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Note

A palladium(II) complex of a new iminophosphine ligand derived from diethylenetriamine and 2-(diphenylphosphino)benzaldehyde

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Abstract

The mononuclear complexes [Pd(oPdien)]X_2 {oPdien = *N*-(2-diphenylphosphinobenzylidene)diethylenetriamine: (**4a**) $X_2 = [ZnCl_4]^{2-}$; (**4b**) X = $[PF_6]^-$; (**4c**) X = Cl^-} are described. Complex **4a** formed in high yield when [Pd(oPCHO)$_2$Cl$_2$] [oPCHO = 2-(diphenylphosphino)benzaldehyde] (**1**) and [Zn(dien)Cl$_2$] (**2**) were reacted together in an unsuccessful attempt to template formation of a bimetallic iminophosphine-bridged complex. The X-ray crystal structure of **4b** has been determined. The ligand oPdien is the first iminophosphine derived from dien and has been isolated and used to prepare **4c**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Palladium complexes; Iminophosphine complexes

1. Introduction

Our recent work on the functionalisation of phosphines with N-donor groups [1] has led us to investigate the synthesis of potentially multinucleating iminophosphine ligands. The presence of both soft and hard base donor atoms in these types of ligand has already prompted reports of their use in preparing heteronuclear complexes [2]. Mononuclear complexes of these same polydentate iminophosphine ligands have also attracted much recent interest due to the role they play in facilitating catalytic reactions by stabilising metal centres in a variety of oxidation states [3–6].

The use of 2-(diphenylphosphino)benzaldehyde (oPCHO) as a building block for iminophosphines was first reported in the Schiff-base condensation with ethylenediamine [7,8] and has since been extended to a wide variety of other amines [9–13]. Diethylenetriamine (dien) is another key component in the synthesis of imine-type ligands and has been employed extensively in the synthesis of metal complexes which show important catalytic and dioxygen binding properties [14–17]. In this report we describe the reaction between a preformed Pd(II) complex of oPCHO and a Zn(II) complex of dien in an attempt to template the preparation of an iminophosphine-bridged Pd, Zn dimer. The reaction resulted in the adventitious formation of a mononuclear Pd(II) complex of the iminophosphine derived from dien and oPCHO, the synthesis and characterisation of which is discussed. The ligand is the first example of an iminophosphine prepared from dien.

2. Experimental

2.1. Materials

2-(Diphenylphosphino)benzaldehyde was synthesised by the method of Rachfuss [18], bis(benzonitrile)palladium(II) dichloride by the method of Anderson [19] and diethylenetriaminezinc(II) dichloride by the method of Curtis [20].

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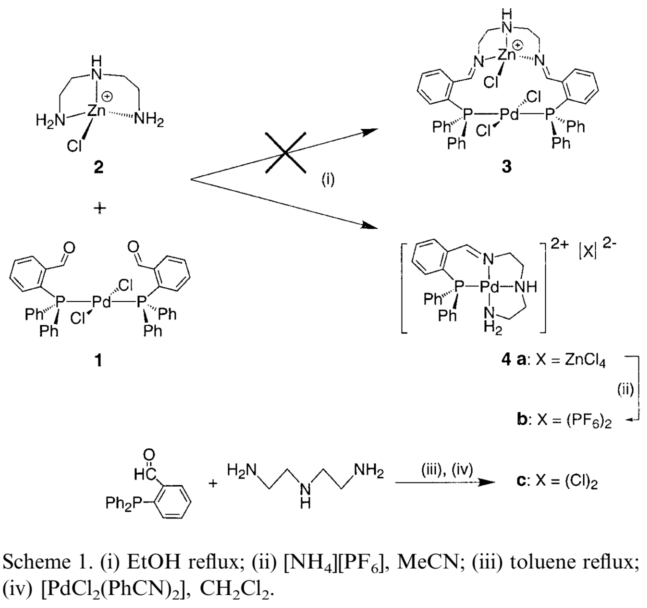
2.2. Synthesis of $[Pd^{II}Cl_2(oPCHO)_2]$ (**1**)

A solution of 2-(diphenylphosphino)benzaldehyde (0.974 g, 3.36 mmol) in dichloromethane (20 cm^3) was added dropwise to an ice cooled stirred solution of $[Pd(PhCN)_2Cl_2]$ (0.645 g, 1.68 mmol) in dichloromethane (45 cm^3). The solution was allowed to warm to room temperature gradually over 2 h and the orange solid that formed was collected by filtration. Additional compound was obtained by adding diethyl ether to the initial filtrate. The complex was recrystallised from dichloromethane–diethyl ether to give orange crystals of $[Pd(PCHO)_2Cl_2]$ (1.02 g, 80%). Found: C, 59.84; H, 4.06. $C_{38}H_{30}Cl_2O_2PdP_2$ requires: C, 60.22; H, 3.99%. P NMR ($CDCl_3$): δ 20.81 (s). H NMR ($CDCl_3$): δ 10.47 (1 H, s), 8.0 (1 H, d), 7.99 (1 H, d), 7.81 (4 H, q), 7.57 (1 H, t), 7.43 (6 H, m), 7.03 (1 H, q).

2.3. Synthesis of $[Pd^{II}(oPdien)][Zn^{II}Cl_4]$ (**4a**)

A suspension of $[Zn(dien)Cl_2]$ (0.415 g, 1.74 mmol) and $[Pd(PCHO)_2Cl_2]$ (1.32 g, 1.74 mmol) in ethanol (100 cm^3) was heated at reflux for 2 h with the yellow colour gradually fading. The cream solid was collected by filtration and recrystallised from methanol–diethyl ether to give white flowers of $[Pd(oPdien)][ZnCl_4]$ (0.973 g, 81%). Found: C, 40.13; H, 4.18; N, 5.34. $C_{23}H_{26}Cl_4N_3PdPZn \cdot 2(CH_3OH)$ requires: C, 39.87; H, 4.55; N, 5.58%. P NMR ($(CD_3)_2SO$): δ 27.35 (s). H NMR ($(CD_3)_2SO$): δ 8.89 (1 H, s), 8.12 (1 H, t), 7.93 (2 H, m), 7.80–7.50 (10 H, m), 7.43 (1 H, t), 4.44 (1 H, m), 4.33 (1 H, m), 3.08 (6 H, m). ES MS *m*/*z*: 240 $\{[Pd(oPdien)]^{2+}\}$.



Scheme 1. (i) EtOH reflux; (ii) $[NH_4][PF_6]$, MeCN; (iii) toluene reflux; (iv) $[PdCl_2(PhCN)_2]$, CH_2Cl_2.

2.4. Synthesis of $[Pd^{II}(oPdien)][PF_6]_2$ (**4b**)

A suspension of $[Pd(oPdien)][ZnCl_4]$ (0.498 g, 0.722 mmol) in acetonitrile (50 cm^3) was treated with $[NH_4][PF_6]$ until the complex completely dissolved. The solution was filtered while still hot, the volume reduced and water added until the first signs of cloudiness were observed. The white solid which formed on standing in a freezer for several hours was collected by filtration and recrystallised from acetonitrile–isopropanol to give colourless plates of $[Pd(oPdien)][PF_6]_2$ (0.376 g, 94%). Found: C, 35.07; H, 3.52; N, 5.31. $C_{23}H_{26}F_{12}N_3PdP_3$ requires: C, 35.79; H, 3.39; N, 5.45%. P NMR ($(CD_3)_2SO$): δ 27.51 (s), -143.11 [sept, *J*(PF) 707 Hz]. H NMR ($(CD_3)_2SO$): δ 8.85 (1 H, s), 8.11 (1 H, t), 7.93 (2 H, m), 7.80–7.40 (10 H, m), 7.22 (1 H, br s), 5.66 (1 H, br s), 4.91 (1 H, br s), 4.44 (1 H, m), 4.26 (1 H, m) and 3.07 (6 H, m). ES MS *m*/*z*: 240 $\{[Pd(oPdien)]^{2+}\}$. A small portion of the sample was recrystallised from 1-butanol–methanol to yield colourless crystals suitable for X-ray analysis.

2.5. Synthesis of $[Pd^{II}(oPdien)]Cl_2$ (**4c**)

A solution of oPCHO (1.30 g, 4.48 mmol) in toluene (60 cm^3) was added slowly over about 15 min via a cannula to a stirred solution of dien (1.85 g, 17.9 mmol) at reflux in toluene (20 cm^3) in a Dean–Stark apparatus. Heating of the solution at reflux was continued for 20 h followed by cooling to room temperature and removal of the solvent under vacuum to give an orange oil (oPdien) which was used without further purification. P NMR ($CDCl_3$): δ -15.48 (s), -16.63 (s). ES MS *m*/*z*: 376 $\{[H(oPdien)]^{+}\}$. A stirred solution of this crude oil (0.46 g, 1.2 mmol) in dichloromethane (12 cm^3) was cooled in an ice bath and treated with a solution of $[Pd(PhCN)_2Cl_2]$ (0.42 g, 1.1 mmol) in dichloromethane (10 cm^3) resulting in the immediate formation of a white precipitate. Stirring was continued for 4 h allowing the solution to gradually warm to room temperature. The white precipitate was collected by filtration and washed with diethyl ether to give $[Pd^{II}(oPdien)]Cl_2$ (0.509 g, 75%). P NMR ($(CD_3)_2SO$): δ 27.06 (s). H NMR ($(CD_3)_2SO$): δ 8.91 (1 H, s), 8.11 (1 H, t), 7.92 (2 H, m), 7.80–7.50 (10 H, m), 7.39 (1 H, m), 5.55 (1 H, br s), 4.42 (2 H, m) and 3.10 (6 H, m). ES MS *m*/*z*: 240 $\{[Pd(oPdien)]^{2+}\}$.

3. Results and discussion

Our objective was to synthesise a bimetallic complex bridged by an iminophosphine ligand derived from dien, e.g. **3** in Scheme 1. Molecular models suggest that the ligand derived from the condensation of two molecules of oPCHO with dien is ideally set-up to

Table 1
Numerical crystal and refinement data for **4b**

Formula	$C_{23}H_{26}F_{12}N_3P_3Pd$
Formula mass	771.8
Crystal size	0.30 × 0.19 × 0.06
Space group	$P2_1/c$
a (Å)	8.841(4)
b (Å)	18.606(4)
c (Å)	17.505(9)
α (°)	90
β (°)	91.74(2)
γ (°)	90
T (°C)	21(1)
Z	4
D_{calc} (g cm^{-3})	1.78
Diffractometer; scan mode	Enraf–Nonius CAD-4, $\theta/2\theta$
Radiation (λ, Å)	Mo Kα 0.71073
μ (cm^{-1})	8.96
F(000)	1536.0
Max., min. transmission factors	0.91, 0.77
$2\theta_{max}$	25
Number of intensity measurements	5238
R_{merge} for number of equivelent reflections	0.011 (178)
Number of observed reflections in final refinement [$I/\sigma(I) > 3$]	3479
Number of variables in final refinement	237
R	0.039
R_w	0.054
Goodness of fit	1.84
Max., min. peaks in final difference map (e Å^{-3})	0.84, −0.88

Table 2
Selected bond lengths (Å) and angles (°) for **4b**

Pd–P	2.232(1)
Pd–N1	1.978(4)
Pd–N2	2.064(4)
Pd–N3	2.043(5)
N1–C7	1.283(7)
P–Pd–N1	93.5(1)
P–Pd–N2	178.0(1)
P–Pd–N3	98.7(1)
N1–Pd–N2	84.6(2)
N1–Pd–N3	166.0(2)
N2–Pd–N3	83.3(2)
Pd–N1–C7	132.4(4)
Pd–N1–C8	109.4(3)
C7–N1–C8	117.6(5)
Pd–N2–C9	106.0(3)
Pd–N2–C10	106.3(3)
C9–N2–C10	119.3(5)
Pd–N3–C11	109.8(4)

coordinate to one metal by the two phosphine groups and to a second metal centre via the N_3-donor set of the dien moiety. We thought that a metal template 'type' reaction where two pre-formed metal complexes of the required stoichiometry were reacted together should provide a feasible route to bimetallic complexes such as **3**. It was envisaged that by initially conferring the required geometry onto the metal ions, the formation of the targeted complex should be facilitated.

To test these ideas a reaction between a palladium(II) complex of oPCHO, [Pd(oPCHO)$_2$Cl$_2$] (**1**), and a zinc(II) complex of dien, [Zn(dien)Cl$_2$] (**2**) [20], was carried out. The palladium(II) complex, **1**, was chosen to give the required transoid geometry and the diamagnetism of the metal centres in **1** and **2** enabled convenient monitoring of the reaction by ^{1}H and ^{31}P NMR spectroscopy. First, **1**, a new complex, was prepared in 80% yield from oPCHO [18] and [Pd(PhCN)$_2$Cl$_2$] [19] in dichloromethane. Then a suspension of **1** and **2** was heated at reflux in ethanol for several hours with the colour changing from yellow to cream. The suspension was then cooled and the cream precipitate, **4a**, collected by filtration. A metathesis reaction of **4a** with excess [NH$_4$][PF$_6$] gave colourless plates of **4b**.

Elemental analyses identify **4a**,**b** as complexes of the new iminophosphine, *N*-(2-diphenylphosphinobenzylidene)diethylenetriamine (oPdien), formed from the condensation of dien and one equivalent of oPCHO. Whilst the elemental and ICP analyses reveal **4a** to be a 1:1 Pd–Zn complex, the absence of zinc in the analyses of **4b** confirms the presence of the tetrachlorozincate anion in **4a** which is replaced by the hexafluorophosphate anion in **4b**. Complexes **4a** and **4b** give identical spectroscopic data with a characteristic imine resonance at about δ 8.9 in the ^{1}H NMR spectra, a singlet at about δ 27 in the ^{31}P NMR spectra and a single peak at m/z 240 in the ES mass spectra corresponding to the [Pd(oPdien)]$^{2+}$ molecular ion.

The complicated ^{1}H NMR spectra of both **4a** and **4b** precluded unequivocal assignment of the structure of the cation and, therefore, an X-ray crystallographic study of crystals of **4b** obtained from methanol–1-butanol was undertaken. Numerical crystal and refinement data for **4b** are summarised in Table 1, and key bond lengths and angles are listed in Table 2. The molecular structure of the cation of **4b** (Fig. 1) confirms the N_3P-coordination of oPdien to palladium. The sum of the bond angles about palladium is 704° which compares to 720° for a perfect square planar arrangement. A slight 'puckering' of the complex about the P to N2 vector causes the deviation from perfect square planar geometry and results in the N1–Pd–N3 bond angle of 166.0(2)° compared to the P–Pd–N2 bond angle of 178.0(1)°. The Pd–N(amine) and Pd–P bond lengths are comparable to those in a similar palladium(II) complex with a N_3P-donor ligand, [Pd(pybox)(PPh$_3$)][BF$_4$]$_2$ [pybox = 2,6-bis{4′-(*S*)-benzyloxazoline-2′-yl}pyridine], a complex which also has two five-membered rings about the palladium centre [21].

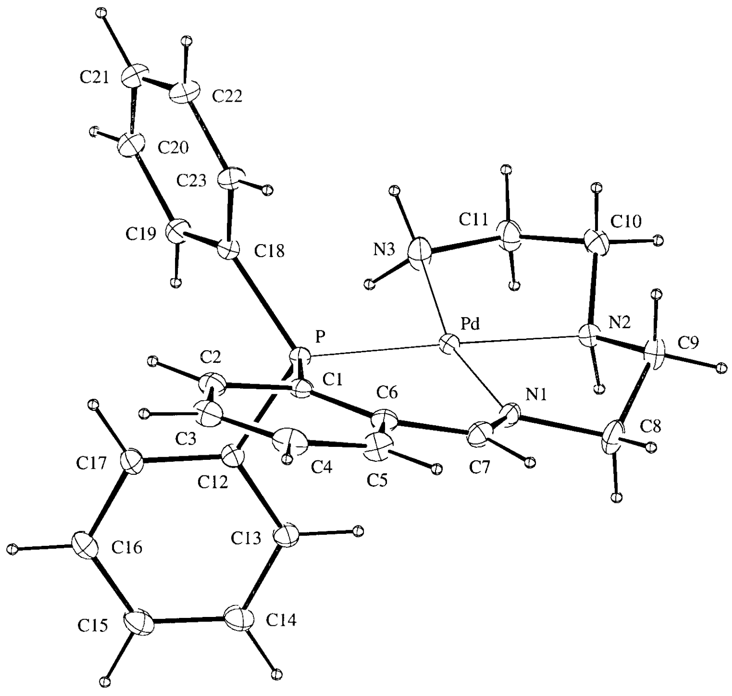


Fig. 1. Drawing of the complex cation **4b** showing the 10% thermal ellipsoids at 294 K.

Another palladium(II) complex with a N_2P-donor ligand, $[Pd(PNN)CH_3]^+$ [PNN = *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine] [22], exhibits a Pd–P bond length of 2.2007(16) Å compared to 2.232(1) Å in **4b** whilst the Pd–N(imine) bond in $[Pd(PNN)CH_3]^+$ at 2.131(5) Å is slightly longer than that observed in **4b** [1.978(4) Å], differences attributable to the formation of three chelate rings in **4b**.

The formation of mononuclear **4** from the stable bis(phosphino)palladium(II) complex **1** indicates a strong driving force for the coordination of the N donor groups to palladium. The preference for chelate ring formation realised in the formation of two five membered and a six membered ring about the palladium centre is the most likely explanation for the rearrangements observed. An alternative coordination mode for the N_3P-donor group of oPdien is found in the complex, $[Ag_3\{(PN)_3N\}_2]^{3+}$ [$(PN)_3N = \{(o\text{-}Ph_2PC_6H_4)CH{=}NCH_2CH_2\}_3N$] (**5**) prepared by the Ag^+ templated reaction of *N*,*N*,*N*-tris(2-aminoethyl)amine and oPCHO [23]. In the resulting complex (**5**) the five-coordinate silver ions were bound by two iminophosphine arms and the amine with the remaining iminophosphine arm bridging to the adjacent four-coordinate Ag^+ ion, Fig. 2. Notably, it was reported that attempts at direct synthesis of $[(PN)_3N]$ were unsuccessful and the complex could only be synthesised in a metal template reaction. This lead us to investigate whether or not free oPdien could be prepared.

Therefore, oPCHO was reacted with an excess of dien in toluene to give an oil which gave a peak at *m*/*z* 376 in its ES mass spectrum corresponding to the protonated free ligand, $[H(oPdien)]^+$. The ^{31}P NMR spectrum of the ligand shows peaks at δ − 16.63 and − 15.48 for free oPdien and the isomer resulting from addition of the secondary amine group to the imine bond, as is observed in similar dien-based ligands [14]. These isomers equilibrate in solution [14], and the crude oil was treated with $[Pd(PhCN)_2Cl_2]$ to give a complex **4c** in 75% yield (Scheme 1). Complex **4c** gave identical spectroscopic data to **4a** and **4b** confirming that it contains the $[Pd(oPdien)]^{2+}$ cation. This demonstrates that the free ligand, oPdien, can be prepared directly from its organic constituents and that using pre-formed oPdien is the best route to **4**.

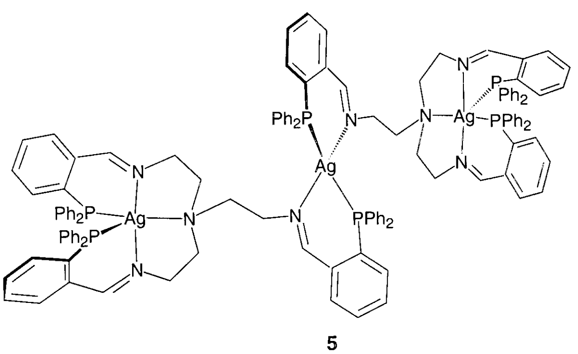


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Fig. 2. Drawing of $[Ag_3\{(PN)_3N\}_2]^{3+}$ (**5**) [23].

4. Conclusions

The synthesis of the first iminophosphine ligand based on dien through the Schiff-base condensation with 2-(diphenylphosphino)benzaldehyde is described. The new ligand, oPdien, is unique amongst iminophosphines in that it has the potential to coordinate either as a tetradentate P,N,N,N-donor as in **4b**; as a tridentate N,N,N-donor like dien in a complex with an uncoordinated, dangling phosphine group; as a bidentate P,N-donor analogous to a molybdenum complex reported briefly by Rauchfuss [7]; and even as a unidentate P-donor comparable to other selective N,P-donor ligands [1,24]. The variation in possible coordination modes for oPdien and the potential to vary chelate ring sizes closely resembles the demonstrated 'intrinsic flexibility' of the related P,N,N-donor ligand, PNN [22]. The ability of PNN to stabilise metals in a variety of oxidation states leads to the observed catalytic activity of a palladium complex of it [4], a result suggesting that complexes of oPdien might display equally novel reactivities.

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