Journal of Organometallic Chemistry, 131 (1977) C11—C13

Preliminary communication

The X-ray Structure of {1-(o-Diphenylarsinephenyl)-2-methoxyethyl-As,C^1} hexafluoroacetylacetonatoplatinum(II), a Tertiary Arsine Chelate Complex Containing a Platinum(II)-Carbon σ-Bond.

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(Received February 22nd, 1977)

SUMMARY

The X-ray structure analysis of {1-(o-diphenylarsinephenyl)-2-methoxyethyl-As,C^1}hexafluoroacetylacetonatoplatinum(II) confirms that the tertiary arsine chelate ring is five-membered with a Pt(II)-C σ-bond and shows a strong trans-influence of the arsine group.

It was shown from nmr evidence that the complex {1-(o-diphenylarsine-phenyl)-2-methoxyethyl-As,C^1}hexafluoroacetylacetonatoplatinum(II) (I) has a five-membered tertiary arsine chelate ring.[1]

We now report the X-ray structure determination of (I) which confirms the presence of the five-membered chelate ring with a Pt(II)-C σ-bond.

Crystals of $C_{25}F_6H_{21}O_3AsPt$ are orthorhombic, spacegroup Pbca, a = 24.078, b = 12.327, c = 18.500 Å, V = 5491.0 Å^3, Z = 8, D_c = 1.80 g cm^{-3}. Solution and refinement were based on 2345 unique reflections $I/\sigma(I)>3.0$ 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 Å). Refinement of the group and atomic parameters (Pt and As anisotropic) has given an R-value of 0.057. The molecular geometry and principal bond lengths are shown in Fig. 1.

The tertiary arsine and the first carbon of the methoxyethyl chain C(1) are bonded to the platinum giving a five-membered chelate ring. The platinum(II) atom and the coordinated atoms, O(1), O(2), As and C(1), are planar to within 0.02 Å.

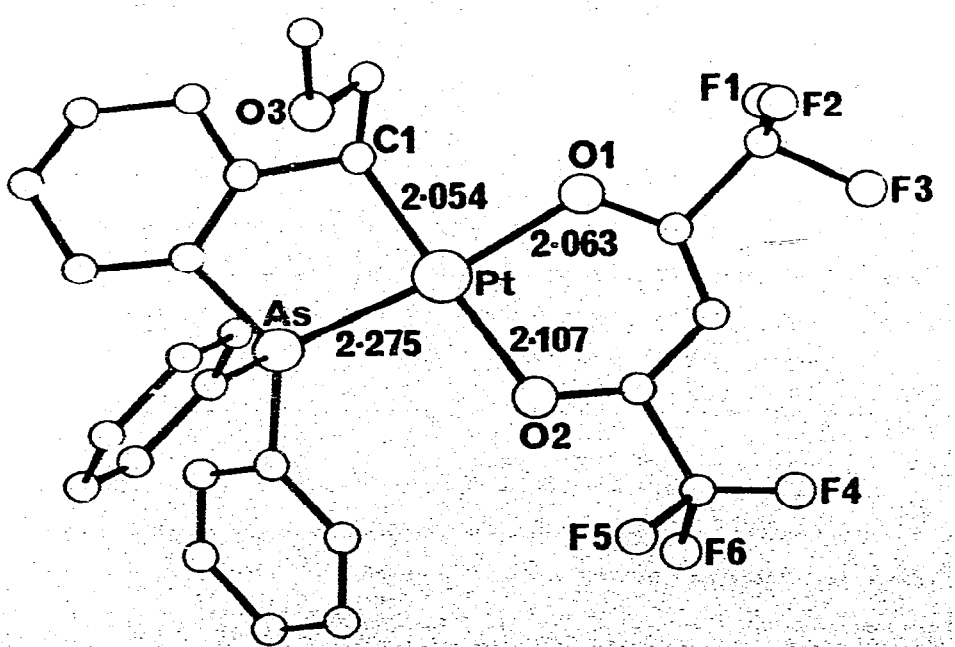

Fig. 1 The structure of (I) and the principal bond lengths (Å). E.s.d.'s are Pt - As 0.002, Pt - C 0.016, Pt - O 0.011 Å.

It is well established that σ-bonded carbon atoms have a very large trans-influence in platinum(II) complexes.[2] A typical example, which is relevant to this case, is the bisacetylacetonatochloroplatinate(II) anion[3] (one acetylacetonato group is mono-dendate, coordinated through a Pt-C σ-bond) in which the Pt-O bond trans to be σ-bonded C atom is 0.104 Å longer than the Pt-O bond trans to the chlorine atom. In the present study the Pt-O(1) bond trans to the σ-bonded C(1) atom is only 0.044 Å longer than the Pt-O(2) bond trans to the tertiary arsine group. Very few X-ray structure analyses of Pt(II) - As complexes are available, but this result supports a previous study in which a comparatively strong trans-influence has been observed for the arsine group in di-μ-chlorobis-(trimethylarsine)platinum(II) (II).[4]

It is significant that the Pt-As bond in the present study is 0.033 Å shorter than the Pt(II)-trimethylarsine bond[4] in (II). This may be attributed to better π-acceptor properties for the tri-aryl arsine ligand.

REFERENCES

1. M.K. Cooper, P.J. Guerney, J.H. Ling, and R.S. Nyholm, J. Organometal. Chem. 91 (1975) 117.

2. R. McWeeny, R. Mason, and A.D.C. Towl, Disc. Faraday Soc., 47 (1969) 20.

3. R. Mason, G.B. Robertson, P.J. Pauling, J. Chem. Soc., A, (1969) 485.

4. S.F. Watkins, J. Chem. Soc. A, (1970) 168.