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# Dithioether Complexes of Palladium(II): the Relationship between Ligand Chain Length and Structure About Palladium

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*Dithioether ligands* $PhS(CH_2)_mSPh$ *form* cis-*chelated complexes of palladium(II) when* m = *2 or 3, but form ligand-bridged complexes of* trans-*geometry when* m = *1, 4, 5, 6, or 8. Different forms of the complex* $[PdCl_2(PhS(CH_2)_2SPh)]$ *exist, the infra-red spectra of which differ significantly. Reaction of equimolar amounts of* $(PhS)_2CH_2$ *and* $K_2[PtCl_4]$ *gives a complex of 2:1 stoicheiometry, in contrast to the reactions of dithioether ligands with* m $\geqslant$ *2.*

## Introduction

The reactions of $M'_2[MCl_4]$ ($M' = Na, M = Pd; M' = K, M = Pt$) with the ligands $PhS(CH_2)_mSPh$ (*1*, $m$ = 2, 3) gave mononuclear *cis*-chelated complexes $[MCl_2(PhS(CH_2)_mSPh)]$ [1, 2]. The long chain ligand *1* ($m$ = 12) *trans*-chelated the same metals but the ligands *1* ($m$ = 6, 8) gave ligand-bridged polynuclear complexes of *trans*-geometry [2]. Similar complexes of $MeS(CH_2)_nSMe$ were also reported [2]. Herein we describe an alternative method of synthesis of complexes of this series, and, for the first time, the preparation of the 'missing' complexes in which $m$ = 1, 4, 5. Further, by analogy with the related series of complexes of the diphosphines $Ph_2P(CH_2)_lPPh_2$ [3], a rationale for the abrupt change in the nature of the complexes within the now continuous series $m$ = 1–6 with the change in $m$ is postulated. The reactions of *1* ($m \geqslant 2$) with equimolar amounts of $K_2[PtCl_4]$ give $[PtCl_2(1)]_x$ [2]. In contrast the reaction of *1* ($m$ = 1) with $K_2[PtCl_4]$ gives $[PtCl_2\{(PhS)_2CH_2\}_2]$. The complexes of *1* ($m$ = 1) herein described represent the first of a series [4] of complexes of this ligand or $PhS(O)CH_2S(O)Ph$ with platinum-group metals.

## Experimental

The ligands $PhS(CH_2)_mSPh$ were prepared by literature methods [2, 5]. Complexes were prepared either by literature methods [1, 2], or as described below.

### *Alternative Synthesis of the Complexes*

*Example 1.*

Under an atmosphere of dinitrogen $[PdCl_2(PhCN)_2]$ (0.332 g, 0.867 mmol) was slowly added to a solution of $(PhS)_2CH_2$ (0.202 g, 0.871 mmol) in acetone (25 mL). The palladium complex dissolved slowly, and a brown precipitate was formed. The precipitate was removed by filtration, washed with acetone, and dried under vacuum to yield, as a brown powder, $[PdCl_2(PhS)_2CH_2]$ (99%) (Analysis found: C, 38.92; H, 2.95; Cl, 17.32%. Calc.: C, 38.11; H, 2.95; Cl, 17.31%). The material was only sparingly soluble in acetone, dichloromethane, or other organic solvents, thus precluding accurate determination of the molecular weight (Found: $M \leqslant 5425$. Calc.: $M$, 410).

*Example 2.*

In a similar procedure to Example 1, a mixture of $[PdCl_2(PhCN)_2]$ (0.310 g, 0.832 mmol) and $PhS(CH_2)_2SPh$ (0.210 g, 0.853 mmol) in acetone (25 mL) was successively stirred (20 min), filtered, the precipitate was washed with acetone (30 mL), and dried under vacuum to yield, as orange-yellow crystals, $[PdCl_2(PhS(CH_2)_2SPh)]$ (74%) (Analysis found: C, 39.64; H, 3.26; Cl, 16.90; S, 14.94%. Calc.: C, 39.69; H, 3.33; Cl, 16.73; S, 15.13%).

The reactions of dithioethers *1* ($m$ = 1–6) with $[PtCl_2(PhCN)_2]$ gave mixtures of products from which only impure starting materials were recovered.

### *Reaction of* $(PhS)_2CH_2$ *with* $K_2[PtCl_4]$

An aqueous solution (10 mL) of $K_2[PtCl_4]$ (0.260 g, 0.627 mmol) and an ethanolic solution (35 mL) of $(PhS)_2CH_2$ (0.149 g, 0.642 mmol) were intimately agitated (1 hr). The mixture was sequentially filtered, washed with water (40 mL), and dried under vacuum (25 °C) to yield, as a pale yellow powder, $[PtCl_2$-

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$\{(PhS)_2CH_2\}_2]$ (Analysis found: C, 41.31; H, 3.19; Cl, 9.83%. Calc.: C, 42.73; H, 3.31; Cl, 9.70%).

Analyses were performed by the microanalytical service of the Department of Chemistry of the University of Alberta. Infra-red spectra were obtained from Nujol mulls using a Perkin-Elmer 283 instrument.

## Results and Discussion

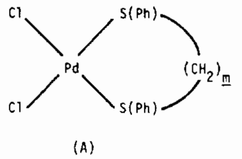
Displacement of labile ligands from complexes $[PdCl_2(L)_2]$ (L = PhCN) by $PhS(CH_2)_mSPh$, (*1*), is a convenient method of synthesis for complexes $[PdCl_2(1)]_x$, but not the platinum(II) analogues. Care must be taken to allow sufficient time for the reaction to go to completion, or PhCN may be retained in the product. In this respect, the reaction of $[PdCl_4]^{2-}$ with a dithioether is a superior synthetic method [1, 2]. The alternative synthesis described above has value in that the reaction is rapid, reflux conditions are not necessary, and the less rigorous conditions may be appropriate for the synthesis of complexes of less stable ligands.

The assignment of infra-red bands in the region 250–350 $cm^{-1}$ for *cis*-chelated complexes is a matter of some dispute. An early report compared the spectra of $[PdCl_2(PhS(CH_2)_mSPh)]$ ($m$ = 2, 3) with the analogous bromo- and diselenoether complexes [1]. Bands in the range 262–286 $cm^{-1}$ were assigned as $\nu$(Pd–Cl), and bands 308–331 $cm^{-1}$ were assigned as $\nu$(Pd–S); weak bands or shoulders 343–350 $cm^{-1}$ were unassigned. In contrast, a comparison of the spectra of the same dithioether complexes of palladium(II) and platinum(II) with the bromo- and iodo-analogues, and with complexes of $MeS(CH_2)_mSMe$ ($m$ = 2, 3), led to an assignment of bands 296–324 $cm^{-1}$ as $\nu$(Pd–Cl) [2]. In this latter report $\nu$(Pd–S) bands were described as moderately intense, often broad, and with ill-defined maxima in the range 290–350 $cm^{-1}$. The agreement between the spectroscopic data for $[MCl_2(PhS(CH_2)_3SPh)]$ (M = Pd, Pt) in the two reports [1, 2] was excellent, but the assignments differed. However, there was no coincidence between the spectroscopic data reported for $[PdCl_2(PhS(CH_2)_2SPh)]$. For this complex we observed bands at 324(s), 308(s), and 269(m) $cm^{-1}$ in the region in question. These values are intermediate between the major features in the earlier reports. The weak bands and shoulders previously reported were not observed. By comparison with the data and arguments in the latter report [2] we assign the bands at 324 and 308 $cm^{-1}$ as $\nu$(Pd–Cl). The bands $\nu$(Pd–S) may be submerged beneath these bands. The assignment of two bands in the range 296–324 $cm^{-1}$ as $\nu$(Pd–Cl) is appropriate for a *cis*-complex, (A) [2, 6]. Similar complexes have also been described for the chelating ligands $o$-$C_6H_4(SPh)_2$ and *cis*-PhSCH=CHSPh [2].

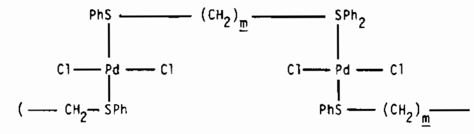
TABLE I. Complexes $[PdCl_2(PhS(CH_2)_mSPh)]_x$.

| $m$ | $x$ | $\nu$(Pd–Cl)$^a$ | Structure | Source |
|---|---|---|---|---|
| 1 | ⩽ 14 | 355 | *trans*, bridged | b |
| 2 | 1 | 315, 296 | *cis*, chelated | c |
| | | 324, 308 | | b |
| 3 | 1 | 324, 308 | *cis*, chelated | c |
| 4 | ⩾2 | 340 | *trans*, bridged | b |
| 5 | ⩾2 | 346 | *trans*, bridged | b |
| 6 | ⩾2 | 343 | *trans*, bridged | b, c |
| 8 | ⩾2 | 346 | *trans*, bridged | c |
| 12 | 1 | 352 | *trans*, chelated | c |

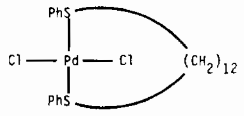
$^a$Nujol mulls; values in wave-numbers. $^b$This work. $^c$Ref. 2.



(A)



(B)



(C)

The non-coincidence of the spectra reported [1, 2] for $[PdCl_2(PhS(CH_2)_2SPh)]$ is not an unprecedented phenomenon. Three forms of *cis*-$[PtCl_2(SMe_2)_2]$ exist for which distinctly different vibrational spectra have been recorded [7]. We therefore suggest that at least two forms of the above chelate complex exist, depending on the method of synthesis and solvent of crystallisation.

The single strong band assigned as $\nu$(Pd–Cl) for each of the novel complexes of *1* ($m$ = 1, 4, 5), and also ($m$ = 6, 8, 12) [2], falls within the range 340–355 $cm^{-1}$ (Table I). The value of this band, and the observation of only one palladium–chlorine stretching mode in each i.r. spectrum, demonstrates that these complexes are of *trans*-geometry about palladium [2, 6, 7].

The complexes $[PdCl_2(PhS(CH_2)_mSPh)_2]_x$ ($m$ = 1, 4, 5, 6, 8) are of very low solubility in appropriate solvents. Nevertheless, for $m$ = 1 an upper average limit of 14 can be placed on the value of $x$. The ligands therefore bridge palladium atoms in complex systems, or mixtures of systems, with high degrees of aggregation, (B). When $m$ = 12 it has been demonstrated that the long-chain ligand *trans*-chelates palladium, (C) [2].

The ligands $Ph_2P(CH_2)_lPPh_2$, (*2*, $l$ = 1, 2, 3) also chelate palladium(II) [3]. However, steric interaction between ligating $Ph_2PCH_2$– groups and neighbouring chloro-ligands increases with increasing value of $l$ due to the widening angle between the phosphine ligating groups. Consequently, the complex of *2* ($l$ = 4) is not chelated, but a ligand-bridged trinuclear complex.

It is therefore proposed that the nature of the dithioether complex formed changes from a *cis*-chelating ($m$ = 2, 3) to a ligand-bridged *trans*-complex due to the increased interaction of thioether ligating groups with the neighbouring chloro-ligands in the proposed chelated product, (A). As the value of $m$ increases so the angle S–Pd–S increases, thereby increasing the interaction between the neighbouring chloro-ligand and the ligating $S(Ph)(CH_2$–) moiety, which also has a lone pair of electrons to be considered. When this interaction is sufficiently destabilising to offset the free energy gain achieved by chelation, but the length of the chain is insufficiently large to permit *trans*-chelation, the complex adopts a *trans* geometry about palladium with bridging dithioether ligands.

The reactions of dithioethers *1* ($m \geq 2$) with equimolar amounts of $K_2[PtCl_4]$ gave $[PtCl_2(1)]_x$ [2]. It is noteworthy that the reaction of an aqueous solution of $K_2[PtCl_4]$ with an ethanolic solution of *1* ($m$ = 1) gave neither $[Pt\{(PhS)_2CH_2\}_2][PtCl_4]$ nor $[PtCl_2(PhS)_2CH_2]_x$, but gave instead a complex of 2:1 stoicheiometry: $[PtCl_2\{(PhS)_2CH_2\}_2]$, despite the equimolar ratio of the reagents.

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