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THE MOLECULAR STRUCTURE OF A PLATINUM–ALLENE COMPLEX

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A study of the crystal structure of the rhodium–allene complex $(C_5H_7O_2)Rh(C_7H_{12})_2$ gave important information on the molecular geometry of the allene ligand, which has since been confirmed by crystal-structure analyses of iodobis(triphenylphosphine)allene rhodium[2], and $(C_5H_7O_2)Rh[CH_2CC(CH_3)_2]$ and $(CO)_2Rh_2(C_5H_7O_2)_2(CH_2CCH_2)$[3]. The preliminary results presented here of the crystal structure analysis of $[Cl_2Pt(C_7H_{12})]_2$ show that this compound, too, is a simple allene complex and that the geometry of the allene ligand is as previously found.

The complex $[Cl_2Pt(C_7H_{12})CCl_4]_2$ crystallizes from carbon tetrachloride as cubic crystals in the orthorhombic space group *Pbca* (D_{2h}^{15}, No. 61)[4], with cell parameters $a = 20.738 \pm 3$, $b = 13.014 \pm 2$, $c = 11.568 \pm 2$, $U = 3122.0$ Å^3, $z = 8$, $M = 1032.4$, $D_X = 2.196$. The crystallographic asymmetric unit is $Cl_2Pt(C_7H_{12})CCl_4$, the dimer molecule having strict C_i symmetry. Complete three-dimensional data to $\sin\theta = 0.42$ (MoKα radiation) were collected on the Nonius three-circle automatic single-crystal diffractometer, using the θ–2θ scan method. The structure was solved by conventional Patterson and

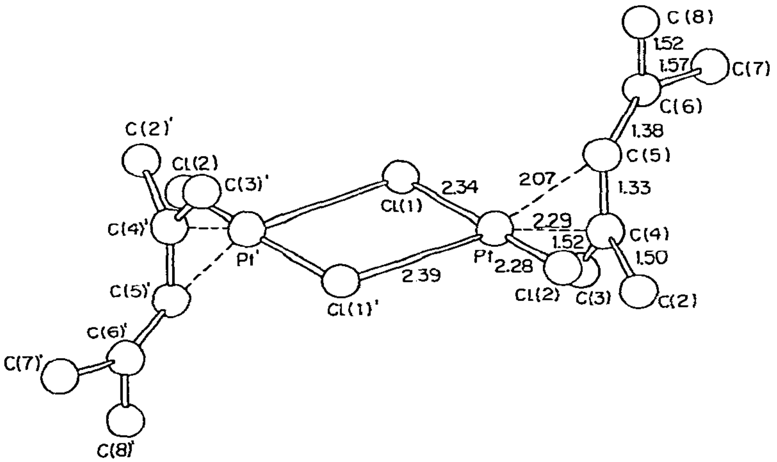

Fig.1. The molecular structure of $[Cl_2Pt(C_7H_{12})]_2$ (bond lengths in Å). Estimated standard deviations are ± 0.01 Å for Pt–Cl ± 0.02 Å for Pt–C and ± 0.03 Å for C–C.

Fourier methods and refined to an *R*-factor of 0.049 for 911 independent reflections by full matrix least squares.

The molecular structure and important bond lengths and angles are shown in the figure. The complex has the expected dimer structure with the Pt^{II} ion in square planar coordination; angle Cl(1)–Pt–Cl(1)′ = 82.8°, Cl(1)′–Pt–Cl(2) = 89.7°, Cl(2)–Pt–centre C(4)-C(5) bond = 93.3° and Cl(1)–Pt–centre C(4)-C(5) bond = 95.0°. The deviation of the centre of the C(4)-C(5) bond from the coordinating plane is -0.48 Å. In contrast to what is found in Zeise's salt[5], the *trans* weakening influence of the tetramethylallene ligand is seen to be significant, as evidenced by the Pt–Cl bond lengths, *i.e. cis* 2.34 Å, 2.28 Å and *trans* 2.39 Å. The difference in length between the terminal and bridging Pt–Cl bonds is also significant.

The tetramethylallene ligand functions as a π-bonded monoolefin, the olefinic bond being approximately orthogonal to the plane containing the platinum and chlorine atoms (the dihedral angle between the Pt, Cl(1), Cl(2) plane and the C(4), C(5), C(6) plane equals 96.2°). There is considerable asymmetry in the metal–olefin bonding, the long bond being that to the carbon atom bearing two methyl substituents. This pattern of metal–carbon bond lengths has also been observed with methoxy[6]- and phenyl-substituted olefins[7]. The unsubstituted allene complexes show a similar asymmetry, which indicates that the formal *sp* character of C(5) as opposed to sp^2 of C(4) may be important. The distance from the Pt^{II} ion to the centre of the C(4)–C(5) bond is 2.08 Å. Both this distance and the Pt–C(5) length are close to the length of a Pt–C σ bond[8].

The change in ligand geometry observed previously[1,2,3] is also observed here, the C(6)–C(5)–C(4) angle being 151.4°; the dihedral angle between the planes C(6), C(7), C(8) and C(2), C(3), C(4) equals 92.0°. The average value of the olefinic bonds is large compared with the free ligand value (1.309 in H_2C–C–CH_2)[9], but this difference as well as the difference between C(4)–C(5) and C(5)–C(6) is hardly significant. The latter does, however, occur in the opposite direction to that found in the rhodium–allene complexes.

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