Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The crystal and molecular structure of *trans*-diiodobis(t-butylisonitrile) palladium(II)

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(Received February 10th, 1972)

In view of the current interest in the chemistry of isonitrile complexes of transition metals[1—5] and of the uncertainty in the detailed geometry of the coordinated ligand (see comment in ref. 6) in the fairly small number of single-crystal structures previously reported[6—10], the authors decided to investigate the system $Pd{-}i_2{-}X_2$ where i represents tertiary butyl isonitrile and X is a halogen. The dichloro complex crystallises as the *cis* isomer and the diiodo complex as the *trans* isomer[11]. Initial studies on the *cis*-dichloro complex were suspended when investigations revealed the presence of a complex super-lattice in the triclinic crystal system with at least eight molecules in the primitive unit cell. The results reported are for the *trans*-diiodo complex which is, as far as the authors are aware, the first structure of a *trans*, square-planar, isonitrile complex of a transition metal in oxidation state II.

Crystal data. Crystals were orange needles obtained from chloroform/ethanol; orthorhombic; $a = 18.30(5)$; $b = 10.62(3)$; $c = 17.74(5)$ Å, $V = 3448$ Å^3; $Z = 8$ for $PdI_2N_2C_{10}H_{18}$, mol. wt. 526.5; D_m 2.03, D_c 2.028; space group is *Pbca* (D_{2h}^{15}, No. 61); μ (Mo-K_α radiation, λ 0.7107 Å) 46.5 cm^{-1}.

Three-dimensional, X-ray data of the type *hk*0-4 and 0-4*kl* were collected by precession methods using Zr-filtered, Mo-K_α X-radiation and were estimated visually. The normal corrections were applied but, so far no corrections have been made for absorption; the total data set (after inter-layer scaling) comprised 839 independent reflexions. The structure was solved by conventional Patterson and Fourier methods and was refined by block-diagonal, least-squares techniques to a current value of $R = 0.093$; anisotropic thermal vibration being allowed for palladium and iodine atoms.

The essential geometry is shown in Fig. 1 the *trans* square-planar geometry is confirmed, and the isonitrile groups are shown to be substantially linear; any deviations from linearity being less than 2.0 σ. Such deviations may be attributed to crystal packing forces, particularly to a short (3.42 Å) intermolecular contact between methyl groups. All bond lengths and angles in the tertiary butyl groups are within 3 σ of expected values; the

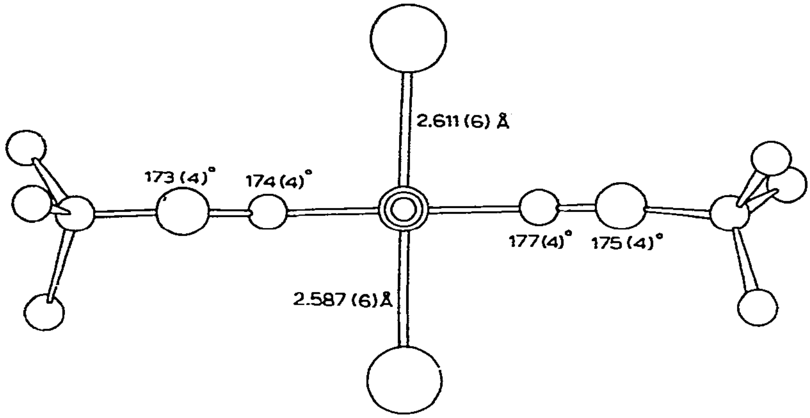

Fig. 1. The essential geometry of *trans*-diiodobis(t-butylisonitrile)palladium(II) (estimated standard deviations in parentheses).

Pd—I distances are similar to each other and to previously reported values. Mean values of Pd—C, C≡N and N—C bond lengths are similar to corresponding values in previously reported isonitrile complexes of transition metals, being 1.92(4), 1.15(5) and 1.46(6) Å respectively.

The structure, therefore, is an additional example of those in which little if any distortion from linearity is observed in the coordinated isonitrile. The only isonitrile complex so far reported which exhibits a significant deviation from linearity at either the donor carbon or the nitrogen atom appears to be *cis*-dichloro(phenylisonitrile)triethylphosphineplatinum(II)[6], in which a C—N—C angle of 165(3.0)° is reported. A similar distortion does not, however, seem to occur in the closely related molecule *cis*-dichloro(ethylisonitrile)diethylphenylphosphineplatinum(II)[6]. Further structural investigations on isonitrile complexes will therefore be necessary before it is possible to determine whether this single significant deviation from linearity has an electronic or a steric origin.

ACKNOWLEDGEMENT

The authors wish to thank Dr. M.G.H. Wallbridge and co-workers for supplying crystals of the compound under study.

REFERENCES

1 E.M. Badley, J. Chatt, R.L. Richards and G.A. Sim, *Chem. Commun.*, (1969) 1322.
2 E.M. Badley, J. Chatt and R.L. Richards, *J. Chem. Soc. A*, (1971) 21 and references therein.
3 A. Araneo, F. Bonatti and G. Minghetti, *J. Organometal. Chem.*, 25 (1970) C25.
4 G.A. Larkin, R. Mason and M.G.H. Wallbridge, *Chem. Commun.*, (1971) 1054.
5 J.W. Dart, M.K. Lloyd, J.A. McCleverty and R. Mason, *Chem. Commun.*, (1971) 1197.
6 B. Jovanovic, L. Manojlovic-Muir and K.W. Muir, *J. Organometal. Chem.*, 33 (1972) C75.
7 F.A. Cotton, T.G. Dunne and J.S. Wood, *Inorg. Chem.*, 3 (1964) 1495.
8 F.A. Cotton, T.G. Dunne and J.S. Wood, *Inorg. Chem.*, 4 (1965) 318.
9 J.K. Stalick and J.A. Ibers, *J. Amer. Chem. Soc.*, 92 (1970) 5333.
10 R.S. Dickson, J.A. Ibers, S. Otsuka and Y. Tatsuno, *J. Amer. Chem. Soc.*, 93 (1971) 4636.
11 G.A. Larkin, R.P. Scott and M.G.H. Wallbridge, *J. Organometal. Chem.*, 37 (1972) C21.