

Transition metal complexes of the *trans*-spanning ditertiary phosphine, bis{3-[bis(3-trifluoromethylphenyl)-phosphinomethyl]phenyl} ether *

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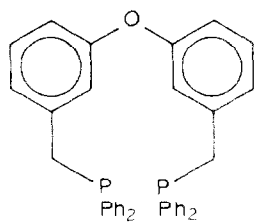
Abstract

The bidentate ditertiaryphosphine ligand, bis{3-[bis(3-trifluoromethylphenyl)phosphinomethyl]phenyl} ether (L–L) forms monomeric *trans*-square planar complexes $[MX_2(L-L)]$ (M = Ni, Pd or Pt, X = Cl; M = Ni, X = NCS) as well as *trans*-[PtHCl(L–L)]; ^{31}P and ^1H NMR, and selected IR parameters are reported.

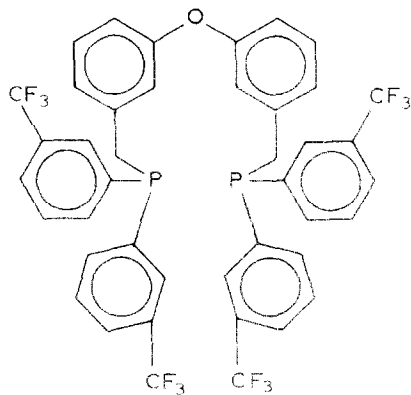
Introduction

Recently, there has been considerable interest in the synthesis of bidentate ditertiary phosphine ligands [1] with either a large backbone [2] or a rigid backbone [3], in order to examine the precise rôle that the nature of the backbone plays in determining the stereochemistry of the complexes with transition metals. The most systematic and extensive attempts in this direction were due to Shaw and coworkers [4] and Venanzi and coworkers [5], who had investigated the ligands $R_2P(CH_2)_nPR_2$ ($n = 10, 11$ or 12) and 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (P–P). The latter ligand (P–P) proved to form a great variety of *trans*-spanning square-planar chelates [6]. However, it was also observed that, despite its rigid backbone and steric hindrance exerted by the four phosphine phenyl groups, this ligand also forms *cis* square-planar [7], as well as six-coordinate, species [8]. A similar type of *trans*-spanning ligand, bis{3-[diphenylphosphinomethyl]phenyl} ether (POP) with a more flexible backbone compared to P–P, was also shown to form *trans*-chelate complexes [9]. In this paper we report the synthesis of similar type of ligand, bis{3-[bis(3-trifluoromethylphenyl)phosphinomethyl]phenyl} ether (L–L) and its metal complexes with nickel(II), palladium(II) and platinum(II).

* Dedicated to my teacher and mentor, Prof. C. Eaborn FRS, on his 65th birthday.



(POP)



(L-L)

Experimental

The physical measurements and experimental techniques were carried out as described elsewhere [9,10].

Synthesis of bis{3-[bis(3-trifluoromethylphenyl)phosphinomethyl]phenyl} ether (L-L)

Bis(3-trifluoromethylphenyl)phosphine (2.4 g, 7.45 mmol) [11] and butyllithium (4.4 ml; 1.78 M in thf) were added from syringe to deoxygenated anhydrous thf (20 ml), with stirring at 0°C, under dinitrogen. A dark orange solution was produced. Bis{3-(bromomethyl)phenyl} ether (1.3 g, 3.7 mmol) [12] dissolved in thf (20 ml) was slowly added, thus producing a pale yellow solution. The reaction mixture was left stirring at 0°C for 2 h. The solvent was then removed under reduced pressure. The orange brown residue was dissolved in trichloromethane (30 cm³) and washed with water (3 × 20 cm³). The organic layer was dried over anhydrous Na₂[SO₄] and filtered. The filtrate, on evaporation, gave a yellow spongy solid, which was purified by dissolving in ethanol (10 cm³) and cooling at -78°C to produce a pale yellow solid (2.2 g, 73%).

IR: 3080–3000, 2910, 1320, and 1150 cm⁻¹. ¹H NMR (CDCl₃), δ 7.4–6.4 (m, 24 H), 3.2 (2, 4 H) ppm. ³¹P NMR (CDCl₃) δ -9.12 ppm (with reference to H₃PO₄).

The *trans* complexes [NiCl₂(L-L)], [Ni(NCS)₂(L-L)], [PdCl₂(L-L)], [PtCl₂(L-L)] and [PtHCl(L-L)] were prepared by a method described elsewhere [9,10]. The analytical data and physical properties of these complexes are summarized in Table 1.

Results and discussion

The reaction of the title ligand L-L, with MCl₂ (M = Ni, Pd or Pt) and Ni(NCS)₂ yielded the complexes *trans*-[MX₂(L-L)]. The hydride complex *trans*-[PtHCl(L-L)] was obtained by ligand exchange from *trans*-[PtHCl(PPh₃)₂] [13], with retention of configuration. The mononuclear nature of these complexes was confirmed by molecular weight determination. It is noteworthy that introduction of a CF₃ group in the 3-position of the *P*-bonded phenyl group of L-L results in the formation of complexes which are soluble in hydroxylic solvents.

Table 1
Analytical and spectroscopic ^b data

Compound	Colour	Analysis (found/calcd, %)			Mol. wt. ^a (CH ₂ Cl ₂)	³¹ P NMR δ/ppm ^c	¹ H NMR		
		C	H	N			δ (aromatic)(ppm)	δ(CH ₂)(ppm)	
L-L	yellow	59.23 (60.15)	3.16 (3.36)	7.10 ^d (7.39) ^d		-9.12		7.4-6.4(m)	3.2(s)
[NiCl ₂ (L-L)]	purple violet	51.82 (52.10)	2.83 (2.91)	7.16 (7.33)	953 (968)	+6.9	9.1(s)	7.2-6.5(m)	3.4(t) J(PH) 10.0 Hz
[Ni(NCS) ₂ (L-L)]	orange red	52.33 (52.15)	2.72 (2.78)	2.63 ^e (2.76) ^e	980 (1013)	+12.6	8.80(s)	7.0-6.2(m)	3.18(t) J(PH) 9.0 Hz
[PdCl ₂ (L-L)]	yellow	49.36 (49.65)	2.63 (2.77)	6.80 (6.99)	1008 (1015)	+19.6	8.3(s)	7.1-6.4(m)	3.78(t) J(PH) 8.2 Hz
[PtCl ₂ (L-L)]	white	45.30 (45.67)	2.48 (2.55)	6.20 (6.45)	1080 (1104)	+15.8 ¹ J(PtP) 2580.6 Hz	8.41(s)	7.0-6.4(m)	3.84(t,t) J(PH) 8.3 Hz
[PtHCl(L-L)] ^f	white	47.0 (47.14)	2.68 (2.73)	3.20 (3.32)	-	+25.3 ¹ J(PtP) 2508 Hz	8.50(2)	6.9-6.3(m)	J(PtH) 26.8 Hz 3.76(t,t) J(PH) 7.3 Hz J(PtH) 37.0 Hz

^a Theoretical values in parentheses. ^b Measured in CDCl₃. ^c Measured relative to external H₃PO₄; positive to low field. ^d %P. ^e %N. ^f δ(HPt) -14.2 ppm, ¹J(PtH) 1190 Hz, ²J(PH) 27 Hz.

The ^{31}P NMR parameters obtained for the complexes are listed in Table I. Nickel(II) and palladium(II) complexes show a single resonance accompanied by the appropriate satellites, with $^1J(\text{PtP})$ of 2581 and 2508 Hz for $[\text{PtCl}_2(\text{L-L})]$ and $[\text{PtHCl}(\text{L-L})]$, respectively, consistent with their *trans* configuration [14]. The lack of paramagnetic shifts and line broadening in the NMR spectra of the nickel(II) complexes suggest the absence of a tetrahedral species in equilibrium with the *trans* square-planar configuration.

The ^1H NMR spectra also support a *trans*-square planar configuration for these complexes, a triplet pattern for the CH_2 protons being obtained. This virtual coupling ($\{^2J(\text{PH}) + ^*J(\text{PH})\}$) is indicative of the *trans* configuration of phosphorus donor atoms [5,9,10]. The hydride complex $[\text{PtHCl}(\text{L-L})]$ shows a hydride resonance at $\delta -14.2$ ppm with $^2J(\text{PH})_{\text{Pt}}$ 27.0 Hz and $^1J(\text{PtH})$ 1190 Hz.

The IR spectra of the complexes are similar to those of free ligand. All these complexes show very strong broad bands at ca. 1320 and 1150 cm^{-1} , characteristic of $\nu(\text{C-F})$. The band at ca. 1250 cm^{-1} for the $\nu(\text{C-O})$ vibration overlaps with $\nu(\text{C-F})$ vibrations. A band at 2080 cm^{-1} in the IR spectrum of $[\text{Ni}(\text{NCS})_2(\text{L-L})]$ was observed, which is characteristic for the *N*-bonded thiocyanate group. A band at 2210 cm^{-1} was observed in the IR spectrum of $[\text{PtHCl}(\text{L-L})]$, due to $\nu(\text{Pt-H})$ vibrations.

In conclusion, the coordination chemistry of L-L is analogous to that of POP, except that introduction of a 3- CF_3 group on the phenyl ring attached to the phosphorus donor atom increases the solubility of the resulting transition metal complexes. On the basis of above studies, the complexes $[\text{MX}_2(\text{L-L})]$ and $[\text{PtHCl}(\text{L-L})]$ can be assigned *trans* square-planar structure.

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