Metal π-Complexes of Dienes with Crossed Double Bonds: Dichloro-(5-methylenecycloheptene)platinum(II)

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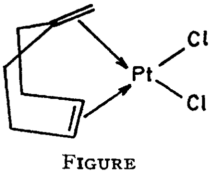
Summary Reaction of sodium tetrachloroplatinate(II) with 5-methylenecycloheptene leads to dichloro-(5-methylenecycloheptene)platinum(II), a complex with mutually perpendicular double bonds one of which is presumed to lie in the plane of co-ordination.

CRYSTAL structures[1] of platinum(II) and palladium(II) olefin complexes, as well as n.m.r. spectral measurements,[2] show the double bonds perpendicular to the co-ordination plane of the metal, or nearly so, and therefore the possibility of a diene complex with double bonds perpendicular to one another, one of them in the plane of co-ordination, seemed interesting. Barriers to rotation of olefins in platinum acetylacetonate complexes have been found to be 10·9—15·8 kcal mol^{-1}, and the barrier maximum is thought to be in the plane of co-ordination.[2] Consequently a diene complex with crossed double bonds might be considerably less stable (10—16 kcal) than those with double bonds perpendicular to the plane of co-ordination. The favoured perpendicular stereochemistry of the double bond is due to



FIGURE

backbonding of the metal d_{xz} and d_{yz} orbitals which overlap better than the d_{xy} orbital because of hybridization with the vacant p_z orbital of the metal.[3]

A methanol solution of 5-methylenecycloheptene[4] and sodium tetrachloroplatinate(II) was stirred for one day giving a white solid, m.p. 210—215°(decomp.). Elemental analysis, a cryoscopic molecular weight determination, and i.r. and n.m.r. spectra were satisfactory for the diene complex (Figure). The n.m.r. spectrum in trifluoroacetic acid shows resonances (downfield from tetramethylsilane) at $-5\cdot92$ p.p.m. ($J_{\mathrm{Pt,H}}$ 70 Hz, 2H), $-4\cdot92$ p.p.m. ($J_{\mathrm{Pt,H}}$ 60 Hz, 2H), and $-2\cdot80$ p.p.m. (very broad *ca.* 60 Hz, 8H). The two downfield signals appear as unresolved multiplets of halfwidth 9 and 2 Hz respectively with satellites on either side due to coupling with ^{195}Pt (33·7% abundance).

The compound is only a little less stable than dichloro(cyclo-octa-1,5-diene)platinum(II) [m.p. 220—278° (decomp.)][5] although the difference between the C=C stretching frequencies of the free olefin and that of the complex (100 cm^{-1}) is rather small compared to cyclo-octadiene and the cyclo-octadiene complex (227 cm^{-1}). The ^{195}Pt–H coupling constants in the cyclo-octadieneplatinum chloride complex are 68 Hz which suggests that the methylene of methylenecycloheptene complex is less closely bound to the platinum. A similar reaction of the diene with sodium tetrachloropalladate(II) gave palladium black and as yet uncharacterized methoxy-substituted organic products in a few minutes.

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