X-Ray Crystallographic Determination of the Molecular Structure of Bis-(μ-*NN*-dimethylthiocarbamoyl)-bis[chloro(trimethyl phosphite)palladium(II)]

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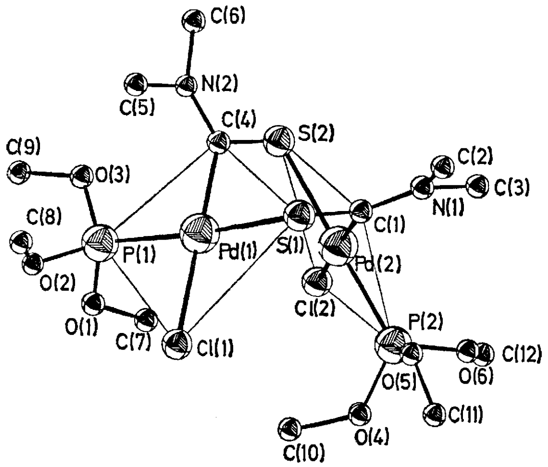
Summary An *X*-ray crystallographic investigation of the complex dimer, $[(MeO)_3P]_2Pd_2(Cl)_2(CSNMe)_2$, revealed two bridging $C(S)NMe_2$ ligands which link the two Pd atoms by co-ordinating through the C and S atoms; this is the first example of a metal complex containing thiocarbamoyl bridging ligands.

Many transition-metal complexes containing carbamoyl, $MC(O)NR^1R^2$, and thiocarbamoyl, $MC(S)NR^1R^2$, ligands have been prepared.[1] Unlike their organic analogues, little is known about their chemistry. Organic amides are known to co-ordinate to metal ions through their chalcogen (O or S) atom.[2] The structure reported here is the first example of inorganic amide chalcogen co-ordination to a metal ion.

The reaction of $Pd[P(OMe)_3]_4$ with $ClC(S)NMe_2$ afforded a yellow dimeric complex with composition, $[(MeO)_3P]_2Pd_2(Cl)_2(CSNMe_2)_2$. Crystals were obtained by slow evaporation of a CH_2Cl_2 solution. *Crystal data:* $C_{12}H_{21}Cl_2N_2O_6P_2Pd_2S_2$, $M = 699{\cdot}07$, monoclinic, $a = 9{\cdot}29(1)$, $b = 18{\cdot}17(2)$, $c = 19{\cdot}92(2)$ Å, $\beta = 128{\cdot}68(1)°$, $U = 2102$ Å^3, $D_m = 2{\cdot}2(1)$, $D_c = 2{\cdot}2$ g cm^{-3}, space group $P2_1/c$. All unique data with $\theta \leqslant 30°$ (for Mo-K_α radiation) were collected and corrected for experimental effects leaving 3340 as judged observed. The structure was solved by the heavy-atom method and refined to $R = 0{\cdot}059$ for the observed reflections.

Each Pd exhibits essentially square-planar co-ordination (see Figure) with a Pd–Cl distance of 2·383(3) Å, a Pd–P distance of 2·26(1) Å, and a Pd–S distance of 2·382(2) Å. These parameters are similar to those reported[3,4] for other palladium complexes containing these donor atoms. The Pd–C(sp^2) bond distance to the thiocarbamoyl ligand is 1·99(1) Å. This is the same as that observed (1·99 Å) for the Pd–C(sp^2) bond of *trans*-$(2\text{-}PhN{=}NC_6H_4)PdCl(PEt_3)_2$.[5]

These are close to the sum (2·05 Å) of the covalent radii; hence there appears to be little, if any, π-bonding between the Pd and C.



FIGURE

The planar thiocarbamoyl ligand has bond distances: C=S 1·72(1), C–N 1·30(1), and N–Me 1·46—1·50 Å. The angles around the carbon atom are ∠PdCS 116(1)°, ∠PdCN 123(1)°, and ∠NCS 121(1)°, similar to those of organic thioamides.[6] The plane of the thioamide group is at an angle of 67° to the square co-ordination plane around the Pd.

The sulphur atom of each thiocarbamoyl group co-ordinates to the other Pd atom. The ∠PdSC, 102·2°(3), at the sulphur is smaller than in other metal complexes of organic thioamides such as Cu(MeCSNH$_2$)$_4^+$,[7] and Pd(NH$_2$CSNH$_2$)$_4^{2+}$,[4] where 110° is found. This angle, together with the geometry around the thiocarbamoyl carbon atom, causes the two square co-ordination planes around the Pd atoms to intersect at an angle of 57°. This moves the Pd atoms to within 3·220(1) Å of each other.

Although complexes are known[8] in which both the C and S of a thiocarbamoyl ligand co-ordinate to the same metal, this is the first in which the S co-ordinates to a second metal atom. The structure reported herein suggests that thiocarbamoyl complexes, like their organic analogues, may also be a general type of ligand for co-ordination to metals.

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