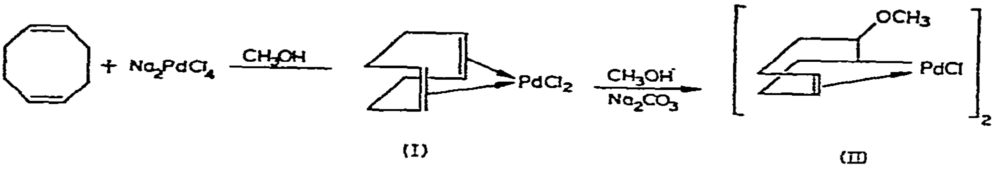
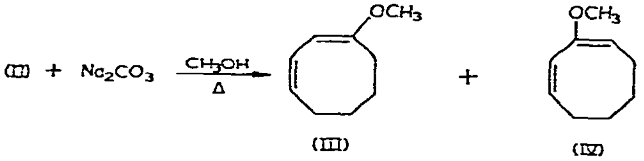
Some reactions of 1,5-cyclooctadienepalladium(II) dichloride

The preparation of 1,5-cyclooctadienepalladium(II) dichloride (I) was first reported by Chatt[1] by the reaction of sodium chloropalladite and 1,5-cyclooctadiene in methyl alcohol or acetone. In the presence of hot methanolic sodium carbonate the transformation of the diene complex to a σ-bonded methoxy complex (II) was reported. Later studies on these and other diolefinic complexes confirmed these structural assignments[2–5].



We now wish to report a simplified preparation of the methoxy complex (II) in which decomposition is completely avoided. When a suspension of the olefin complex (I) and sodium carbonate was stirred in methanol at 25° an excellent yield of the methoxy complex (II) was obtained. A preliminary study has indicated that the organic moieties produced when the complex (II) is totally decomposed in hot methanolic sodium carbonate are the isomeric methoxyoctadienes (III) and (IV). The most probable explanation for this observation is a palladium metal catalyzed isomerization of a non-conjugated methoxy diene produced as a primary product of the reaction.



Experimental

1,5-Cyclooctadienepalladium(II) dichloride. Sodium chloropalladite [14.7 g, 0.05 mole] was dissolved in 400 ml water containing 5 ml concentrated hydrochloric acid and 5.75 g [0.053 mole) of 1,5-cyclooctadiene was added. The mixture was stirred at 25° for 2.5 h. During this time the solution changed in color from red-brown to pale yellow and a bright yellow precipitate formed. The precipitate was filtered, washed with water and air dried yielding 13.2 g (92.7 % of theory) of 1,5-cyclooctadienepalladium(II) dichloride, dec. pt. 210–215°.

Di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium (II). A mixture of 2.85 g (0.01 mole) of 1,5-cyclooctadienepalladium(II) dichloride and 0.53 g (0.005 mole) of sodium carbonate was suspended in 75 ml methanol and stirred at 25° for 3 h. After 1 h of reaction all the yellow color of the diolefin complex (I) had disappeared. The suspension was filtered, washed with methanol and triturated with 75 ml water. The aqueous suspension was filtered, washed with water and air dried yielding 2.62 g (93.3 %) of di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium (II), dec. pt. 136–140°.

Decomposition of the methoxy complex (II). A mixture of 14.25 g [0.05 mole] of 1,5-cyclooctadienepalladium(II) dichloride and 15.9 g [0.15 mole] of sodium carbonate was suspended in 250 ml methanol and stirred at 25° for 1 h. During this time the yellow color of the diolefin complex faded and a white solid formed. This mixture was then heated at reflux for 1 h. After 10 min at reflux there was extensive precipitation of palladium. The reaction mixture was then cooled and filtered. The filtrate was evaporated to small volume and the residue partitioned between benzene and water. The benzene solution was washed with three portions of water and then dried over sodium sulfate. After the benzene was evaporated the residue was distilled giving 2.51 g (36.4 %) of a fraction, b.p. 115–117° at 85 mm. A nuclear magnetic resonance spectrum on the neat liquid showed peaks at δ -5.7 (olefinic protons, relative intensity 3); -3.27 and -3.23 (OCH_3, total rel. intensity 3); -2.25 ($CH_2C{=}C$, rel. intensity 4); and -1.60 ppm ($C{-}CH_2{-}C$, rel. intensity 4) indicating the assigned structures (III) and (IV).

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The preparation of ferrocenylmethyl alkyl sulfides from alkyl ferrocenethiolcarboxylates

Esters of aromatic acids are reduced by lithium aluminum hydride to form two alcohols that correspond to the components of which the ester is composed (eqn. 1)[1]. Corresponding products have been obtained in the reduction of thiol esters by lithium aluminum hydride (eqn. 2). The alcohol is derived from the acyl fragment as before and the mercaptan is derived from the thiol portion[2]. In certain instances when the reduction of an aromatic ester is carried out in the presence of excess lithium aluminum hydride, the reduction of the acyl portion proceeds further with the formation of a methyl group[3,4,*]. Numerous reductions by lithium aluminum hydride have been

$$ArCO_2R \xrightarrow{LiAlH_4} ArCH_2OH + ROH \qquad (1)$$

$$RCOSR' \xrightarrow{LiAlH_4} RCH_2OH + R'SH \qquad (2)$$

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[*] The report that methylferrocene results from treatment of ferrocenoic acid or its methyl ester with excess lithium aluminum hydride[4] must be attributed to the *in situ* preparation of this latter reagent from lithium hydride and aluminum bromide. These reductions when carried out in our laboratories using commercially available lithium aluminum hydride (Metal Hydrides, Inc.) led only to the formation of ferrocenylmethanol. Methylferrocene was obtained only when added aluminum chloride was present in the reducing medium. These latter results are in agreement with the findings of Benkeser and Bach[5].