9.44 g. (98%). An analytical sample was prepared by twofold recrystallization from chloroform–cyclohexane; m.p. 65.5–67°.

Anal. Calcd. for $C_{17}H_{15}O_5N$: C, 65.17; H, 4.83; N, 4.48. Found: C, 65.14; H, 4.87; N, 4.42.

Preparation of II in the Presence of Potassium Chloride.—To a solution of 0.3133 g. (0.001 mole) of I in 3 ml. of 5 *N* ammonium hydroxide were added 0.0292 g. (0.0005 mole) of sodium chloride plus 0.0328 g. (0.0005 mole) of potassium chloride. The solution was diluted with water to 5 ml., divided into two equal portions, and placed in cork-stoppered vessels. After 4 hr., the precipitate in the first vessel was filtered and air-dried; 0.1200 g. (74%) of II resulted. A flame test on II prepared in this manner revealed the presence of a small amount of potassium.

The precipitate in the second vessel gradually changed to an oil on standing for 2 days.

π-Allyl-π-Cyclopentadienylcobalt Halides

R. F. HECK

Research Center, Hercules Powder Company,
Wilmington, Delaware

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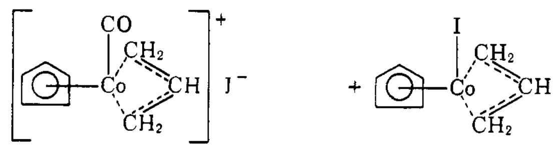
Fischer has reported the preparation of the ionic compound, π-allyl-π-cyclopentadienylcobalt carbonyl bromide by the reaction of allyl bromide with π-cyclopentadienylcobalt dicarbonyl.[1] We have found that allyl iodide reacts with π-cyclopentadienylcobalt dicarbonyl at 25° in tetrahydrofuran solution to give two products, a yellow-green insoluble, ionic material as the major product and about 10% of a soluble covalent compound. The ionic compound reacts with hexafluorophosphate ion to give an insoluble yellow product which is identical with the π-allyl-π-cyclopentadienylcobalt carbonyl hexafluorophosphate prepared by Fisher,[1] indicating that the original compound was probably π-allyl-π-cyclopentadienylcobalt carbonyl iodide. The covalent compound, obtained as very dark red needles by evaporation of the tetrahydrofuran solution and recrystallization, melted with decomposition at 95.5–97°. The compound is oxidized by air quite rapidly, particularly in solution. The compound sublimed in high vacuum at 50–60°. It is soluble in organic solvents but insoluble in water. The compound has no carbonyl bands in its infrared spectrum. Analyses and the nuclear magnetic resonance spectrum indicate that the compound is π-allyl-π-cyclopentadienylcobalt iodide. The n.m.r. spectrum at 60 Mc. in deuteriochloroform had four bands with an area ratio of 5:2:1:2 at 71, 88 (doublet), 112 (multiplet), and 198 (doublet) c.p.s., respectively, relative to an external benzene standard.

$CH_2{=}CH{-}CH_2I + \pi{-}C_5H_5Co(CO)_2 \longrightarrow$



Under the same conditions, allyl bromide reacts with π-cyclopentadienylcobalt dicarbonyl to give only a few per cent of π-allyl-π-cyclopentadienylcobalt bromide, the major product being π-allyl-π-cyclopentadienylcobalt carbonyl bromide as observed by Fischer.[1] The covalent bromide is a dark red crystalline compound of m.p. 96–98° dec. The properties and spectra are very similar to those of the iodide. The n.m.r. spectrum in deuteriochloroform had four bands in the area ratios of 2:5:1:2 at 70, 80, 120, and 220 c.p.s., respectively, referred to an external benzene standard.

Allyl chloride reacts with π-cyclopentadienylcobalt dicarbonyl to yield only a bright green salt which is probably π-allyl-π-cyclopentadienylcobalt carbonyl chloride, since it gives the same insoluble hexafluorophosphate as is obtained from the bromide.

Experimental

π-Allyl-π-Cyclopentadienylcobalt Iodide.—Cyclopentadienylcobalt dicarbonyl (3.0 ml.), 10 ml. of purified tetrahydrofuran and 2.0 ml. of allyl iodide were injected into a nitrogen-filled tube which had been closed with a self-sealing rubber cap. A yellow solid soon began to separate. After standing for 2 days the gas formed was allowed to escape and the solid was separated from the very dark solution by centrifuging. The solid was washed several times under nitrogen with tetrahydrofuran. The combined tetrahydrofuran solutions were evaporated *in vacuo* at room temperature to about 4 ml. The yellowish solid which separated was removed by centrifuging again. Addition of 10 ml. of pentane to the solution and cooling to −80° gave very dark red, nearly black crystals. Several recrystallizations from tetrahydrofuran and pentane gave 0.37 g. shiny black needles, m.p. 95.5–97° dec. The solid compound could be handled in the air for short periods but it oxidizes readily. In solution it decomposes very rapidly in air.

Anal. Calcd. for $C_8H_{10}ICo$: C, 32.90; H, 4.11; I, 43.5. Found: C, 32.86; H, 3.51; I, 43.3.

The infrared spectrum in carbon tetrachloride had bands at 3.25 μ (w), 3.33 (w), 4.70 (w), 5.50 (w), 5.80 (vw), 6.12 (vw), 6.38 (w), 7.01 (m), 7.12 (m), 7.23 (m), 7.41 (w), 8.20 (w), 8.30 (w), 8.99 (w), 9.50 (w), 9.81 (m), 9.90 (m), 10.10 (m), 10.85 (m), 11.10 (w), 11.50 (w), and 11.92 (m). There were additional bands in carbon bisulfide solution at 12.15 μ (s) and 13.10 (w).

The tetrahydrofuran-insoluble, yellow solid obtained in the above reaction was readily soluble in water. The aqueous solution gave a yellow precipitate with an aqueous solution of potassium hexafluorophosphate. The solid was recrystallized from aqueous acetone. The infrared spectrum of a Nujol mull of the product had a strong carbonyl band at 4.79 μ.

The reactions of allyl bromide and chloride with π-cyclopentadienylcobalt dicarbonyl were carried out as described for the allyl iodide reaction.

Acknowledgment.—The nuclear magnetic resonance spectra were measured by C. R. Boss.

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[1] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16b**, 475 (1961).