cations such as the tetrafluoroborates have been reported previously.[7-9]

Experimental

Hexafluorophosphoric acid in 65% aqueous solution was purchased from the Ozark-Mahoning Company. The propionic anhydride was Eastman White Label grade used without further purification. Cyclopentadienyliron dicarbonyl iodide was prepared by a published method[10] which can be scaled up without difficulty to produce the material in pound quantities in nearly quantitative yields.

Cyclopentadienyliron Tricarbonyl Hexafluorophosphate.—A mixture of 13 ml. of 65% aqueous hexafluorophosphoric acid and 50 ml. of propionic anhydride was prepared by very slow addition with stirring since much heat is generated. After cooling to room temperature, this mixture and 10 g. (32.9 mmoles) of cyclopentadienyliron dicarbonyl iodide were charged into a shaker tube of 300 ml. capacity. The tube was pressurized with 5350 p.s.i. carbon monoxide and heated to 150–151° for 2 hr., the pressure dropping from 7100 to 7025 p.s.i. The tube then was cooled to room temperature and vented. The solid was separated by filtration. Unreacted $C_5H_5Fe(CO)_2I$ was removed by washing with four 100-ml. portions of dichloromethane, and white water-soluble impurities (possibly formed by corrosion of the bomb) then were removed by washing with four 100-ml. portions of water. After further washing with ethanol and dichloromethane, the yellow air-stable, water-insoluble crystals of $[C_5H_5Fe(CO)_3][PF_6]$ weighed 6.9 g. (60% yield).

This reaction can be scaled up to give more than 20 g. of product.

Anal. Calcd. for $C_8H_5O_3F_6PFe$: C, 27.4; H, 1.4; F, 32.5; P, 8.9; Fe, 16.0. Found (two independent preparations): C, 27.4, 27.4; H, 1.5, 1.6; F, 32.3, 31.9; P, 8.9, 8.8; Fe, 15.6, 15.7.

Infrared Spectrum.—C–H at 3160 (w) cm.$^{-1}$; carbonyl bands at 2090 (s) and 2150 (s) cm.$^{-1}$; P–F band at 835 (vs) cm.$^{-1}$; other bands at 1440 (w) and 880 (m) cm.$^{-1}$.

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Mercury and Sodium Tetracarbonylcobaltate(−I)

BY SHRIKANT V. DIGHE AND MILTON ORCHIN

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The standard procedure[1] for the preparation of sodium tetracarbonylcobaltate(−I), $NaCo(CO)_4$, consists of treating an ether solution of dicobalt octacarbonyl with 1% sodium amalgam. In searching for alternate solvents, we noted that solutions of $Co_2(CO)_8$ in hexane, when treated with amalgam, became yellow before turning colorless. Investigation revealed that the yellow color was due to mercury(II) tetracarbonylcobaltate(−I), $Hg[Co(CO)_4]_2$. Isolation of the mercury compound and subsequent treatment of its ether solution with amalgam resulted in rapid conversion to $NaCo(CO)_4$. Apparently, therefore, in the ether (as well as in the hexane) preparation of $NaCo(CO)_4$ from dicobalt octacarbonyl and sodium amalgam, $Hg[Co(CO)_4]_2$ is an intermediate. Indeed it was possible to isolate a small amount of the mercury compound during the ether preparation.

We also wish to report that treating a hexane solution of dicobalt octacarbonyl with mercury alone at room conditions under carbon monoxide gives a quantitative yield of $Hg[Co(CO)_4]_2$. Since this carbonyl precipitates elemental mercury when warmed with pyridine,[2] a novel purification of mercury thus is available.

Experimental

A mixture of 45 g. of 1% Na–Hg was stirred under carbon monoxide with a solution of 1.80 g. of dicobalt octacarbonyl in 100 ml. of hexane. After 24 hr. of stirring, the conversion to sodium tetracarbonylcobaltate(−I) was complete. However, after only 1.5 hr., the solution contained approximately 1 mmole each of dicobalt octacarbonyl and mercury(II) tetracarbonylcobaltate(−I). Analysis was made by treating aliquots with pyridine, which reacts only slowly[2] with the mercury compound but very rapidly[3] with the cobalt carbonyl to liberate 8/3 moles of carbon monoxide per mole of $Co_2(CO)_8$. Addition of water to the mixture, followed by separation and evaporation of the hexane layer, gave pure $Hg[Co(CO)_4]_2$, m.p. 81–82°, identical with an authentic sample[4] prepared from ammonia, cobalt carbonyl, and mercuric chloride.

In a similar preparation, at 0° with ether as a solvent, an aliquot was withdrawn after 45 min. and evaporated to dryness. The residue was taken up in hexane; pyridine and then water were added. Separation and evaporation of the hexane layer gave a small quantity of $Hg[Co(CO)_4]_2$, m.p. 80–81°.

A solution of 0.130 g. of $Hg[Co(CO)_4]_2$ in dry ether was added to 20 g. of 1% Na–Hg under carbon monoxide. The yellow color of the solution disappeared completely after 15 min. The presence of $NaCo(CO)_4$ was confirmed by addition of methyl iodide followed by triphenylphos-

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phine and the isolation of the known[5] $CH_3COCo(CO)_3P(C_6H_5)_3$.

A solution of 0.950 g. of $Co_2(CO)_8$ in about 50 ml. of hexane was stirred with mercury under carbon monoxide. After about 20 hr., the yellow solution was evaporated to dryness in a stream of carbon monoxide, giving a quantitative yield of $Hg[Co(CO)_4]_2$.

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CONTRIBUTION FROM THE
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Resolution of Chromium(III) Hexafluoroacetylacetonate by Gas Chromatography

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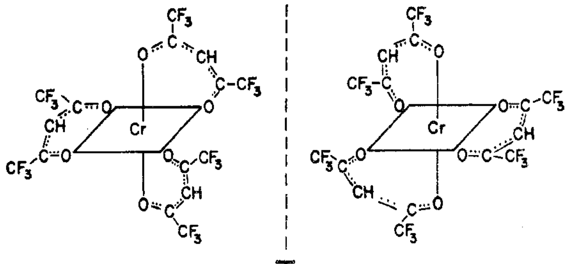
We wish to report the partial resolution of *dl*-tris-(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-chromium(III) (structure I) by gas–solid chromatography.



I

This complex can be prepared by allowing 1,1,1,-5,5,5-hexafluoro-2,4-pentanedione to react with chromium(III) nitrate nonahydrate in absolute ethanol. Two g. (0.005 mole) of the chromium salt and 3.12 g. (0.015 mole) of the ligand were combined in 20 ml. of absolute ethanol and heated on a steam bath for 5 min. The solution was evaporated almost to dryness under an air stream, with the formation of green crystals. The product (yield, 1.5 g. or 42%) was separated by filtration and recrystallized from carbon tetrachloride. *Anal.* Calcd. for $Cr(C_{15}H_3F_{18}O_6)$: C, 26.76; H, 0.45; Cr, 7.73; F, 50.80. Found: C, 27.00; H, 0.93; Cr, 7.92; F, 50.57.

The complex is soluble in most common organic solvents and is moderately soluble even in hexane. It is remarkably volatile and sublimes rapidly at room temperature at 0.05 mm. and can even be steam distilled from boiling water. More impressively, the complex steam distils from boiling aqua regia. Increased volatility of the hexafluoroacetylacetonato complexes as compared with corresponding acetylacetonato complexes has been observed for a number of metal ions.[1-4]

A separation of optical isomers by gas chromatography is possible if the column employed is packed with an optically active substrate. In gas–solid chromatography the separation is based on the differences in the adsorptive tendencies of the isomers on the surface of the solid.

Experimental

A column packed with powdered *dextro* quartz (80–120 mesh) was used in this study. Large natural *dextro* quartz crystals were first broken down to pea-size pieces in a jaw crusher. The pieces were heated to 300° and then dumped into ice water.[5] The resulting thermal shock caused numerous ruptures and fissures, and consequently the grinding process was greatly facilitated. The powdered quartz was washed with hot concentrated hydrochloric acid and with distilled water several times. It was dried for 1 hr. at 200° and packed in a Teflon tube 12 ft. long with an inner diameter of 0.25 in. The tube was coiled and inserted in a constant temperature air bath in a Burrell Model K-7 gas chromatography apparatus. The column was conditioned for 1 week at 100° with a stream of purified helium.[6] For the remainder of the experiment the column temperature was maintained at 55°. The flash vaporizer chamber was thermostated at 125° and the detector cell at 150°. The flow rate of the carrier gas was 80 ml./min. Components in the effluent helium stream were collected in a trap immersed in liquid nitrogen.

The sample was taken from a saturated carbon tetrachloride solution of the chromium complex. Fifteen μl.

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(5) The authors wish to thank Dr. L. Spialter for suggesting this procedure for pulverizing quartz.

(6) When the column was used without prolonged conditioning, the adsorptive ability of the quartz was greatly reduced. Retention times were considerably longer after conditioning for 1 week as compared with 1 day. It is suspected that mono- or poly-layers of adsorbed water are responsible for the erratic adsorptive behavior of the quartz.