69\%(V) \quad \text{trace}, n = 1, 2, 3
\end{array} \qquad (4)
$$

"$(C_6F_5)_2Co$"

I

$$
\begin{array}{ll}
\xrightarrow{\text{240}^\circ} & C_6F_5H + C_{12}F_{10} + C_6F_5(C_6F_4)_nX \\
& 32\% \qquad 8\%(V) \quad X = H, F; n = 1, 2, 3, 4
\end{array} \qquad (5)
$$

$$
\begin{array}{ll}
\xrightarrow{\text{S}} & C_6F_5SH + C_6F_5SSC_6F_5 + C_{12}F_{10} \\
& 30\%(VI) \quad 35\%(VII) \qquad 7\%(V)
\end{array} \qquad (6)
$$

$$
\begin{array}{ll}
\xrightarrow{\text{I}_2} & C_6F_5I \\
& 83\%(VIII)
\end{array} \qquad (7)
$$

$$
\begin{array}{ll}
\xrightarrow{\text{ICN}} & C_6F_5I \\
& 71\%(VIII)
\end{array} \qquad (8)
$$

undergoes hydrolysis to produce pentafluorobenzene in quantitative yield. In contrast, it does *not* react with carbon dioxide or with trimethylchlorosilane to give

* A cobalt phosphine complex [1,2-bis(diphenylphosphino)ethane]bis(pentafluorophenyl)cobalt has been synthesized by Phillips and co-workers[7] through the reaction between (pentafluorophenyl)magnesium bromide and bis(triphenylphosphine)cobalt dibromide. Its solutions in organic solvent decompose in air.
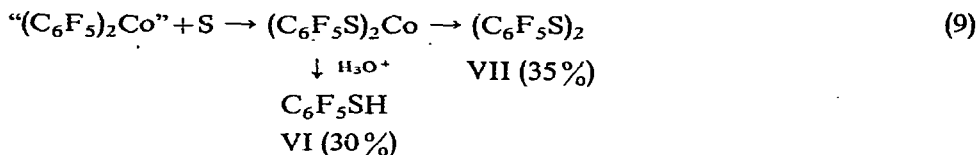
pentafluorobenzoic acid and trimethyl(pentafluorophenyl)silane[9,10], respectively.

The organocobalt complex (I), unlike pentafluorophenylmagnesium bromide, can be readily oxidized to decafluorobiphenyl (V) in good yield, with concurrent formation of trace quantities of perfluoropolyphenylenes (eqn. 4). The decafluorobiphenyl could have arisen from a simple bimolecular process leading to the coupling of the organic groups, or from the coupling of pentafluorophenyl free radicals. The free radical mechanism would account for the presence of the perfluoropolyphenylenes. Both mechanisms are quite feasible, and characteristic of organometallic compounds[2b].

Thermal decomposition of the organocobalt complex (I) (eqn. 5) under nitrogen is similar to that of its hydrogen analog[11], and gives further evidence for the formation of free radicals, especially in the formation of the pentafluorobenzene, which could have only arisen by hydrogen abstraction from the solvent[2b].

Unlike the pentafluorophenyl organometallics of lithium and copper, the organocobalt complex (I) showed no reaction with iodotrifluoroethylene[12] or acetyl chloride[13], with quantitative yields of pentafluorobenzene being recovered after hydrolysis of the reaction mixtures.

In the reactions of (I) with sulfur (eqn. 6), two major products were obtained after hydrolysis, pentafluorothiophenol (VI) and bis(pentafluorophenyl) disulfide (VIII). In addition, a small amount of decafluorobiphenyl (V) was also obtained. This reaction could occur by a stepwise mechanism (eqn. 9), leading to a bis(pentafluorothiophenyl)cobalt intermediate, which subsequently decomposes to (VII).

$$\text{``}(C_6F_5)_2Co\text{''} + S \longrightarrow (C_6F_5S)_2Co \longrightarrow (C_6F_5S)_2 \tag{9}$$

$$\downarrow \text{ }_{H_3O^+} \qquad VII\ (35\%)$$

$$C_6F_5SH$$

$$VI\ (30\%)$$

The presence of the decafluorobiphenyl again gives rise to the possibility of a free radical mechanism also occurring under these conditions[2b].

The reaction of the organocobalt complex (I) with iodine and cyanogen iodide gave iodopentafluorobenzene (VIII) in good yield (eqns. 7, 8).

EXPERIMENTAL

Tetrahydrofuran was distilled from metallic Na followed by CaH_2 prior to use. Dioxane was distilled from $LiAlH_4$. All other solvents used were analytical grade. Reactions involving organometallic reagents were carried out under dry nitrogen with the usual precautions for the rigorous exclusion of moisture and air. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected. Infrared spectra were run on a Perkin–Elmer Infracord spectrophotometer as KBr pellets or as liquid films. GLC analysis were performed on an F & M Model 700 instrument using a 6 ft., 10% polyphenylether (6 ring) on Chromosorb P column and a 6 ft., SE-30 on Chromosorb W column. All products were characterized by GLC retention time with calibrated known samples. Yields of all products were determined by GLC analysis using appropriate hydrocarbon internal standards. Mass spectral analysis were performed on a CEC-21-110B mass spectrometer.

Preparation of the bis(pentafluorophenyl)cobalt complex

Bromopentafluorobenzene (61.7 g, 0.250 mole) was added dropwise with stirring to a mixture of magnesium (6.8 g, 0.275 mole) in THF (250 ml), previously cooled to $5°$. The addition rate was such that the temperature never rose above $20°$. After $1\frac{1}{2}$ h stirring at room temperature, the mixture was filtered and the filtrate added rapidly to a solution of cobaltous bromide (27.4 g, 0.125 mole) in THF (200 ml). The mixture was refluxed for 2 h, cooled to room temperature and treated with anhydrous dioxane (70 ml), which caused precipitation of a white solid. The mixture was filtered under dry nitrogen, and the filtrate concentrated on a rotary evaporator. The dark blue solid was washed with pentane (3 × 100 ml), dissolved in THF (350 ml) and filtered through a medium porosity funnel into a storage bottle. The concentration of the solution was determined to be 0.437 M in pentafluorobenzene (61 % overall yield) by hydrolyzing an aliquot and analyzing via an internal standard by GLC for pentafluorobenzene. The solution showed little change during storage and was used for the following experiments.

Reaction with tri-n-butylphosphine

Bis(pentafluorophenyl)cobalt complex (0.0109 mole) in THF was added rapidly to tri-n-butylphosphine (4.42 g, 0.0218 mole) giving a dark green mixture. The mixture was stirred 15 min, hydrolyzed, extracted with diethyl ether (15 ml) and filtered, yielding 1.89 g (44 %) of a pale yellow solid. The solid was recrystallized from hot hexane yielding 1.73 g (40 %) of a green crystalline solid, bis(pentafluorophenyl)-bis(tri-n-butylphosphine)cobalt, decomp. 136–150°. (Found: C, 54.20; H, 6.57; Co, 7.41; F, 24.69; P, 7.76. $C_{36}H_{54}CoF_{10}P_2$ calcd.: C, 54.25; H, 6.80; Co, 7.37; F, 23.90; P, 7.76%.) It is insoluble in H_2O, 6 N HCl, acetone, very slightly soluble in hexane, diethyl ether, dioxane, and soluble in THF. It decomposes rapidly in refluxing dioxane or THF, giving quantitative yields of pentafluorobenzene. An infrared spectrum (KBr pellet) exhibited absorptions characteristic of the pentafluorophenyl group at 1065, 954 and 780 cm^{-1}. Mass spectral analysis gave parent ion peak at 797, calcd. for (IV) 797.

Oxidation

Dry air was bubbled through a THF solution of the bis(pentafluorophenyl)-cobalt complex (0.0109 mole) for 2 h, producing a dark green mixture. The mixture was hydrolyzed (3 N HCl), extracted with diethyl ether (2 × 25 ml) and the ether extracts were dried. GLC analysis showed that decafluorobiphenyl (69%) was the major product, with a trace of perfluoropolyphenylenes.

Thermal stability of bis(pentafluorophenyl)cobalt complex

The bis(pentafluorophenyl)cobalt complex (0.0109 mole) in THF was heated to reflux, distilling over the solvent. Heating was continued to 240°, and held at this temperature for 20 min. GLC analysis of the distillate showed pentafluorobenzene (32 %) and decafluorobiphenyl (2.2 %) to be present. The black residue was hydrolyzed (3 N HCl), extracted with diethyl ether (10 ml) and filtered, leaving a gray magnetic solid, believed to be free cobalt. GLC/mass spectral analysis of the diethyl ether solution indicated the presence of decafluorobiphenyl (5.9 %), 1-hydrononafluoro-biphenyl (1.6 %) and a series of monohydro and perfluoropolyphenylenes.

Reaction with sulfur

Sulfur (0.35 g, 0.0109 mole) was added to a THF solution of the bis(pentafluorophenyl)cobalt complex (0.0109 mole). The mixture was stirred 45 min at room temperature, and then heated to reflux for 1 h, yielding a dark black mixture. The mixture was hydrolyzed (6 N HCl), filtered, extracted with diethyl ether (2 × 25 ml), and the diethyl ether extracts dried. GLC/mass spectral analysis revealed the presence of pentafluorobenzene (14.7 %), pentafluorothiophenol (30 %), bis(pentafluorophenyl) disulfide (35 %), and decafluorobiphenyl (7 %).

Reaction with iodine

The bis(pentafluorophenyl)cobalt complex (0.0109 mole) was added dropwise (15 min) to a solution of iodine (2.78 g, 0.0109 mole) in THF (10 ml). The dark green solution was stirred 3 h at room temperature, hydrolyzed (6 N HCl), extracted with diethyl ether (2 × 25 ml), and the extracts washed with saturated $Na_2S_2O_3$ solution to remove excess iodine. GLC analysis revealed iodopentafluorobenzene (83 %) as the major product. Mass spectral analysis indicated a parent ion peak at 294, calcd. for (VIII) 294.

Reaction with cyanogen iodide

The bis(pentafluorophenyl)cobalt complex (0.0109 mole) was added dropwise (5 min) to a solution of cyanogen iodide (1.67 g, 0.0109 mole) in THF (20 ml). The mixture was stirred 20 min at room temperature, then heated to reflux for 1 h. The dark green mixture was cooled, hydrolyzed (3 N HCl), extracted with diethyl ether (2 × 25 ml), and the extracts washed with saturated $Na_2S_2O_3$ solution. GLC analysis showed iodopentafluorobenzene (71 %) to be the major product. Mass spectral analysis indicated a parent ion peak at 294, calcd. for (VIII) 294.

Attempted reaction with acetyl chloride

Acetyl chloride (0.86 g, 0.0109 mole) was added dropwise to a THF solution of bis(pentafluorophenyl)cobalt complex (0.0109 mole). The mixture was stirred for 10 min, then heated to reflux for 0.5 h, cooled, hydrolyzed, extracted with pentane (2 × 25 ml) and dried. GLC showed a quantitative yield of pentafluorobenzene.

Attempted reaction with trimethylchlorosilane

Trimethylchlorosilane (0.48 g, 0.0044 mole) was added to a THF solution of the bis(pentafluorophenyl)cobalt complex (0.0022 mole). After it had been stirred for 15 min at room temperature, the mixture was refluxed for 1 h, cooled, and a sample was removed for analysis. GLC analysis revealed pentafluorobenzene (82 %) as the major product with no trace of the desired silane.

Attempted reaction with iodotrifluoroethylene

Iodotrifluoroethylene (2.2 g, 0.012 mole) was added dropwise to a THF solution of the bis(pentafluorophenyl)cobalt complex (0.0109 mole). The solution was heated to reflux for 1 h, cooled, hydrolyzed, extracted with diethyl ether (2 × 25 ml) and dried. GLC analysis showed pentafluorobenzene (98 %) as the only product.

Attempted reaction with carbon dioxide

Dry carbon dioxide was bubbled through a THF solution of the bis(penta-

fluorophenyl)cobalt complex (0.0109 mole) for 1 h. The solution was hydrolyzed, extracted with diethyl ether (2 × 25 ml), and dried. GLC analysis revealed only pentafluorobenzene (98 %) recovered.

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