

Preliminary communication

The X-ray Structure of the Complex

Dichloroorthovinylidiphenylarsineplatinum(II)

MERVYN K. COOPER and PHILIP J. GUERNEY

(School of Chemistry, University of Sydney, Sydney 2006, Australia)

MICHAEL ELDER

(Rutherford Laboratory, Chilton, Didcot, Oxon, OX11 0QX)

MARY McPARTLIN

(Department of Chemistry, The Polytechnic of North London, London N7 8DB)

(Received May 24th, 1977)

SUMMARY

The X-ray structure analysis of the olefinic tertiary arsine complex dichloroorthovinylidiphenylarsineplatinum(II) shows a square planar coordination geometry with the coordinated olefin making an angle of 83.6° with this plane.

Platinum(II) chelate complexes of olefinic tertiary Group V ligands have been widely studied,^{1,2,3} but so far no X-ray structural information has been reported for platinum(II) complexes with arsine ligands of this type. We therefore report the principal features of a single crystal X-ray structure analysis of the complex dichloroorthovinylidiphenylarsineplatinum(II) (I).

Crystals of $C_{20}H_{17}AsCl_2Pt$ (I) are monoclinic, spacegroup $P2_1/c$, $a = 9.288$, $b = 18.112$, $c = 12.413$ Å, $\beta = 118.3^\circ$, $v = 1838.1$ Å³, $D_c = 2.48$ g cm⁻³ for $Z = 4$. Solution and refinement were based on 2258 unique reflections ($I/\sigma I > 3$) measured with a Philips PW1100 four-circle diffractometer using graphite crystal monochromated Mo-K α

radiation. The two non-chelating phenyl rings were treated as rigid groups (C-C 1.395 \AA). Refinement of the group and atomic parameters (Pt, As and Cl anisotropic) has given an R-value of 0.047. The molecular structure and principal bond lengths are shown in Fig.1.

The platinum atom has square planar coordination with bonds from two chlorine atoms and a chelate ring bonded through the tertiary arsine and the olefin group. The mid-point of the olefin is 0.2 \AA out of the least square plane through Pt, As, Cl(1) and Cl(2). The olefin bond C(1) - C(2) makes an angle of 83.6 $^\circ$ with this plane.

The Pt-As bond produces a marked trans-influence on the Pt-Cl(1) bond which is 0.044 \AA (10 σ) longer than the Pt-Cl(2) bond trans to the olefin. That arsine groups have a strong trans-influence is also evident in the structures of di- μ -chlorobis(trimethylarsine)platinum(II)⁴ (II) and {1-(o-diphenylarsinephenyl)-2-methoxyethyl-As,C¹}hexafluoroacetylacetonatoplatinum(II)⁵ (III).

The very short Pt-As bond length of 2.275 \AA in (II) was attributed to the good π -acceptor properties of the tri-aryl ligand.⁵ In contrast the tri-arylsarsine-Pt bond in (I) is 0.042 \AA (35 σ) longer than in (II). The Pt-As bonds in (I) and (II) are trans to a chlorine and an oxygen

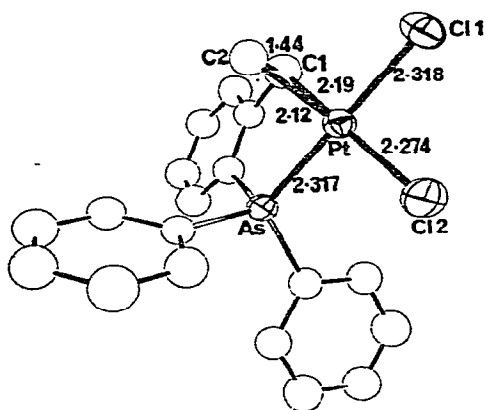


Fig. 1. Molecular structure and principal bond lengths of dichloroorthovinyldiphenylarsineplatinum(II) (I).

atom respectively, both atoms which appear to have low trans-influence in Pt(II) complexes.⁶ The lengthening of the tri-arylsarsine-Pt(II) bond in (I) relative to that in (II) may be largely attributed to a cis-influence⁷ of the π -bonding olefin ligand in (I), i.e. the withdrawal of electron density from the platinum atom by the olefin has reduced the π -component of the Pt-As bond.

REFERENCES

- 1 R.S.Nyholm, Rev. Pure Applied Chem., 27 (1971) 127
- 2 D.I.Hall, J.H.Ling and R.S. Nyholm, Struct. Bonding (Berlin), 15
(1973) 427
- 3 M.A.Bennett and I.B.Tomkins, J. Organometal. Chem., 51 (1973) 289
- 4 S.F.Watkins, J. Chem. Soc., A (1970) 168
- 5 M.K. Cooper, P.J.Guerney, P. Donaldson and M. McPartlin,
J. Organometal. Chem., 131 (1977) C11
- 6 F.R.Hartley, The Chemistry of Platinum and Palladium Applied
Science, London, 1973, P.301
- 7 P. Hitchcock, M. McPartlin and R. Mason, Chem. Comm.(1969), 1367 •