A Simple Method for Preparing Metallocenes

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Many sorts of metallocenes have already been synthesized in various methods by many investigators. However, only a one-step method for the preparation of ferrocene has been proposed;[1] this method consists of a direct reaction between ferric chloride and cyclopentadiene in the presence of an organic base, without the reduction procedure of ferric chloride to ferrous chloride. No simple and convenient method for the direct preparation of metallocenes other than ferrocene has yet been reported.

The present authors wish to report on a simple method for the preparation of such metallocenes as cobaltocene and nickelocene as well as of ferrocene. They can be synthesized in good yields by this convenient procedure.

The reactions of ferric chloride, cobaltous chloride, and nickel chloride with cyclopentadiene were carried out in the presence of an excess of diethylamine. The yields of metallocenes were 84% for ferrocene, 28% for cobaltocene, and 66% for nickelocene. In this procedure the formation of the metallocenes is considered to proceed through the following mechanism: by the reaction of the metal chloride and diethylamine, a corresponding ammine-complex salt of the metal is formed, and the complex salt reacts with cyclopentadiene, which has previously been de-protonated by strongly basic diethylamine.[2]

The infrared spectra of all these metallocenes have essentially identical absorption peaks at 3100 (ν_{C-H}), 1430—1400 (ν_{C-C} ring), 1110—1100 (ring breathing), 1000 (δ_{C-H}), 820—760 (δ_{C-H}) and 1800—1550 cm^{-1}.

The Synthesis of Ferrocene.—Anhydrous ferric chloride (210.5 g., 1.30 mol.) was placed in a three-necked flask, equipped with a dropping funnel, a nitrogen inlet tube, a reflux condenser, and a stirrer. A stream of nitrogen was introduced, and dry diethylamine (320.5 g., 4.38 mol.) was added dropwise with stirring and cooling in an ice-water bath. A dark brown suspension was obtained. A mixture of dry cyclopentadiene (320.5 g., 4.85 mol.) and dry diethylamine (420.7 g., 5.76 mol.), previously cooled to 0—−15°C with an ice-salt bath, was added with vigorous stirring into the suspension over several minutes. After vigorous stirring for an hour, additional gentle stirring was continued for 3 hr. The entire reaction mixture was then heated so as to evaporate almost to dryness, and then it was submitted to steam distillation in order to collect the ferrocene. During the distillation, a part of separated ferrocene was apt to accumulate in the condenser tube. It was dissolved out by benzene, which was occasionally supplied into the distilling flask. The combination of the steam distillation and the dissolution with benzene was continued until no more ferrocene was distilled out.[3] A mixture of ferrocene and other materials was then collected as a benzene solution. On concentration and cooling, ferrocene was crystallized from the solution, collected on a filter, washed with a small amount of ether, and air-dried. The mixture of the filtrate and the ethereal washing was further concentrated, and a second crop of ferrocene was obtained by a similar treatment. The procedure was repeated several times; the total yield of ferrocene amounted to 210.4 g. (84% based on ferric chloride).

The Synthesis of Cobaltocene.—In the same manner as was used with ferrocene, a deep blue mixture was prepared in a stream of nitrogen by the reaction of blue anhydrous chloride[4] obtained from its hydrate ($CoCl_2 \cdot 6H_2O$, 48.2 g., 0.20 mol.) and dry diethylamine (117.0 g., 1.60 mol.). After this mixture had been stirred for half an hour, a cold mixture of dry cyclopentadiene (49.3 g., 0.75 mol.) and dry diethylamine (64.9 g., 0.89 mol.) was added with stirring into the mixture over a 15-min. period. After the reaction mixture had been stirred for an hour, it was refluxed for 15 min. with stirring. The reaction mixture was then cooled to room temperature, and hexane was added in 3 portions (100, 100, and 50 ml.) which

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[1] R. L. Pruett and E. L. Morehouse, *Advances in Chem. Ser.*, **23**, 368 (1959), "The Amine Method for Preparing Ferrocene".

[2] F. Ephraim, *Z. physik. Chem.*, **81**, 513 (1913); E. O. Fischer and R. Jira, *Z. Naturforsch.* **8b**, 217, 327, 692 (1953); E. O. Fischer and W. Hafner, ibid., **8b**, 444 (1953); Brit. Pat. 774529 (May 8, 1957); *Chem. Abstr.*, **52**, 2928 (1958); J. F. Cordes, *Chem. Ber.*, **95**, 3084 (1962).

[3] The method of removing the clogged ferrocene with benzene was first realized in this laboratory by K. Hata, I. Motoyama, K. Azuma and K. Urushibara.

[4] "Inorganic Syntheses," Vol. 5, 153 (1957).

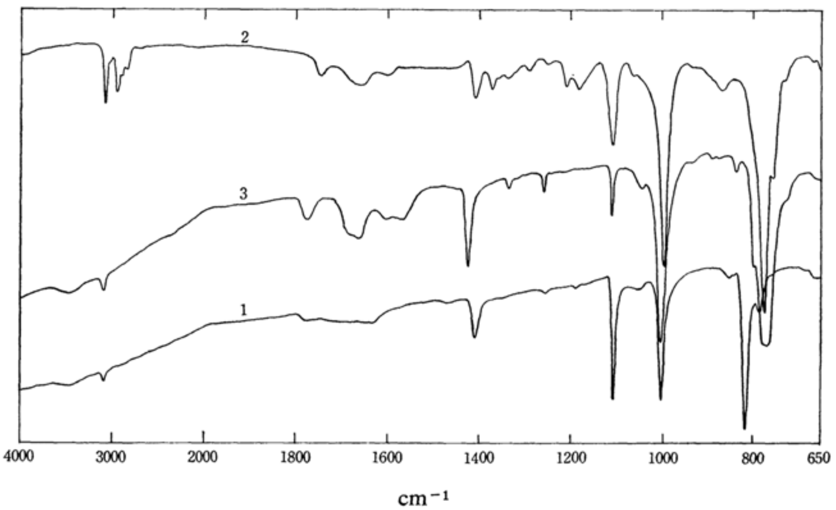

Fig. 1. The infrared spectra of the three metallocenes.
1: Ferrocene in a KBr disk 2: Cobaltocene in a CS_2 solution
3: Nickelocene in a KBr disk

has been previously deoxygenated by treatment with nitrogen. After each addition, the combined mixture was agitated thoroughly and left to stand until a violet-brown organic phase was separated as an upper layer. The organic layer was transferred to a round-bottomed flask by means of nitrogen pressure through a siphon, the inlet tube of which was covered with glass wool. The entire violet-brown organic solution was evaporated in a stream of nitrogen to give 12.0 g. of crude cobaltocene, which was then submitted to vacuum sublimation to obtain 10.5 g. (yield, 28%) of the pure substance as large, black-violet, glittering crystals.

The Synthesis of Nickelocene.—A deep violet-blue mixture was obtained by the reaction between yellow anhydrous nikel chloride4) prepared from its hydrate ($NiCl_2 \cdot 6H_2O$, 47.7 g., 0.20 mol.) and dry diethylamine (117.0 g., 1.60 mol.) in the same as manner described above. The following procedure was similar to that used with cobaltocene, except for the addition of 250 ml. deoxygenated petroleum ether in place of hexane. The entire reaction mixture was then filtered, in air, as rapidly as possible. The deep green filtrate thus obtained was evaporated in a stream of nitrogen to give crude nickelocene, which was submitted to vacuum sublimation to obtain 25.1 g. (yield, 66%) of the pure substance as large, deep green, glittering crystals.

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