

## Preliminary communication

### X-ray structure analysis of platinum(II) isonitrile complexes

BORJANA JOVANOVIĆ,\* LJUBICA MANOJLOVIĆ-MUIR and K.W. MUIR

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received October 18th, 1971)

Interest in the structural features of coordinated isonitriles has been revived by recent investigations of the reactivity of transition metal-isonitrile complexes<sup>1-3</sup>. It has been shown, for example, that the addition of alcohols and amines to the carbon-nitrogen bond in *cis*-PtCl<sub>2</sub>(CNR)(PR'<sub>3</sub>) compounds gives platinum-carbene complexes<sup>1</sup>. The C-N-C<sub>6</sub>H<sub>5</sub> angle in *cis*-PtCl<sub>2</sub>(CNC<sub>6</sub>H<sub>5</sub>)[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] is 165.5(30)<sup>o</sup><sup>4</sup>, and it has been suggested that this significant non-linearity of the isonitrile ligand and the addition reaction described above may both reflect an electronic change in isonitrile caused by coordination to platinum<sup>2</sup>. In order to provide further information on the mode of platinum-isonitrile bonding we have determined, by X-ray methods, the crystal structures of the complexes *cis*-PtCl<sub>2</sub>(CNC<sub>2</sub>H<sub>5</sub>)[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>] (I) and *cis*-PtCl<sub>2</sub>(CNC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (II).

Compound I is orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 15.16(1), *b* = 10.72(1), *c* = 10.48(1) Å, *Z* = 4; compound II is monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 9.936(4), *b* = 11.825(7), *c* = 13.088(4) Å, β = 101.75(3)<sup>o</sup>, *Z* = 4. The structure analysis of I is based on 1062 photographic intensity data, and that of II on 1644 data measured on a four circle diffractometer. For both compounds the intensities were corrected for absorption effects and the structural parameters were refined by full matrix least-squares methods. The final *R*-factors are 0.062 for I and 0.046 for II.

In each complex the coordination around the platinum atom is square planar.

The Pt-C distances in I and II (Table 1) are not significantly different. Their weighted mean, 1.89(2) Å, may be compared with the Pt-C distances in other mononuclear platinum(II) complexes containing organic ligands: Pt-C (alkyl) of 2.079(14) Å in *trans*-PtCl[CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>][P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>2</sub><sup>5</sup>, Pt-C(carbene) of 1.98(2) and 2.020(16) Å in *cis*-PtCl<sub>2</sub>[C(OC<sub>2</sub>H<sub>5</sub>)NH·C<sub>6</sub>H<sub>5</sub>][P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sup>1</sup> and *trans*-PtCl<sub>2</sub>[C(C<sub>6</sub>H<sub>5</sub>NCH<sub>2</sub>)<sub>2</sub>]-[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sup>6</sup>, respectively, and Pt-C(carbonyl) of 1.74(4) Å in *trans*-PtCl<sub>2</sub>(CO)(ONC<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>)<sup>7</sup>. Allowing for the effect of hybridisation on the covalent radius of the carbon atom, these distances clearly indicate that in platinum(II) complexes isonitrile is a stronger π-acceptor than carbene and an appreciably weaker π-acceptor than carbonyl.

\*Present address: Institute of Nuclear Sciences "Boris Kidrich", Vincha, Belgrade, P.O. Box 522 (Yugoslavia).

TABLE 1

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) IN *cis*-PtCl<sub>2</sub>(CNC<sub>2</sub>H<sub>5</sub>)[P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>] (I) AND *cis*-PtCl<sub>2</sub>(CNC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (II)

Bond	<i>trans</i> -atom	I	II	
Pt-C	Cl	1.83 (4)	1.88 (2)	1.91 (2)
Pt-Cl	C	2.314(10)	2.313(4)	2.303(5)
Pt-Cl	P	2.390(8)		
Pt-P	Cl	2.244(8)		
Angle				
Pt-C-N		174(4)	170(2)	178(2)
C-N-R		172(3)	178(2)	175(2)

The Pt-C-N and C-N-R angles in I and II (Table 1), with weighted means of 174.0° and 175.5° respectively, suggest that the pronounced non-linearity, observed in *cis*-PtCl<sub>2</sub>(CNC<sub>6</sub>H<sub>5</sub>)[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>], is not a general feature of the Pt-C-N-R system. The slight bending which occurs at both carbon and nitrogen atoms may be ascribed to the effects of crystal packing. On the other hand, since isonitrile appears to be a π-acceptor in these complexes, it is possible that different occupancies of the ligand π\* orbitals may also contribute to the bending, in the way suggested for metal carbonyl complexes<sup>8</sup>.

Judged by the length of the appropriate *trans*-Pt-Cl bonds (Table 1), the relative *trans*-influence of isonitrile is smaller than that of phosphine. The length of the Pt-Cl bond *trans* to carbonyl in *cis*-PtCl<sub>2</sub>(CO)[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sup>4</sup> is 2.31(2) Å. It thus appears that the *trans*-influence of isonitrile is comparable with that of carbonyl, although both the π-acceptor and σ-donor properties of the two ligands are believed to be appreciably different.

#### ACKNOWLEDGEMENTS

We thank Professor J. Chatt and Drs. E.M. Badley and R.L. Richards for providing crystals, Professor G.A. Sim for use of the diffractometer, the Federal Fund for Scientific Research of Yugoslavia for a grant (to B.J.), and the S.R.C. for financial support.

#### 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. Bonati and G. Minghetti, *J. Organometal. Chem.*, 25 (1970) C25; G.A. Larkin, R. Mason and M.G.H. Wallbridge, *Chem. Commun.*, (1971) 1054; J.W. Dart, M.K. Lloyd, J.A. McCleverty and R. Mason, *Chem. Commun.*, (1971) 1197.
- 4 E.M. Badley, *D. Phil. Thesis*, University of Sussex, 1969.
- 5 B. Jovanović, Lj. Manojlović-Muir and K.W. Muir, to be published.
- 6 D.J. Cardin, B. Cetinkaya, M.F. Lappert, Lj. Manojlović-Muir and K.W. Muir, *Chem. Commun.*, (1971) 400; Lj. Manojlović-Muir and K.W. Muir, to be published.
- 7 M. Orchin and P.J. Schmidt, *Coord. Chem. Rev.*, 3 (1968) 345.
- 8 S.F.A. Kettle, *Inorg. Chem.*, 4 (1965) 1661.