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# NICKEL(II), PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF *trans* SPANNING DITERTIARY PHOSPHINE 3,3′-OXYBIS-[(DI-*meta*-TOLYLPHOSPHINO)METHYL]BENZENE

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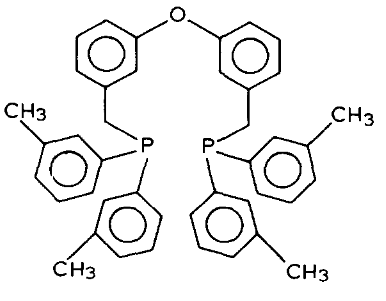
## Summary

The synthesis of the *trans*-spanning bidentate diphosphine ligand, 3,3′-oxybis-(di-*meta*-tolylphosphino)methyl]benzene (I) and its complexes with $Ni^{II}$, $Pd^{II}$ and $Pt^{II}$ are described. The ligand I forms monomeric *trans* square planar complexes $[MX_2(I)]$ (M = Ni, Pd or Pt, X = Cl or X = NCS in case of Ni). $^{31}P$ and $^1H$ NMR parameters are reported.

## Introduction

Venanzi et al. [1] have extensively studied the coordination chemistry of the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene(*P–P*) which induces the preferential formation of square planar *trans* chelate complexes with a



(I)

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variety of metal centres. This ligand has found application in mechanistic as well as structural studies. A similar type of *trans*-spanning ligand 3,3′-oxybis[(diphenylphosphino)methyl]benzene (POP) with a more flexible backbone was also shown to form *trans* chelate complexes [2,3]. Under certain circumstances, both the ligands also form *cis*-chelate complexes [3,4]. The platinum complexes of POP were also shown to undergo cyclometallation [2,5]. In order to impart different solubility or different electronic and steric properties in metal complexes of (P–P), a variety of ligands with different R groups were synthesised [6,7]. In this paper, we report the synthesis of the ligand 3,3′-oxybis[(di-*meta*-tolylphosphino)methyl]benzene (I) and its metal complexes with $Ni^{II}$, $Pd^{II}$ and $Pt^{II}$. This study was undertaken in order to prepare more soluble complexes, so that the $^{31}P$ NMR studies could be carried out.

## Experimental

Physical measurements and experimental techniques were as described elsewhere [1,6,7].

*Synthesis of 3,3′-oxybis[(di-meta-tolylphosphino)methyl]benzene (I)*

Di-*m*-tolylphosphine [8] (3.6 g, 16.8 mmol) and butyllithium (10 ml, 1.7 *M*) were added from a syringe to deoxygenated anhydrous tetrahydrofuran (20 ml) with stirring at 0°C under nitrogen. 3,3′-Oxybis(bromomethyl)benzene [9], (3.0 g, 8.4 mmol) in deoxygenated THF (20 ml) was then added during 20 min. The mixture was stirred at 0°C for 1 h then at room temperature for 1 h, and the solvent then removed under reduced pressure. The orange brown residue was shaken with water and chloroform and the water layer was discarded. The chloroform layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to leave an oil, which on extraction with petroleum ether (30–60°C) gave white solid which was recrystallised from ethanol at −10°C to give a white solid (3.4 g, 65%), m.p. 100–103°C. Analysis. Found: C, 80.96; H, 6.46; P, 9.71, Mol. Wt. 615.0. ($CH_2Cl_2$). $C_{42}H_{40}P_2O$ calcd.: C, 81.04; H, 6.43; P, 9.96%. Mol. Wt. 622.5. IR ($cm^{-1}$): 3080–3000 ($\nu$(CH) aromatic), 2920 ($\nu$(C–H) aliphatic) 1250 ($\nu$(C–O)). $^1H$ NMR ($CDCl_3$): $\delta$ 7.5–6.50 (m) (aromatic protons, 24 H); 3.3 (s) (methylene protons, 4H); 2.28 (s) (methyl protons, 12H). $^{31}P$ NMR ($CDCl_3$): $\delta$ −9.77 ppm (with reference to $H_3PO_4$).

*trans-[NiCl$_2$(I)]*

A suspension of $NiCl_2 \cdot 6H_2O$ (0.15 g, 0.63 mmol) was heated to reflux in 30 ml of n-butanol and ligand I (0.4 g, 0.64 mmol) was added, the solution which immediately become purple violet, was refluxed for 2 h then cooled, and the purple violet solid which separated out was filtered off, washed with n-butanol, and dried (0.33 g, 69%).

*trans-[Ni(NCS)$_2$(I)]*

Ligand I (0.36 g, 0.58 mmol) was added to a solution of $Ni(NCS)_2$ (0.1 g, 0.57 mmol) in n-butanol (20 ml). A red solution being immediately produced. This was refluxed for 1 h then filtered, and the filtrate was cooled to give red-orange crystals (0.36 g, 78%), which were recrystallized from $CH_2Cl_2$/benzene.

*trans-[$PdCl_2$(I)]*

A mixture of $PdCl_2$ (0.075 g, 0.43 mmol) and acetonitrile (40 ml) was refluxed for 2 h to produce a clear solution and ligand I (0.27 g, 0.43 mmol) was then added. The mixture was refluxed for 3 h and the acetonitrile was removed under reduced pressure to leave a yellow solid. Recrystallization from a solution of benzene/ethanol gave yellow crystals (0.23 g, 65%).

*trans-[$PtCl_2$(I)]*

$PtCl_2(CH_3CN)_2$ (0.2 g, 0.57 mmol) was refluxed for 2 h with ligand I (0.36 g, 0.58 mmol) in 30 ml of $CH_3CN$. A pale yellow solid separated out. The $CH_3CN$ was removed under reduced pressure and the residue was crystallised from benzene/ethanol to give a pale yellow solid (0.32 g, 63%).

## Results and discussion

Complexes of ligand I were prepared in reasonable yield and some of their physical properties and analytical data are given in Table 1. Their mono-nuclear nature was established by molecular weight determination. All the isolated complexes were homogeneous, and the $^{31}P$ NMR spectra showed a single resonance in all cases (Table 2) for $Ni^{II}$ and $Pd^{II}$ complexes and a single resonance accompanied by the appropriate satellites for $Pt^{II}$ complex. The value of $J(^{195}Pt-^{31}P)$ 2592.7 Hz is consistent with a *trans* configuration. Their $^1H$ NMR spectra are also consistent with *trans* square planar configuration (Table 2); thus a simple triplet pattern for the $CH_2$ protons being observed and such virtual coupling $(^2J(P-H)+^4J(P-H))$ is generally indicative of *trans* configuration of the phosphorus donor atoms. It has also been observed for the analogous complexes of ligand (P–P) and (POP) [2,3,7]. No line broadening was observed in NMR spectra of the $Ni^{II}$ complex, which suggests the absence of tetrahedral species.

The IR spectra of the complexes are similar to those of the free ligands. All these complexes show one medium to strong band at ~ 1250 $cm^{-1}$ which is characteristic of (C–O) vibrations of the ligand.

It is evident that ligand I can readily form normal square-planar *trans* chelate complexes having electronic and NMR parameters very similar to those of the complexes containing the ligand (P–P) or (POP). The only difference is that the complexes described here are much more soluble in hydrocarbon solvents than those

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES OF LIGAND I

| Compound | Colour | Analysis (Calc (Found) (%)) | | | Mol. wt ($CH_2Cl_2$) |
|---|---|---|---|---|---|
| | | C | H | Cl | |
| [$NiCl_2$ (I)] | Purple violet | 67.07(67.21) | 5.32(5.48) | 9.43(9.54) | 752.1(752.0) |
| [$Ni(NCS)_2$(I)] [a] | Orange red | 66.28(65.99) | 5.02(5.13) | 3.51(3.37) [b] | 797.3(811.4) |
| [$PdCl_2$(I)] | Yellow | 63.07(63.14) | 5.04(5.18) | 8.87(8.92) | 799.8(865.3) |
| [$PtCl_2$(I)] | Pale yellow | 56.77(56.87) | 4.51(4.65) | 7.98(8.08) | 888.5(926.2) |

[a] $\nu$(NCS) 2080 $cm^{-1}$. [b] Nitrogen.

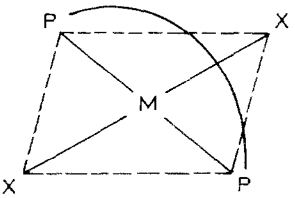
TABLE 2

$^{31}$P AND $^{1}$H NMR DATA FOR THE COMPLEXES *trans*-[MX$_2$(I)] [a]

| Compound | $^{31}$P NMR [b] | Ring proton | $^{1}$H NMR [c] aromatic protons | Methylene protons | Methyl protons |
|---|---|---|---|---|---|
| Ligand (I) | −9.77 | – | 6.5–7.5(m) | 3.33(s) | 2.28(s) |
| [NiCl$_2$(I)] | +7.16 | 9.33(s) | 6.1–7.3(m) | 3.54(t)<br>*J*(P–H) 10.28 Hz | 2.28(s) |
| [Ni(NCS)$_2$ (I)] | +12.90 | 8.96(s) | 6.0–7.3(m) | 3.44(t)<br>*J*(P–H) 9.67 Hz | 2.34(s) |
| [PdCl$_2$ (I)] | +20.39 | 8.45(s) | 6.1–7.3(m) | 3.85(t)<br>*J*(P–H) 8.5 Hz | 2.27(s) |
| [PtCl$_2$ (I)] | +16.65<br>*J*(Pt–P)<br>2592.7 Hz | 8.54(s) | 6.1–7.4(m) | 3.92(t, t)<br>*J*(P–H) 8.24 Hz,<br>*J*(Pt–H) 27.76 Hz | 2.28(s) |

[a] All the spectra were recorded with CDCl$_3$ solutions. [b] Relative to an external H$_3$PO$_4$ standard; shifts to higher field are denoted as negative and those to lower field as positive. [c] Relative to TMS.

containing (POP). This higher solubility being exploited in a study of the cyclometallation reactions.



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