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PREPARATION OF DICYCLOPENTADIENYLIRON AND DICYCLOPENTADIENYLNICKEL

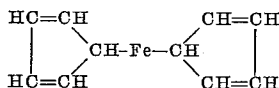
Charles L. Hobbs, Jr., Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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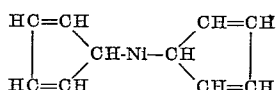
9 Claims. (Cl. 260-439)

This invention relates to a process for the manufacture of dicyclopentadienyliron and dicyclopentadienylnickel.

Dicyclopentadienyliron and dicyclopentadienylnickel are recently discovered organo metallic compounds which are of great theoretical and practical interest because they are the only known compounds in which these metals are directly attached by principal valence to a hydrocarbon radical. The iron compound is described and claimed in pending U.S. application Serial No. 291,567, filed June 3, 1952 now Patent No. 2,680,756 and the corresponding nickel compound is described and claimed in pending U.S. application Serial No. 298,170, filed July 10, 1952 now Patent No. 2,680,758. Several structural formulas have been proposed for these compounds, the simplest being the following:



and



These compounds may also be called bis-cyclopentadienyl iron and bis-cyclopentadienyl nickel.

One known method for their preparation is by the Grignard reaction between a cyclopentadienyl magnesium halide and the anhydrous halide of iron or nickel dissolved in ether. The yields, particularly in the case of the nickel compound, are small and in addition the process is expensive and suitable only for small scale production.

Another method of preparing dicyclopentadienyliron involves reacting cyclopentadiene and a specially prepared iron catalyst. The main disadvantage with this process is that the catalyst loses its activity readily and becomes inoperable in a very short time.

Another method of making dicyclopentadienyliron, which is not applicable to the manufacture of dicyclopentadienylnickel, is described and claimed in pending U.S. application Serial No. 292,388, filed June 7, 1952 now Patent No. 2,791,597. It involves the reaction between cyclopentadiene and iron pentacarbonyl. This method is suitable for large scale production but involves the use of high temperatures and in some cases of high pressures.

It is an object of the present invention to provide a process for preparing dicyclopentadienyliron and dicyclopentadienylnickel which is adapted to commercial scale operation and which produces satisfactory yields without the use of elevated temperatures or pressures. A further object is the provision of a method which employs inexpensive starting materials. Further objects will appear from the description of this invention which follows:

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According to the present invention, dicyclopentadienyliron or dicyclopentadienylnickel is obtained by reacting an anhydrous halide of the corresponding metal with cyclopentadienyl sodium.

The reaction is preferably carried out in a liquid medium which is inert with respect to the sodium compound and which has some solvent action with respect to the metal halide. For this purpose, the media ordinarily used for Grignard reactions are suitable. These include various ethers, such as diethyl ether, diamyl ether, anisole and the like, and tertiary amines such as diethylamine and dimethylaniline. The solvent may be diluted with hydrocarbons such as benzene or refined petroleum fractions. It is of course important to exclude moisture, both from the solvent and from the reactants. Any compounds capable of reaction with the cyclopentadienyl sodium should also be excluded.

The preferred halides are the chlorides and bromides. Either ferrous or ferric halides may be employed, as the latter are reduced to the ferrous state by the cyclopentadienyl sodium.

Cyclopentadienyl sodium is conveniently made by the reaction of cyclopentadiene with sodium acetylide, as described and claimed in my copending U.S. application Serial No. 312,659, filed October 1, 1952, now Patent No. 2,763,700.

The reaction between the metal halide and the cyclopentadienyl sodium is preferably carried out at a temperature between 0 and 50° C., although higher and lower temperatures are operable. The product may be recovered by filtering off the sodium halide which is formed during the reaction and separating the dicyclopentadienyliron or dicyclopentadienylnickel from the filtrate by evaporation of the solvent. In general the products may be recovered and purified either by virtue of their solubility in organic solvents such as ethers, alcohols and aliphatic and aromatic hydrocarbons, or of their volatility at slightly elevated temperatures.

The process of this invention is illustrated by the following examples, in which parts are by weight.

Example 1

Cyclopentadienyl sodium is prepared by adding 33 parts of freshly distilled cyclopentadiene to a solution of sodium acetylide, formed from 11.5 parts of sodium and an excess of acetylene, in 275 parts of liquid anhydrous ammonia. The charge is permitted to reflux at -32° C. with agitation and under a blanket of nitrogen. The ammonia is replaced by dry ethyl ether and the mixture is refluxed at 35° C. for one hour. Twenty-eight (28) parts of anhydrous ferric chloride dissolved in dry ethyl ether are added and the mixture is agitated at room temperature for 16 hours. The mixture is then filtered and the filter cake is washed with ethyl ether. The combined filtrate is concentrated and the last traces of ether are removed under reduced pressure. The yield is dicyclopentadienyliron, M.P. 173° C., is 14.9 parts. This corresponds to a yield of 44.1% based on the ferric chloride.

Example 2

Cyclopentadienyl sodium is prepared as described in Example 1 and in the same amount. To the slurry of cyclopentadienyl sodium in ether are then added 22.4 parts of anhydrous nickel chloride, prepared by heating

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$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a stream of dry hydrogen chloride until all of the water is removed and then powdering. The mixture is agitated at room temperature for 16 hours and then filtered. The filter cake is washed with ethyl ether. The combined filtrate is concentrated and the last traces of ether are removed under reduced pressure. The product is sublimed from the residue at 1.3 mm. pressure at 95–98° C. The yield of dicyclopentadienylnickel is 12.0 parts. This corresponds to a yield of 37.2% based on nickel chloride.

Analysis	Theory	Found
Percent Carbon.....	63.60	63.37
Percent Hydrogen.....	5.30	5.03
Percent Nickel.....	31.10	30.75

By the previously known reaction between a cyclopentadienyl magnesium halide and nickel halide, yields of only about 4% of dicyclopentadienylnickel are obtained.

The process of this invention is adaptable to operation on either a small or large scale, using cheap and readily available starting materials. It eliminates the use of expensive Grignard reagents and also the need for high temperatures and pressures. It permits the manufacture of either dicyclopentadienyliron or dicyclopentadienylnickel in commercially practical yield. These products are useful in the preparation of anti-knock fuels, as a source of free organic radicals and as concentrated sources of organic-soluble iron and nickel.

I claim:

1. The process of preparing a compound from the class consisting of dicyclopentadienyliron and dicyclopentadi-

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enylnickel which comprises reacting an anhydrous halide of the corresponding metal with cyclopentadienyl sodium.

2. A process according to claim 1 in which the reaction is carried out in the presence of a solvent for the metal halide which is inert with respect to the sodium compound.

3. A process according to claim 2 in which the solvent is an ether.

4. A process according to claim 1 in which the metal halide is a member of the class consisting of chlorides and bromides.

5. The process of preparing dicyclopentadienyliron which comprises reacting an anhydrous iron halide with cyclopentadienyl sodium.

6. The process of preparing dicyclopentadienyliron which comprises reacting an anhydrous iron chloride with cyclopentadienyl sodium in the presence of ethyl ether.

7. The process of preparing dicyclopentadienylnickel which comprises reacting an anhydrous nickel halide with cyclopentadienyl sodium.

8. The process of preparing dicyclopentadienylnickel which comprises reacting an anhydrous nickel chloride with cyclopentadienyl sodium in the presence of ethyl ether.

9. The process of preparing dicyclopentadienyliron which comprises reacting anhydrous ferric chloride with cyclopentadienyl sodium.

References Cited in the file of this patent

- Kealy et al.: Nature, vol. 168, pp. 1039–40, Dec. 15, 1951.
 Miller et al.: J. Chem. Soc. (London), pp. 632–635, February 1952.