X-Ray Structure of *Cis*- and *Trans*-bis(*o*-amidophenyldiphenylphosphine)platinum(II)

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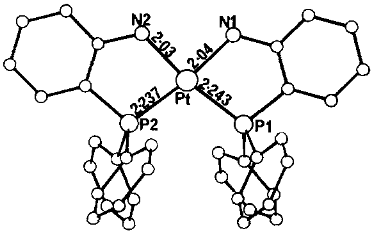

Fig. 1. The structure of the *cis* isomer (I) showing the principal bond lengths (Å). E.s.d.s average Pt–P 0.003 and Pt–N 0.009 Å. The angles of the Pt coordination sphere are P(1)–Pt–P(2) 104.2(1), P(1)–Pt–N(1) 84.0(3), P(2)–Pt–N(2) 83.9(3), and N(1)–Pt–N(2) 87.8(4)°.

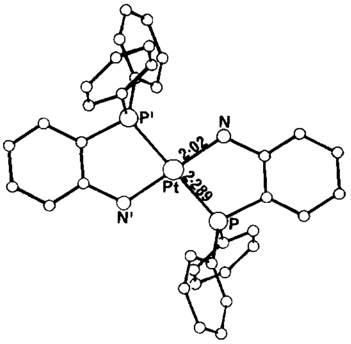

Fig. 2. The centrosymmetric structure of the *trans* isomer (II) with the average values of the principal bond lengths (Å) for the two crystallographically independent molecules. E.s.d.s average Pt–P 0.004 and Pt–N 0.013 Å. The mean angles of the coordination sphere are P–Pt–N 82.6(3) and P'–Pt–N 97.4(3)°.

We have recently reported the preparation of the new hybrid ligand *o*-aminophenyldiphenylphosphine (PNH_2) [1]. Rare examples of bis-chelate geometrical isomers of platinum(II) were described which contained the ligand in either its neutral or deprotonated (PNH^-) form. The stereochemistries were assigned using ^{31}P NMR spectroscopy. The ligand in its deprotonated form contains the comparatively rare amido donor group. We present here a preliminary account of the X-ray crystal structures of one set of geometrical isomers, *cis*- and *trans*-$[Pt(PNH^-)_2]$ (I) and (II), which confirm the spectroscopic assignment of the stereochemistries and yield data of relevance to the *trans* influence of the amido group.

The title compounds (I) and (II) were prepared as described elsewhere [1]. Crystals suitable for X-ray structure analysis were grown as follows. A vigorously stirred suspension of the complex in acetonitrile was treated with a 10% solution of trifluoroacetic acid in acetonitrile until dissolution was complete and the solution had just become colourless. Well-formed crystals of (I) or (II) each containing one molecule of solvent per molecule of complex formed when triethylamine in acetonitrile (2%) was allowed to diffuse slowly into this solution.

Crystals of both (I) and (II), $C_{36}H_{30}N_2P_2Pt \cdot C_2H_3N$, M = 788.76, were triclinic, space group $P\bar{1}$: for (I) a = 11.948(4), b = 11.236(4), c = 14.880(5) Å, α = 96.69(2), β = 105.96(2), γ = 115.18(2)°, U = 1655.41 Å^3, Z = 2, μ(Mo-Kα) = 41.77 cm^{-1}; for (II) a = 13.686(5), b = 11.661(4), c = 11.170(4) Å, α = 96.25(2), β = 106.21(2), γ = 85.54(2)°, U = 1699.51 Å^3, Z = 2, μ(Mo-Kα) = 40.69 cm^{-1}).

The X-ray structure determinations were undertaken using 3538 reflections for (I) and 3144 reflections for (II) with $I > 3\sigma(I)$ measured with a Philips PW1100 four-circle diffractometer using Mo-Kα radiation from a graphite crystal monochromator. Refinement of positional and thermal parameters for all non-hydrogen atoms was performed using full-matrix least-squares procedures [2]. In both compounds the platinum, phosphorus and solvent atoms were assigned anisotropic temperature factors, the chemically equivalent pairs of bond lengths in the chelating phenyl rings were constrained to be equal and the other phenyl rings were refined as rigid groups (C–C 1.395 Å). Hydrogen atoms, which were given fixed temperature factors (0.1 Å^2), were allowed to ride on the carbon atoms in the rings (C–H 1.08 Å). A final R of 0.056 was obtained for compound (I) and 0.054 for compound(II). The structure of the complex molecule in (I) is shown in Fig. 1 with the bond lengths of the coordination sphere. The *trans* compound(II) has crystallographic C_i symmetry there being two independent molecules in the unit cell (the platinum atoms are at 0, 0, 0, and ½, 0, ½). There are no significant differences in bond length in the two independent mole-

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cules and the average values for the principal bond lengths are shown in Fig. 2. For both compounds the atoms of the coordination sphere and chelating phenyl rings are coplanar to within 0.05 Å.

The Pt–P bonds in the *trans* compound (II) {mean 2.289(4)} are significantly longer than the Pt–P bonds in the *cis* compound (I) {mean 2.240(3)}.

This difference may be attributed to the competition between the two *trans* phosphorus atoms for π-electron density from the same d-orbitals of the platinum atom in (II).

The Pt–N bonds in the two independent molecules of the *trans* complex (II) {mean 2.02(1)} are shorter than the two independent Pt–N bonds *trans* to phosphorus atoms in this *cis* complex (I) {mean 2.04(1)}. Although these differences are of low significance they are consistent with a smaller *trans* influence of the amido nitrogen compared to the phosphine.

In the structure of I, both phenyl rings attached to P(1) adopt conformations approximately parallel to the corresponding phenyl rings on P(2) (mean dihedral angle 13.4°). Close contact between these rings is apparently avoided by the large P(1)–Pt–P(2) angle of 104.2° so that there are no contacts of less than 3.4 Å between the two ligands.

References

1 M. K. Cooper and J. M. Downes, *Inorg. Chem., 17,* 880 (1978).
2 G. M. Sheldrick, SHELX 76 Program System, University of Cambridge, 1976.