

Chapter Two

ORGANOMETALLIC COMPOUNDS

11. CYCLIC-DIOLEFIN COMPLEXES OF PLATINUM AND PALLADIUM

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Recently compounds containing cyclic polyolefins coordinated to platinum or palladium have received considerable attention as a result of the unique bonding found in these compounds and their possible use as intermediates in a variety of reactions. Several methods have been reported for the synthesis of these compounds, and among these procedures the displacement of ethylene¹ from di- μ -chloro-dichlorobis(ethylene)diplatinum(II) and benzonitrile² from dichlorobis(benzonitrile)palladium(II) are the most generally applied procedures. Both of these methods involve the preparation of intermediates before the isolation of the product, and in addition these intermediates tend to decompose upon storage.

The procedures described in the subsequent preparations are rapid and the starting materials are the commercially available

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palladium(II) chloride and hydrated chloroplatinic acid [hydrogen hexachloroplatinate(2-)].

A. PLATINUM COMPOUNDS

The procedure for the preparation of the platinum compounds is an extension of the method described by Kharasch and Ashford.³ A glacial acetic acid solution of chloroplatinic acid is mixed with the appropriate olefin, and in the ensuing reaction the platinum is reduced from the 4+ oxidation state to the 2+ state. The overall stoichiometry of these reactions is not known; however, the reduction of the platinum is accompanied by the partial oxidation of the olefin.

1. Dichloro(1,5-cyclooctadiene)platinum(II)



Procedure

In a 125-ml. Erlenmeyer flask 5.0 g. (8.41 mmoles) of hydrated chloroplatinic acid is dissolved in 15 ml. of glacial acetic acid and the solution heated to 75°. Six milliliters of 1,5-cyclooctadiene† is added to the warm solution and the mixture swirled gently, cooled to room temperature, and diluted with 50 ml. of water. The black suspension is stored for one hour at room temperature, and the crude product is collected on a Büchner funnel, washed with 50 ml. of water, and finally 100 ml. of ether. The crude product is suspended in 400 ml. of methylene chloride

* ■ *Note.* Several recently purchased samples of the commercially available hydrated chloroplatinic acid, labeled to contain 40% platinum by weight, were actually analyzed as 32.8% by weight, and the yields were computed on the basis of the latter percentage. *Caveat emptor.*

† The following hydrocarbons have been successfully substituted for 1,5-cyclooctadiene in this procedure to yield the corresponding dichloro(olefin)platinum(II) derivatives: 1,3,5,7-cyclooctatetraene, dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene), and bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene).

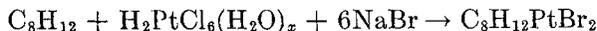
and the mixture heated to the boiling point and kept at this temperature for 5 minutes. The solution is cooled, mixed with 5.0 g. of chromatographic-grade silica gel, and allowed to settle. The supernatant liquid should be colorless; if not, add additional silica gel in 1-g. portions until the solution is clear. The mixture is filtered and the residue washed with two 50-ml. portions of methylene chloride. The methylene chloride solution, approximately 500 ml., is evaporated until the product commences to crystallize, about 75 ml. The hot solution is poured into 200 ml. of petroleum ether (b.p. 60–70°), yielding a finely divided white product. The precipitate is washed with 50 ml. of petroleum ether and dried. Yield is 2.55 g. (80%). *Anal.* Calcd. for $C_8H_{12}PtCl_2$: C, 25.68; H, 3.23. Found: C, 25.73; H, 3.41.

A small amount of product can be recovered by evaporation of the methylene chloride–petroleum ether filtrate. The product can be recrystallized to yield white macroscopic crystals by dissolving the white powder in 150 ml. of boiling methylene chloride and evaporating the solution until crystallization commences.

Properties

Dichloro(1,5-cyclooctadiene)platinum(II) is a white, air-stable solid. The compound is slightly soluble in solvents such as chloroform, acetic acid, sulfolane (tetrahydrothiophene 1,1-dioxide), and nitromethane. It decomposes slowly upon dissolution in dimethyl sulfoxide. The p.m.r. spectrum of the compound in chloroform shows resonances at 4.38 τ , $J_{Pt-H} = 65$ Hz., for the olefinic protons and 7.29 τ for the methylene protons. The infrared spectrum in Nujol has strong absorption maxima at 1334, 1179, 1009, 871, 834, and 782 cm^{-1} .

2. Dibromo(1,5-cyclooctadiene)platinum(II)



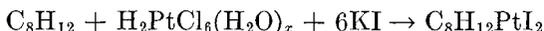
Procedure

A mixture of 5.0 g. (8.41 mmoles) of hydrated chloroplatinic acid and 6.2 g. (60 mmoles) of sodium bromide suspended in 15 ml. of glacial acetic acid in a 125-ml. Erlenmeyer flask is heated at 75° for 10 minutes. Six milliliters of 1,5-cyclooctadiene* is added to the hot solution yielding a brown solution and a black precipitate containing the impure product. The pure product is isolated in *exactly* the same manner as that described for the preparation of dichloro(1,5-cyclooctadiene)-platinum(II). The clarified methylene chloride solution is very pale yellow. The yield of the very pale yellow product in the form of a finely divided powder was 3.22 g. (83%). *Anal.* Calcd. for C₈H₁₂PtBr₂: C, 20.75; H, 2.61. Found: C, 21.21; H, 2.66.

Macroscopic pale yellow crystals can be isolated by the recrystallization procedure described in the preparation of dichloro(1,5-cyclooctadiene)platinum(II).

Properties

Dibromo(1,5-cyclooctadiene)platinum(II) is a very pale yellow, air-stable solid. The solubility of the compound is similar to that of the chloro derivative except that the rate of decomposition in dimethyl sulfoxide is appreciably faster. The p.m.r. spectrum of the compound in chloroform shows resonances at 4.32 τ , $J_{\text{Pt-H}} = 70$ Hz., for the olefinic protons and 7.43 τ for the methylene protons. The infrared spectrum in Nujol has strong absorption maxima at 1334, 1175, 1007, 870, 830, and 780 cm.⁻¹.

3. (1,5-Cyclooctadiene)diiodoplatinum(II)

* The following hydrocarbons have been successfully substituted for 1,5-cyclooctadiene in this procedure to yield the corresponding dibromo(olefin)platinum(II) derivatives: 1,3,4,7-cyclooctatetraene, dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene), and bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene).

Procedure

To a solution of 5.0 g. (8.41 mmoles) of hydrated chloroplatinic acid in 50 ml. of water is added 10 g. (60 mmoles) of potassium iodide followed by 6 ml. of 1,5-cyclooctadiene.*

The brown suspension is stirred magnetically for 30 minutes, and then a solution containing 1.9 g. of *fresh* sodium metabisulfite in 20 ml. of water is added until the solution is colorless. The yellow product is separated on a Büchner funnel and washed with two 50-ml. portions of water and two 100-ml. portions of diethyl ether. The product is redissolved in 300 ml. of boiling methylene chloride, and after cooling, 6.0 g. of chromatographic grade silica gel is added to the solution. The solution is filtered and the silica gel residue washed with two 50-ml. portions of methylene chloride. The combined filtrates and washings are evaporated until crystallization commences (about 75 ml.) and the product recovered by adding the hot solution to 200 ml. of petroleum ether (b.p. 60–70°). The precipitate is washed with 50 ml. of petroleum ether and dried. Yield is 3.60 g. (77%). *Anal.* Calcd. for $C_8H_{12}PtI_2$: C, 17.25; H, 2.17. Found: C, 17.42; H, 2.12.

A small amount of product can be recovered by evaporation of the methylene chloride–petroleum ether filtrate. The product can be recrystallized to yield yellow macroscopic crystals by dissolving the yellow powder in 150 ml. of boiling methylene chloride and evaporating until the solution crystallization commences.

Properties

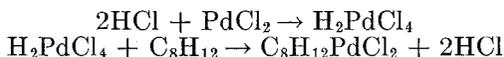
(1,5-Cyclooctadiene)diiodoplatinum(II) is a yellow, air-stable solid. The compound is slightly soluble in solvents such as

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chloroform, acetic acid, sulfolane (tetrahydrothiophene 1,1-dioxide), and nitromethane. It decomposes upon dissolution in dimethyl sulfoxide. The p.m.r. spectrum of the compound in chloroform shows resonances at 4.24 τ , $J_{\text{Pt-H}} = 64$ Hz., for the olefinic protons and at 7.63 τ for the methylene protons. The infrared spectrum in Nujol has strong absorption maxima at 1334, 1172, 1000, 867, 825, and 776 cm^{-1} .

B. PALLADIUM COMPOUNDS

1. Dichloro(1,5-cyclooctadiene)palladium(II)



This compound has been prepared by the reaction of sodium tetrachloropalladate and the olefin⁴ or by the displacement of carbon monoxide from $[\text{COPdCl}_2]_2$ ⁵ or benzonitrile from $(\text{C}_6\text{H}_5\text{C}\equiv\text{N})_2\text{PdCl}_2$. Bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) may be substituted in the following procedure for 1,5-cyclooctadiene to yield (bicyclo[2.2.1]hepta-2,5-diene)dichloropalladium(II).

Procedure

Palladium(II) chloride (2.0 g., 11.3 mmoles) is dissolved in 5 ml. of concentrated hydrochloric acid by warming the mixture. The cool solution is diluted with 150 ml. of absolute ethanol, filtered, and the residue and filter paper washed with 20 ml. of ethanol. To the combined filtrate and washings is added 3.0 ml. of 1,5-cyclooctadiene with stirring. The yellow product precipitates immediately, and after a 10-minute storage is separated and washed with three 30-ml. portions of diethyl ether. Yield is 3.10 g. (96%, based on PdCl_2). *Anal.* Calcd. for $\text{C}_8\text{H}_{12}\text{PdCl}_2$: C, 33.66; H, 4.24. Found: C, 34.26; H, 4.39.

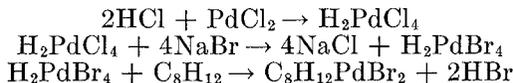
The product can be obtained as macroscopic yellow crystals

by dissolving the yellow powder in 200 ml. of boiling methylene chloride and evaporating the hot solution until crystallization commences.

Properties

Dichloro(1,5-cyclooctadiene)palladium(II) is an air-stable yellow solid. The compound is slightly soluble in solvents such as chloroform, sulfolane (tetrahydrothiophene 1,1-dioxide), and nitrobenzene and reacts with dimethyl sulfoxide to yield dichlorobis(dimethyl sulfoxide)palladium(II). The p.m.r. spectrum of the compound in chloroform shows resonances at 3.68τ for the olefinic protons and at 7.31τ for the methylene protons. The infrared spectrum in Nujol has strong absorption maxima at 1489, 1419, 1337, 1088, 999, 867, 825, 794, 768, 325, and 295 cm.^{-1} .

2. Dibromo(1,5-cyclooctadiene)palladium(II)



The previously reported⁴ procedure, which is a technique of general utility, involves the reaction of dichloro(1,5-cyclooctadiene)palladium(II) with a solution of sodium bromide in acetone. The following procedure gives comparable yields and eliminates the need for the preparation of the dichloro intermediate. Bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) may be substituted in the following procedure for the 1,5-cyclooctadiene to yield (bicyclo[2.2.1]hepta-2,5-diene)dibromopalladium(II).

Procedure

Two grams of palladium(II) chloride (11.3 mmoles) is dissolved in 5 ml. of concentrated hydrochloric acid by warming

the mixture. A solution containing 4.65 g. (45.2 mmoles) of sodium bromide in 7.0 ml. of water is added to the palladium chloride solution and the mixture warmed to 50° for about 5 minutes. The mixture is diluted with 50 ml of absolute ethanol and after cooling for 15 minutes is filtered. The flask and filter paper are washed with three 10-ml. portions of 75% aqueous ethanol to remove the residual palladium salts. To the combined filtrate and washings is added 3.0 ml. of 1,5-cyclooctadiene, and the solution is mixed by swirling the flask. The orange product precipitates immediately and after settling for 10 minutes is collected on a Büchner funnel. The product remaining in the flask is transferred to the funnel with the aid of 50 ml. of water, and the collected product is washed with an additional 50 ml. of water, followed by two 100-ml. portions of ether. Yield is 3.96 g. (93%, based on PdCl₂). *Anal.* Calcd. for C₈H₁₂PdBr₂: C, 25.66; H, 3.23. Found: C, 26.85; H, 3.17.

The product may be obtained as macroscopic orange crystals by dissolving the orange powder in 150 ml. of boiling methylene chloride and evaporating the hot solution until crystallization commences.

Properties

Dibromo(1,5-cyclooctadiene)palladium(II) is an air-stable, orange solid. The compound is slightly soluble in solvents such as chloroform, nitrobenzene, and sulfolane (tetrahydrothiophene 1,1-dioxide), and reacts rapidly with dimethyl sulfoxide to yield dibromobis(dimethyl sulfoxide)palladium(II). The p.m.r. spectrum of the compound in chloroform shows resonances at 3.58 τ for the olefinic protons and 7.40 τ for the methylene protons. The infrared spectrum in Nujol has strong absorption maxima at 1472, 1417, 1333, 1172, 1083, 992, 905, 864, 823, 787, 764, 678, 310, 265, 221, 213, 178, and 126 cm.⁻¹.

References

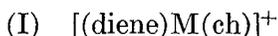
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12. CATIONIC DIENE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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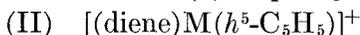
Checked by J. R. DOYLE† and H. LEWIS†

The palladium(II) and platinum(II) ions form stable complexes with a variety of chelating diolefins.¹⁻⁵ These may be either neutral or cationic in character. The preparative routes to the former type are, in general, well-documented. The species (I) through (IV) include all the presently known cationic species, and the preparation of each type is discussed and exemplified.

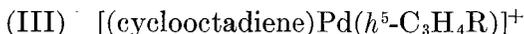


diene = 1,5-cyclooctadiene, 2,5-norbornadiene, or dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene)

ch = conjugate base of acetylacetone (2,4-pentanedione), benzoylacetone (1-phenyl-1,3-butanedione) or dibenzoylmethane (1,3-diphenyl-1,3-propanedione)



diene = 1,5-cyclooctadiene or 1,2,3,4-tetraphenyl-1,3-cyclobutadiene



R = H or 1-Me

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