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Preliminary communication

Trans-BIDENTATE BEHAVIOUR OF A POTENTIALLY TETRADENTATE LIGAND TO PALLADIUM(II) AND PLATINUM(II)

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Summary

The ligand 1,3-bis(3-dimethylarsinopropylthio)propane, L, forms MLX_2 (M = Pd, Pt; X = Cl, Br, I), which are pentacoordinate [MLX]X in the solid state and in nitromethane and planar *trans*-$[MLX_2]$, containing a *trans*-chelating diarsine ligand in dichloromethane; these are the first examples of a potentially tetradentate ligand acting as a *trans*-chelating bidentate.

Despite extensive studies of complexes of bidentate chelating Group VB ligands [1] only one example of a *trans* structure, $Ni\{Cy_2P(CH_2)_5PCy_2\}Br_2$ **, has been reported [2] prior to 1973. However, recent studies in our own and other laboratories [3,4] suggest that *trans*-chelating behaviour may be more common than was hitherto thought. The presence of long chelate backbones and bulky terminal groups have been proposed [3] as factors promoting a *trans* stereochemistry.

During an investigation of the coordination properties of the potentially tetradentate diarsine-dithioether chelate, 1,3-bis(3-dimethylarsinopropylthio)propane, $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$, L, we have prepared nickel(II), palladium(II), and platinum(II) complexes of stoichiometry MLX_2 (X = Cl, Br, I). In the solid state the $PdLX_2$ complexes have a pentacoordinate structure, on the basis of their reflectance spectra (E_{max} = 25-20 × 10^3 cm^{-1}) [5]. We tentatively propose the square pyramidal structure I for this complex because accurate molecular models suggest that this structure is the one of least strain and because a linear tetradentate arsine of similar structure has been shown to adopt this configuration about palladium(II) [6]. The electronic spectra are almost identical in nitromethane and conductivity measurements in this solvent are consistent with 1:1 electrolytes. Thus, we formulate these

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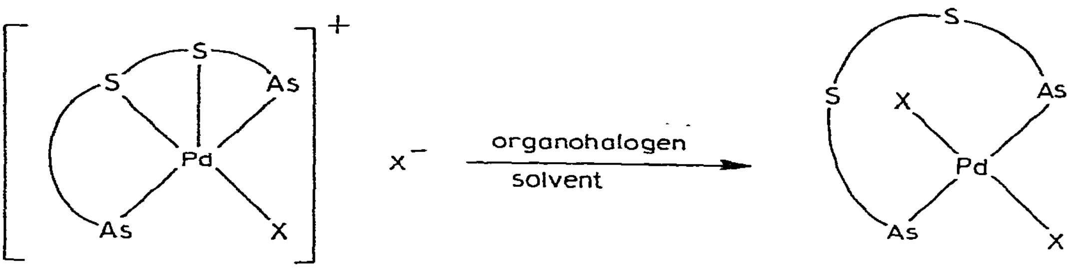
[**] Cy = cyclohexyl.



(I) (II)

complexes as $[PdAs_2S_2X]^+$ chromophores in the solid state and in nitromethane.

However, in dichloromethane or 1,2-dichloroethane the complexes are non-electrolytes and exhibit electronic spectra which are sensitive to change in the X group $\{E_{max} = 29.5$ (Cl), 28.5 (Br), 28.5, 23.9 (I) $\times 10^{-3}\ cm^{-1}\}$ and characteristic of planar palladium(II). Molecular weights in 10^{-3} M chloroform are consistent with monomeric $[PdLX_2]$ species. The ^1H NMR spectra in $CDCl_3$ show single methyl resonances which are X sensitive, ranging from τ 8.20 - 8.58 ppm compared with τ 8.96 ppm in the free ligand, and thus confirming that the Me_2As groups are coordinated.

The structures of species present in organohalogen solvents correspond to planar $[PdLX_2]$ with As_2X_2 donor sets (and do not contain coordinated thioether) in a fourteen-membered chelate ring. The inability of terminal thioether donors to compete with halide ions for coordination positions on palladium(II) has been demonstrated previously [7,8] but this seems to be the first example of the displacement of non-terminal thioether donors. The differing behaviour of these complexes in $MeNO_2$ and CH_2Cl_2 can be rationalised in terms of the polar solvent stabilising the ionic form and reducing the nucleophilicity of the halide ion by solvation.

Molecular models indicate that L cannot readily coordinate as a *cis* bidentate but easily assumes a *trans* stereochemistry, structure II. Infrared spectra in CH_2Cl_2 in the 400-200 cm^{-1} region exhibit only one ν(Pd—X) band at 355 (Cl) and 275 (Br) cm^{-1}, further strong evidence of a *trans*-PdX_2 arrangement [9].

This unexpected behaviour of the $PdLX_2$ complexes in non-polar solvents suggests that under favourable electronic conditions small terminal donor groups (Me_2As), if separated by a sufficiently long chelate backbone can coordinate *trans* across a metal even in the presence of potential donors in the backbone.

The corresponding $PtLX_2$ complexes display analogous behaviour, but for the $NiLX_2$ complexes, even though we observe several different structural types, in all cases the ligand behaves as a tetradentate chelate.

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References

1 C.A. McAuliffe (Ed), Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Donor Ligands, Macmillan Co., London, 1973; W. Levason and C.A. McAuliffe, Adv. Inorg. Chem. Radiochem., 14 (1972) 173.
2 K. Isslieb and G. Hohlfeld, Z. Anorg. Allgem. Chem., 312 (1961) 169.
3 A.J. Pryde, B.L. Shaw and B. Weeks, J. Chem. Soc. Chem. Commun., (1973) 947.
4 N.J. DeStefano, D.K. Johnson and L.M. Venanzi, Angew. Chem., 86 (1974) 133.
5 G. Dyer and L.M. Venanzi, J. Chem. Soc., (1965) 2771.
6 T.L. Blundell and H.M. Powell, J. Chem. Soc. (A), (1967) 1650.
7 W. Levason, C.A. McAuliffe and S.G. Murray, J. Chem. Soc. Dalton, in press.
8 R.L. Dutta, D.W. Meek and D.H. Busch, Inorg. Chem., 9 (1970) 1215.
9 G.E. Coates and C. Parkin, J. Chem. Soc., (1963) 421; R.J. Goodfellow, J.G. Evans, P.L. Goggin and D.A. Duddell, J. Chem. Soc. (A), (1968) 1604.