Inorganica Chimica Acta, 76 (1983) L159–L160

Reaction of *Cis*-bis(amidophenyldiphenyl)platinum(II) with Carbon Disulphide; X-ray Analysis of the CS_2 Adduct

M. K. COOPER, J. M. DOWNES

School of Chemistry, University of Sydney, Sydney 2006, N.S.W., Australia

K. HENRICK, H. J. GOODWIN and M. McPARTLIN

School of Chemistry, The Polytechnic of North London, London N7 8DB, U.K.

Received November 4, 1982

We have previously reported the synthesis [1] and structures [2] of the *cis*- and *trans*- bis chelate Pt(II) complexes of *o*-aminophenyldiphenylphosphine in its neutral (PNH_2) and deprotonated forms (PNH^-). In an extensive investigation [3] of the reactions of the coordinated nitrogen atom in these complexes it has been shown that the presence of the Pt atom has altered the reactions compared to those of the free ligand.

We report here a reaction of the N atom of *cis*-$[Pt(PNH^-)_2]$ which gives the Pt(II) complex of a novel tridentate dithiocarbamato ligand. *Cis*-$[Pt(NH^-)_2]$ (I) reacted with carbon disulphide in chloroform to give an orange solution which slowly turned yellow and deposited well formed pale yellow crystals. Elemental analysis* showed the product to be a 1:1 addition compound $Pt(PNH^-)_2 \cdot CS_2$ (II). The compound (II) was not sufficiently soluble for spectral measurements to be made in solution, but in the solid state ir spectra indicated the presence of an uncoordinated amino group [ν(N–H) 3372 and 3298 cm^{-1}].

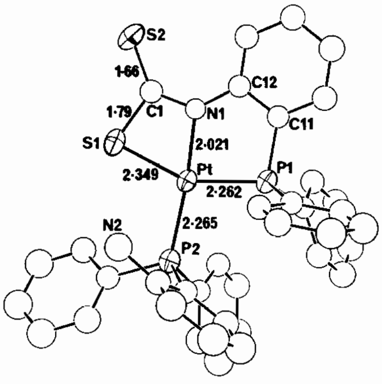

Fig. 1. The structure of the CS_2 adduct of *cis*-$[(PNH^-)_2$-Pt(II)], $[(PN \cdot CS_2)(PNH_2)Pt]$ (II), showing the principal bond lengths (Å). The maximum e.s.d.'s are Pt–S and Pt–P 0.003 and Pt–N 0.010 Å, Important angles are: S(1)–Pt–P(1) 153.0(1), S(1)–Pt–P(2) 105.1(1), P(1)–Pt–P(2) 101.8(1), S(1)–Pt–N(1) 69.5(2), P(1)–Pt–N(1) 83.5(2), P(2)–Pt–N(1) 174.6(2)°. Contact distances Pt···N(2) 3.67 and Pt···C(1) 2.710 Å.

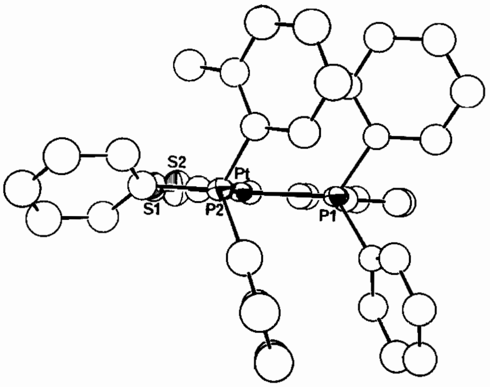

Fig. 2. The structure of the CS_2 adduct (II) viewed along the plane of Pt(II) coordination.

An X-ray crystal structure analysis revealed the presence of a dithiocarbamato(2–) fragment in a P, S, and N-bonded tridentate ligand containing 5- and 4-membered rings fused to the Pt atom. The complex is monomeric and neutral with the structure shown in Fig. 1. The reaction of *cis*-$[Pt(NH^-)_2]$ with CS_2 shows some similarity to those of some monodentate dialkylamido metal complexes with CO_2 which lead to the formation of carbamato metal complexes [4]. However in these compounds the ligand is only coordinated through the O-atoms of the carbamato group (either in mono- or bidentate mode) and the dialkyl-N atom is no longer bonded to the metal.

The PtP_2SN coordination sphere together with the chelating phenyl ring and the S_2CN group in (II) are coplanar to within 0.02 Å (see Fig. 2). Due to the small bite of the N–C–S part of the new tridentate ligand, the angles at the Pt atom, subtended by the donor atoms, differ markedly from those expected for square planar Pt(II) coordination (see legend to Fig. 1). The second ligand (PNH_2) is monodentate coordinated through the P atom with the amino N atom at a distance of 3.67 Å from the metal atom.

---

*Calc. for $C_{37}H_{30}N_2P_2S_2Pt$: C, 53.94; H, 3.67; P, 7.52; S, 7.78. Found: C, 53.56; H, 3.50; P, 7.3; S, 7.8%. The analytical data were obtained on a sample from which the solvent had been removed at 100 °C under vacuum (0.1 mm Hg).

0020-1693/83/0000-0000/$03.00

In view of the asymmetric coordination of the Pt atom the Pt–P distances are remarkably similar (2.262 and 2.265 Å). These distances are intermediate in length between the Pt–P distances in the *cis*-Pt(II) complexes of the (PNH$^-$) and (PNH$_2$) ligands (2.240 and 2.245 Å respectively) and the significantly longer bonds (2.289 and 2.290 Å respectively) observed for the corresponding *trans* isomers of the same complexes where the P ligands are in competition for the same d-orbital electron density. This observation is consistent with there also being some d_π–p_π character in the Pt–S bond.

Crystals of $C_{31}H_{30}N_2P_2S_2Pt\cdot 2CHCl_3$, the bis-chloroformate of (II), are triclinic, space group $P\bar{1}$, a = 14.620(3), b = 13.165(3), c = 13.260(3) Å, α = 114.91, β = 115.01, γ = 87.90°, V = 2056.77 Å^3, Z = 2, μ(Mo-K$_\alpha$) = 38.26 cm^{-1}. A Philips PW1100 four-circle diffractometer with Mo-K$_\alpha$ radiation from a graphite monochromator was used to collect 6066 reflections with $I/\sigma(I) \geqslant 3.0$. Blocked full-matrix refinement of the positional and thermal parameters of the non-hydrogen atoms gave an R of 0.060. The phenyl rings were refined as rigid groups (C–C 1.395 and C–H 1.08 Å). The Pt, Cl, S, and P atoms were assigned anisotropic thermal parameters.

References

1 M. K. Cooper and J. M. Downes, *Inorg. Chem., 17,* 880 (1978).

2 (a) M. K. Cooper, J. M. Downes, H. J. Goodwin, M. McPartlin and J. M. Rosalky, *Inorg. Chim. Acta, 76,* L155 (1983);
(b) M. K. Cooper, J. M. Downes, H. J. Goodwin and M. McPartlin, *Inorg. Chim. Acta, 76,* L157 (1983).

3 J. M. Downes, *Ph.D. Thesis,* University of Sydney (1978).

4 M. H Chisholm and M. W. Extine, *J. Am. Chem. Soc., 99,* 782 (1977);
M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, *Inorg. Chem., 17,* 3536 (1978).