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NOTE

PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF *cis,cis*-1,5-CYCLONONADIENE

G. NAGENDRAPPA AND D. DEVAPRABHAKARA
Department of Chemistry, Indian Institute of Technology, Kanpur (India)

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In an earlier publication we described the structure and physical properties of the silver(I), copper(I) and rhodium(I) complexes of *cis,cis*-1,5-cyclononadiene[1], and we now report studies on complexes of the cyclononadiene with palladium(II) and platinum(II). The Pd^{II} and Pt^{II} complexes of the analogous *cis,cis*-1,5-cyclooctadiene[2,3] and *cis,cis*-1,6-cyclodecadiene[4] are well known.

RESULTS AND DISCUSSION

The orange-yellow diene–palladium complex was prepared by stirring a benzene solution of bis(benzonitrile)palladium(II) chloride with a slight excess of diene at room temperature[5], it decomposes above 150° without melting.

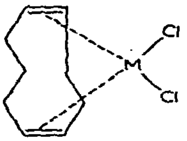
The orange diene–platinum complex was prepared by modification of one of the methods recommended by Chatt[6]; it was precipitated when a 2 *N* AcOH solution of potassium tetrachloroplatinate(II) was stirred with a slight excess of the diene, it also decomposes above 150° without melting.

Analyses showed that each molecule of the diene is complexed with one molecule of MCl_2 ($M = Pd$ or Pt).

Both the palladium and platinum complexes were found to be quite stable, and could be vacuum-dried over drierite without appreciable change in the elemental analysis. They are insoluble in most of the common organic solvents, but dissolve in dimethyl sulfoxide with immediate decomposition. The NMR spectra of both the complexes recorded in dimethyl sulfoxide-d_6 were identical to that of the original diene[1], which shows that the diene does not undergo any isomerization during complexation. The complex of bullvalene with palladium(II) chloride is known to be similarly decomposed by dimethyl sulfoxide[7].

The infrared spectra of the Pd^{II}– and Pt^{II}–diene complexes are very similar. The carbon–carbon double bond frequencies between 1600–1675 cm^{-1} are absent, two new strong bands appear at 1495 and 1505 cm^{-1} and can be assigned to coordinated double bonds. These results are in agreement with the observations made by Chatt[2,3] and Jonassen[4] on Pd^{II} and Pt^{II} *cis,cis*-1,5-cyclooctadiene, and Pd^{II} and Pt^{II} *cis,cis*-1,6-cyclodecadiene complexes, respectively. The three C–H stretching bands at 3000, 2915 and 2855 cm^{-1} of the free *cis,cis*-1,5-cyclononadiene, have merged in the spectra of both its Pt^{II} and Pd^{II} complexes, and a broad band at 2835 cm^{-1} with shoulder at 2970 cm^{-1} has taken their place.

No exact structures can be assigned to the complexes because neither other spectra, such as NMR, nor molecular weights could be made because of their insolubility but it is likely that they have structures similar to that proposed by Jonassen and coworkers for the *cis,cis*-1,6-cyclodecadiene–Pd^{II} chloride complex[4].



or —diene—MCl$_2$—diene—MCl$_2$—

M = Pd(II) or Pt(II)

EXPERIMENTAL

General

cis,cis-1,5-Cyclononadiene was prepared as described earlier[1]. Bis(benzonitrile)palladium(II) chloride was prepared by the method of Kharasch[5].

Elemental analyses were carried out by A. H. Siddiqui, microanalyst of this department.

The IR spectra were recorded on a Perkin–Elmer Model 521 spectrophotometer. The spectra of the liquids were recorded neat using CsBr plates, and those of solids in KBr pellets.

Preparation of palladium(II) complex

3.7 g (0.01 mole) of bis(benzonitrile)palladium(II) chloride was dissolved in benzene and the solution filtered. To the filtrate was added 1.50 g of *cis,cis*-1,5-cyclononadiene. The diene–palladium(II) chloride complex precipitated out. After standing overnight, the precipitate was filtered off, washed with dry petroleum ether and dried over drierite (yield of the complex 2.58 g). (Found: C, 36.26; H, 4.46. $C_9H_{14}Cl_2Pd$ calcd.: C, 36.08; H, 4.67%.) The complex blackens around 150° and decomposes without melting. It is insoluble in common organic solvents and dissolves with decomposition in dimethyl sulfoxide.

Preparation of platinum(II) complex

The diene (0.5 g) was added to a solution of 1.0 g of potassium tetrachloroplatinate(II) in dilute acetic acid (2 *N*), and the mixture was stirred at room temperature. A light-orange complex precipitated out, and was filtered off, washed with absolute ethanol and dried over drierite (yield of the complex 0.77 g). (Found: C, 28.46; H, 3.80. $C_9H_{14}Cl_2Pt$ calcd.: C, 27.83; H, 3.60%.) It decomposes above 150° without melting, is insoluble in most of the common organic solvents, and decomposes in dimethyl sulfoxide.

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