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Preliminary communication

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trans-CHELATION OF THE DITHIOETHER, 1,12-BIS(PHENYLTHIO)-DODECANE TO PLANAR PALLADIUM(II)

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Summary

The dithioether, 1,12-bis(phenylthio)dodecane (dpd) reacts with tetrachloropalladate(II) and tetrachloroplatinate(II) in ethanol/dichloromethane to form *trans*-[M(dpd)Cl_2] (M = Pd, Pt); *trans*-[Pd(dpd)Br_2] has also been isolated. These are the first reported complexes which contain a *trans*-chelating bidentate ligand involving sulphur donors and is thus further evidence that bulky terminal substituents are not a prerequisite for *trans* chelation.

Recent studies [1—6] have shown that bidentate phosphines and arsines with suitably long backbones can chelate *trans* to square planar rhodium(I), iridium(I), palladium(II) and platinum(II). Although the presence of bulky substituents, especially t-butyl groups appears to aid the isolation of *trans*-chelates [1,3], studies by ourselves [5,6], and others [4] have shown that ligands with methyl or phenyl substituents can form this type of complex providing the backbone length is correct. There is renewed interest in the nature of the "chelate effect" [7] and as an extension of our studies on *trans*-chelation we have prepared the dithioether, 1,12-bis(phenylthio)dodecane, $PhS(CH_2)_{12}SPh$, and report here its reactions with palladium(II) and platinum(II) salts which have produced the first *trans* chelates with a sulphur donor ligand.

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Experimental

1,12-Bis(phenylthio)dodecane (dpd). Sodium (4.6 g, 0.2 g-atom) was dissolved in absolute ethanol (200 cm^3) under dinitrogen, and benzenethiol (22.0 g, 0.2 mol) added. The solution was heated to reflux and 1,12-dibromododecane (16.4 g, 0.1 mol) in ethanol (50 cm^3) added. The mixture was refluxed for 1/2 h, most of the ethanol was distilled off, and the residue treated successively with water (200 cm^3) and chloroform (200 cm^3). The chloroform layer was separated, dried with anhydrous sodium sulphate, and evaporated. Recrystallisation of the residue from ethanol yielded a flaky crystalline solid (28 g, 73%). M.p. 85—87°C (dec.). Analysis: Found: C, 76.2; H, 8.5. $C_{24}H_{34}S_2$ calcd.: C, 75.5; H, 8.4%. ^{1}H NMR ($CDCl_3$) 2.8 (m) [5H], 7.2 (t) [2H], 8.75 (m) [10H].

trans-Dichloro-1,12-bis(phenylthio)dodecanepalladium(II). Sodium tetrachloropalladate(II) (0.3 g, 0.001 mol) was dissolved in ethanol (200 cm^3), and a solution of dpd (0.38 g, 0.001 mol) in dichloromethane (50 cm^3) added dropwise with stirring. The solution was refluxed for 1 h, filtered to remove a small amount of precipitate, and evaporated to dryness. The orange oil produced was dissolved in dichloromethane, the solution filtered and concentrated to ca. 10 cm^3. On long standing a yellow-orange solid separated (~80%). *trans*-[Pd(dpd)Br_2] was prepared similarly in the presence of a fivefold excess of NaBr.

trans-[Pt(dpd)Cl_2] was prepared by reaction of K_2PtCl_4 and dpd in a 1/1 ratio in ethanol/dichloromethane/water (2/2/1). Low yields of the desired product (~10%) separated on long standing. The mother liquor yielded a sticky substance on evaporation which appeared to be identical to the solid product, but which could not be solidified.

Results and discussion

The reaction of the appropriate sodium tetrahalopalladate(II) Na_2PdX_4, (X = Cl, Br) with 1,12-bis(phenylthio)dodecane (dpd) in a 1/1 molar ratio in ethanol/dichloromethane resulted in rapid precipitation of small amounts of yellowish solids (~5% by weight), and evaporation of the mother liquor gave orange-brown complexes (70—80%) of stoichiometry [Pd(dpd)X_2] (Table 1). Identical products were obtained using $Pd(PhCN)_2X_2$ as starting material. A similar complex, [Pt(dpd)Cl_2], was also obtained, but repeated attempts to prepare [Pd(dpd)I_2] produced black, insoluble powders of low (and variable) C, H, content, and the majority of the ligand was recovered from the mother liquor. The reasons for this failure are not known. The [M(dpd)X_2] complexes were very soluble in hydrocarbon solvent in which they were non-electrolytes, and had molecular weights in excellent agreement with the values expected for monomeric complexes (Table 1). The far IR spectra contains single ν(M—X) vibrations in the range expected for *trans*-X—M—X groups [8]. In dichloromethane the electronic spectra of the complexes consist of very broad intense absorptions at ~28000—29000 cm^{-1}, with distinct low energy shoulders. Attempts to grow crystals suitable for X-ray studies from a variety of solvents have been unsuccessful; indeed the solid complexes separate very slowly from solution, and as we have previously suggested [5] this may account for the

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF [Pd(dpd)Cl$_2$], [Pd(dpd)Br$_2$] AND [Pt(dpd)Cl$_2$]

Compound	Colour	Analysis (Found (calcd.) (%))			Mol. wt.^{a}	ν(M—X) (cm^{-1})
		C	H	X		
[Pd(dpd)Cl$_2$]	orange	51.7 (51.6)	6.1 (6.3)	13.0 (12.7)	587 (564)	352
[Pd(dpd)Br$_2$]	orange	44.1 (44.2)	5.4 (5.3)	24.6 (24.8)	665 (652)	275
[Pt(dpd)Cl$_2$]	buff	44.8 (44.2)	4.7 (5.2)	10.7 (10.8)	640 (653)	346

Compound	CH$_2$Cl$_2$ Soln. E_{max} (ϵ_{mol}) × 10^{-3} cm^{-1}	Solid State^b E_{max} × 10^{-3} cm^{-1}		
[Pd(dpd)Cl$_2$]	22800 (1080) (sh), 29150 (10000)	22480	29900	
[Pd(dpd)Br$_2$]	21500 (1107) (sh), 28300 (9590)	21620 (sh),	22470	35340
[Pt(dpd)Cl$_2$]	28500 (sh), 30800 (9030)	28000	34000	

^{a}10^{-3} M solutions in CHCl$_3$. ^{b}MgO as diluent.

scarcity until recently, of such complexes. Unlike the PtCl$_2$[t-Bu$_2$P(CH$_2$)$_n$PBu$_2$-t] [1], the dithioether complexes do not sublime in high vacuo. The mass spectra which were recorded to provide an independent check on the molecular weights, exhibited only fragments of low *m/e*, probably the result of S-dealkylation of the ligand backbone.

The small amounts of insoluble by-products from the palladium preparations, also analysed as [Pd(dpd)X$_2$], and are probably oligomeric with bridging dpd, although their insolubility precluded confirmation of this.

The reaction of [Pd(MeCN)$_4$](ClO$_4$)$_2$ with dpd in a 1/2 ratio was examined in the hope of isolating a [Pd(dpd)$_2$](ClO$_4$)$_2$ complex containing two *trans*-chelating ligands, but only an intractable red oil was obtained. Space-filling molecular models suggest that severe steric interactions would be present in this complex, and this may account for our failure to prepare it.

This work demonstrates that *trans*-chelation is not limited to phosphorus and arsenic donor ligands, but also occurs with poorer σ-donor thioethers. The single phenyl groups on each sulphur atom, will exert minimal steric influence on the confirmation adopted by the ligand backbone, and this confirms that bulky terminal substituents are not a prerequisite for *trans* chelation. The formation of *trans* chelated complexes in high yield, with only minor amounts of insoluble oligomers suggests that *trans* chelates are more stable than is generally believed, and it is likely that they are of much wider occurrence than was thought. The small number of examples reported to date may be a reflection both of the difficulty of isolating these complexes from solution, and of the small number of bidentate ligands with sufficiently large "chelate bites" studied, rather than of inherent instability.

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