



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

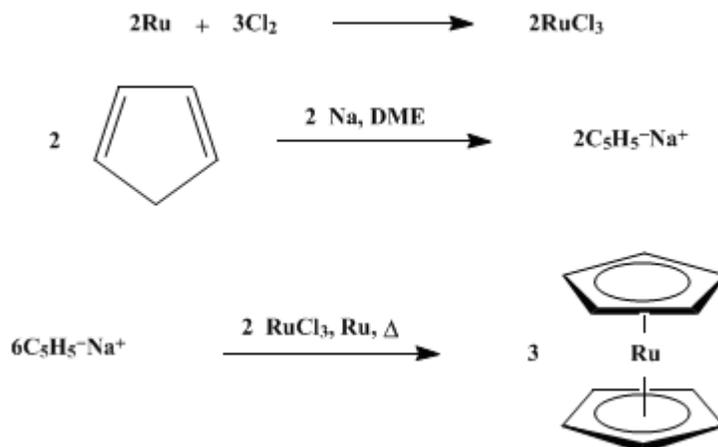
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.1001 (1973); Vol. 41, p.96 (1961).*

## RUTHENOCENE

### [Ruthenium, dicyclopentadienyl-]



Submitted by D. E. Bublitz, William E. McEwen, and Jacob Kleinberg<sup>1</sup>.  
Checked by Hans G. Essler and John H. Richards.

### 1. Procedure

A 500-ml. three-necked flask is equipped with a Trubore stirrer, reflux condenser, and a pressure-equalizing dropping funnel that carries an inlet for admission of **nitrogen**. The system is purged with **nitrogen** (Note 1), and 300 ml. of **1,2-dimethoxyethane** (Note 2) is added, followed by 7.2 g. (0.312 g. atom) of **sodium** either as wire or freshly cut small pieces. The solution is stirred, and 31.0 ml. (0.376 mole) of **cyclopentadiene** (Note 3) is added dropwise. When the evolution of **hydrogen** has almost ceased, the mixture is maintained at slightly below the reflux temperature for 1–2 hours. In the event that all the **sodium** does not dissolve, the solution is cooled to room temperature, a few milliliters more of **cyclopentadiene** added, and the mixture heated again until dissolution of the **sodium** is complete.

A mixture of 14.6 g. (0.07 mole) of **ruthenium trichloride** and 2.4 g. (0.024 g. atom) of **ruthenium metal** (Note 4) is added, and the reaction mixture is heated and stirred under **nitrogen** for 80 hours (Note 5) at slightly below the reflux temperature. With the use of stirring, the solvent is removed at aspirator pressure, and the flask then refilled with **nitrogen**. The solid is transferred to a sublimator in a dry-box containing a **nitrogen** atmosphere (Note 6) and sublimed at 0.1 mm. pressure with a heating bath at 130° (Note 7). The sublimate is dissolved in **benzene** and passed through a 1 × 12-in. column of activated alumina. Evaporation of the **benzene** gives 12.2–15.1 g. (56–69%) of ruthenocene, m.p. 199–200° (Note 8).

### 2. Notes

1. The submitters used prepurified **nitrogen**, obtained from Matheson Company, Inc., East Rutherford, New Jersey, without further purification. The checkers passed Linde (H. P. Dry) **nitrogen** successively through **chromous chloride** solution, solid **potassium hydroxide**, Ascarite, and solid **phosphorus pentoxide**.
2. **1,2-Dimethoxyethane** is dried over **sodium** wire and then distilled under **nitrogen** from **lithium aluminum hydride** just before use.
3. For preparation of **cyclopentadiene** from the dimer, see G. Wilkinson, *Org. Syntheses, Coll. Vol. 4*, 475 (1963). The **dicyclopentadiene** used as starting material was dried by passage through a 1 × 12-in. column of activated alumina prior to cracking.
4. **Ruthenium trichloride** was prepared by chlorination of powdered **ruthenium** at 650–700°<sup>2</sup> with the use of metal obtained from Goldsmith Bros. Smelting and Refining Co., 111. N. Wabash Ave., Chicago

2, Illinois. Complete chlorination could not be effected under these conditions, and on the average about 85% of the metal was converted to trichloride. Consequently, in all the preparations of ruthenocene, mixtures of trichloride and metal, as obtained from the chlorination reaction, were employed. The equations given for the preparation are idealized; the submitters believe that during the course of reaction the trichloride is gradually reduced to dichloride by ruthenium metal, and that it is the dichloride which reacts with sodium cyclopentadienide.

5. Somewhat lower yields than those reported are obtained when the reaction is carried out for a shorter period of time.

6. From this point on, the solid materials are pyrophoric, especially the residual solids from the sublimation process. However, the ruthenocene obtained by sublimation is not pyrophoric. The checkers found that careful addition of the sublimation residues to water under nitrogen destroys their pyrophoric character.

7. The checkers found the use of a Dry Ice-cooled sublimation finger advantageous.

8. The yield reported here is based on the total amount of ruthenium (both Ru<sup>III</sup> and Ru<sup>0</sup>) available for formation of ruthenocene. An additional quantity of ruthenocene may be obtained by extraction of the pyrophoric residue from the sublimation step with benzene in a Soxhlet extractor under a nitrogen atmosphere. The benzene solution is filtered through activated alumina, the solvent evaporated, and the residue sublimed.

### 3. Discussion

Ruthenocene has been prepared in 20% yields by reaction of cyclopentadienylmagnesium bromide with ruthenium(III) acetylacetonate.<sup>3</sup> More recently,<sup>4</sup> the compound has been made in 43–52% yield by treatment of sodium cyclopentadienide with ruthenium trichloride in tetrahydrofuran or 1,2-dimethoxyethane.

### 4. Merits of the Preparation

Ruthenocene is an example of a stable  $\pi$ -bonded organometallic compound which undergoes substitution reactions similar to those displayed by ferrocene. Because ruthenocene has heretofore been relatively unavailable, its chemistry has not been extensively studied.

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### References and Notes

1. Department of Chemistry, University of Kansas, Lawrence, Kans.
2. G. Brauer, "Handbuch der präparativen anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, Germany, 1952, p. 1194.
3. G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6146 (1952).
4. E. O. Fischer and H. Grubert, *Ber.*, **92**, 2302 (1959).

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### Appendix

#### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Ruthenocene

Ascarite

ruthenium(III) acetylacetonate

Benzene (71-43-2)

hydrogen (1333-74-0)  
nitrogen (7727-37-9)  
potassium hydroxide (1310-58-3)  
sodium (13966-32-0)  
Tetrahydrofuran (109-99-9)  
lithium aluminum hydride (16853-85-3)  
chromous chloride (10049-05-5)  
CYCLOPENTADIENE (542-92-7)  
dicyclopentadiene (77-73-6)  
Ruthenium, dicyclopentadienyl-  
ruthenium trichloride (14898-67-0)  
sodium cyclopentadienide (4984-82-1)  
1,2-dimethoxyethane (110-71-4)  
cyclopentadienylmagnesium bromide  
ruthenium (7440-18-8)  
phosphorus pentoxide (1314-56-3)