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Chemistry of Metal Diene Complexes: X-Ray Crystal Structure of Dichloro(1,5-cyclooctadiene)platinum(II)

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Dichloro(1,5-cyclooctadiene)platinum(II) has been used frequently for the synthesis of various complexes by ligand substitution reactions [1–4]. Nucleophilic addition reactions of a variety of nucleophiles with this complex have also been studied in detail [5–7]. The activation of coordinated olefins towards nucleophilic attack has recently been suggested [8] due to an unsymmetrically oriented olefin–metal η^2–π complexation, *i.e.* the two carbons of the olefin are unsymmetrically bonded to the metal center. We have been engaged in the reactions of $(COD)MCl_2$ (M = Pt or Pd; COD = 1,5-cyclooctadiene) with phosphine ligands [9] and various nucleophiles. The nucleophilic addition products $[(C_8H_{12}OCH_3)MX]_2$ (M = Pt or Pd and X = Cl or OCH_3) obtained in the course of our investigations, have been found to be important starting materials for the synthesis of metal hydride complexes [10–12] and coordinatively unsaturated metal(0) complexes [13]. In view of the importance of the dichloro(cyclooctadiene)platinum complex it was considered worthwhile to examine its molecular structure. The crystal structure of the (endodicyclopentadiene)platinum dichloride has been reported twice; however, in the first publication [14] the residual was only to 13% whereas in the second [15] structure no geometrical parameters were reported due to high standard deviation in bond lengths (±0.15 Å) and angles (±5–6°). We wish to present here the X-ray crystal structure of dichloro(cyclooctadiene)platinum(II).

Dichloro(cyclooctadiene)platinum(II) was prepared following the improved procedure of Clark and Manzer [3]. Recrystallization by slow evaporation of a CH_2Cl_2 solution of the complex provided colorless crystals suitable for single-crystal X-ray diffraction. Unit-cell parameters and intensity data were obtained using a Syntex $P2_1$ four-circle diffractometer. The complex crystallized in the orthorhombic space group $P2_12_12_1$ with a = 11.014(3), b = 12.305(3), c = 6 940(3) Å, Z = 4 (MoKα radiation) with d_{exp} = 2.63 g cm^{-3} (d_{cal} = 2.64 g cm^{-3}). A semi-empirical absorption correction using ψ_0 scans was applied to the measured intensities 989 unique reflections having $F \geqslant 3\ \sigma_F$ wre collected.

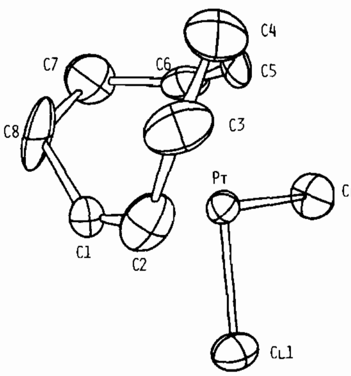

Fig. 1. ORTEP Diagram of $(C_8H_{12})PtCl_2$. Principal bond lengths (Å): Pt–Cl1 = 2.322(5), Pt–Cl2 = 2.299(5), Pt–C1 = 2.215(18), Pt–C2 = 2.203(19), Pt–C5 = 2.209(21), Pt–C6 = 2.156(17), C1–C2 = 1.331(28), C5–C6 = 1.296(29), and bond angles (°): Cl2–Pt–Cl1 = 88.9(2), C1–Pt–Cl1 = 93.0(5), C2–Pt–Cl1 = 90.6(6), C2–Pt–C1 = 35.0(8), C5–Pt–Cl2 = 94.0(5), C6–Pt–Cl2 = 90.3(5), C6–Pt–C5 = 34.5(7), C5–Pt–C1 = 89.1(7), C5–Pt–C2 = 81 5(8), C6–Pt–C1 = 82.8(7), C6–Pt–C2 = 95.5(7), C1–C2–Pt = 73.0(1.1), C2–C1–Pt = 72.0(1.1), C6–C5–Pt = 70.5(1.2), C5–C6–Pt = 75.0(1.2).

The structure was solved [16] using conventional heavy-atom techniques. From a three-dimensional Patterson map, the position of the platinum was determined and subsequent electron density maps provided the positions of all the chlorine and carbon atoms. Hydrogen positions were either calculated by the program or located from Fouriers. The non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least squares refinement of all the atom positions and temperature factors yielded an unweighted residual (R) of 0.037 and a weighted residual (R_w) of 0.042.

Pertinent distances and angles are presented in Fig. 1. The structure (Fig. 1) shows that while both of the chlorines are at normal distances from the central platinum (2.322(S) *vs.* 2.299(S) Å) suggesting equivalent *trans*-groups (*i.e.* both double bonds of 1,5-cyclooctadiene), several geometric deformations are observed upon close examination of the modes of coordinations for the C1=C2 and C5=C6 double bonds to the central platinum atom. The most striking deformation has been observed in the bonding distances of C5–Pt [2.209(21) Å] *vs.* C6–Pt [2.156(17) Å], indicating a slipping of the

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C5=C6 bond axis with respect to $PtCl_2$. Compared to this, only a small variation in the bonding distances of C1–Pt and C2–Pt [2.215(18) *vs.* 2.203(19) Å] has been observed. Thus, a deformation of the type proposed by Hoffman [8] has occurred resulting in the unsymmetrically bound olefin and C5=C6 should show increased activation with respect to nucleophilic attack. In the light of this deformation, one might expect C5 to be the point of nucleophilic attack. Although, similar deformation has been observed earlier in the unsymmetrical (endo-dicyclopentadiene)palladium dichloride [17] and 5-vinylnorbornene•$PdCl_2$ [18], it was not expected in a more symmetrical (1,5-cyclooctadiene)platinum dichloride complex. Since (1,5-cyclooctadiene)platinum dichloride is relatively less reactive compared to the 5-vinylnorbornene complex, the double bonds in the latter should be bonded in an extremely unsymmetrical manner.

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