

Palladium(II) complexes with hemilabile amphiphilic phosphines

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Abstract

A series of *trans*-PdCl₂L₂ complexes were prepared and characterized with the following hemilabile amphiphilic phosphines: R-(C₆H₄)-(OCH₂CH₂)_n-PPh₂ {**1** (R = *tert*-octyl, *n* = 1), **2** (R = *tert*-octyl, *n* = 5), **3** (R = *tert*-octyl, *n* = 13), **4** (R = *n*-nonyl, *n* = 1.4), **5** (R = *n*-nonyl, *n* = 5), **6** (R = *n*-nonyl, *n* = 11)}, CH₃(OCH₂CH₂)₃PPh₂ (**7**), CH₃(OCH₂CH₂)₃PPhR (**8**, R = isopentyl) and HOCH₂CH₂(OCH₂CH₂)₂PPhR (**9**, R = *n*-octyl). The molecular structure of *trans*-PdCl₂(**1**)₂ was determined by X-ray crystallography. The reaction between the *trans*-PdCl₂L₂ complexes and Ag⁺ was studied by ³¹P-NMR spectroscopy. The formation of chelated P⋯O species in tetrahydrofuran solution was observed in complexes with ligands **2**, **3**, **5**, **6**, **7**, **8** and **9**. However, with ligand **1** the formation of chelated species was only observed in the less coordinating solvent dichloromethane. This different behavior can be attributed to the electronic and steric effects of the aryl group bonded to the oxygen atom. Ligand **4** is a mixture of a molecule similar to **1** and molecules with more than one oxygen atom and thus displays both characteristics. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium(II) complexes; Hemilabile amphiphilic phosphines; ³¹P-NMR spectroscopy

1. Introduction

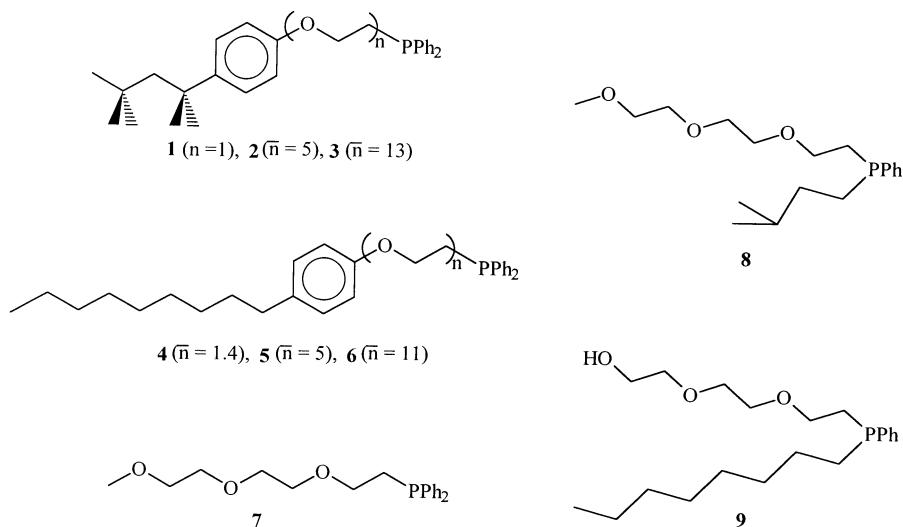
The synthesis and study of new functionalized ligands, which may improve certain properties in transition metal complexes, has become a central topic in inorganic and organometallic chemistry. Functionalized phosphine ligands exhibit a relevant position on this subject since a broad range of groups may be anchored to the phosphorus atom, leading to different functionalized phosphines, e.g. water-soluble [1], asymmetric [2], hemilabile [3], etc. In this way, a new concept of functionalized phosphines has emerged in recent years: amphiphilic phosphines [4]. These ligands contain hydrophilic and hydrophobic groups in the same molecule and can form metal complexes which can aggregate,

yielding to supramolecular arrangements such as micelles and vesicles [5]. These micro-heterogeneous systems are attractive for improving catalytic processes, especially those working in two-phase systems due to phase-transfer limitations [6]. This approach has been recently utilized in the study of a catalytic reaction accelerated by vesicle formation [7].

In a previous paper, we described the synthesis of a new group of amphiphilic phosphines that feature the combination of amphiphilic and hemilabile properties [8] (Scheme 1). Ligands **1–9** were prepared straightforwardly from polyethylene glycol monoalkylethers; common starting compounds since they are used extensively as nonionic surfactants. In this paper, we report the reactivity of ligands **1–9** (Scheme 1) towards Pd(II). New data on the coordination chemistry of **1–9**, thus rounds out our previously reported results with Ru(II) where various coordination modes such as monodentate (*P*), bidentate (*O*, *P*) and tridentate (*O*, *O*, *P*) were described [8].

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Scheme 1.

2. Results and discussion

2.1. Ligands

Ligands **1–6** were synthesized from commercial non-ionic surfactants Igepal¹ [9]. In accordance with the nature of these starting nonionic surfactants, the ligands were obtained as mixtures of compounds with the same structure but with different ethoxylation grades (Scheme 1). The only exception is **1**, which was obtained as a single compound because it crystallized from the reaction mixture as a white solid. Ligands **7–9** were also achieved as single compounds because they were prepared from pure $\text{Cl}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $\text{Cl}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{OH}$.

2.2. PdCl_2L_2 complexes

The reaction of $\text{PdCl}_2(\text{COD})$ with 2 moles of **1–9** in dichloromethane yields orange solutions and except the reaction with **1**, no solids could be isolated. All the ^{31}P -NMR spectra of the palladium complexes obtained from ligands **1–7** display a main signal at 12.4–14.1 ppm and a very small peak at 24.5–26.8 ppm. The upfield and major resonance is assigned to the *trans*- PdCl_2L_2 isomer and the small and downfield resonance to the *cis*- PdCl_2L_2 isomer. These assignments are consistent with data reported previously for PdCl_2L_2 complexes with monodentate phosphine ligands [9–11]. The ^{31}P -NMR spectra of $\text{PdCl}_2(\textbf{8})_2$ and $\text{PdCl}_2(\textbf{9})_2$ display a similar pattern but the resonances are upfield shifted. Thus, the signals assigned to *trans*- PdCl_2L_2 are observed at 10.0 ($\text{L} = \textbf{8}$) and 9.3 ppm ($\text{L} = \textbf{9}$) and the

signals assigned to *cis*- PdCl_2L_2 appeared between 17 and 19 ppm. This is consistent with the replacement of an aryl group bonded to phosphorus by an alkyl group in **8** and **9** with respect to **1–7**. In addition, since ligands **8** and **9** were obtained as racemic mixtures, the ^{31}P -NMR spectra of their *cis*- PdCl_2L_2 complexes display the signals of the respective two diastereoisomers.

In previous studies with $\text{Ru}(\text{II})$ [8b], ligand **1** showed a significantly different behavior from **2** to **6** since it is the sole ligand that is not a mixture of molecules with different ethoxylation grades and only one oxygen atom is available for coordination. As mentioned above, after reaction with $\text{PdCl}_2(\text{COD})$ it was the only ligand that led to the formation of a solid compound, which was isolated and characterized as $\text{PdCl}_2(\textbf{1})_2$ by the usual analytical and spectroscopic methods. As noted above, the *trans*-configuration is anticipated by ^{31}P -NMR spectroscopy and the ^{13}C -NMR spectrum is also consistent with this assignment. A signal at 26.5 ppm assigned to the carbon atom of the methylene group bonded to phosphorus is observed as a triplet. This splitting has been previously described for the carbon atoms linked to phosphorus in *trans*- PdX_2P_2 complexes and attributed to the coupling of these carbon atoms to the two virtually equivalent *trans*-phosphorus atoms [10,12]. Single crystals of *trans*- $\text{PdCl}_2(\textbf{1})_2$ were obtained by recrystallization in acetone–ethanol and their structure was determined by X-ray analysis. A perspective view of the molecule with the labelling scheme is shown in Fig. 1. The palladium atom displays a square-planar geometry with ligands in *trans* disposition, confirming previous assignment from NMR data. Bond distances and angles around the metal centre are similar to other *trans*- PdCl_2L_2 complexes with monodentate phosphine ligands [11,13]. The phenyl groups bonded to the phosphorus atoms are nearly eclipsed. This is evidenced by

¹ These products are ethoxylated alkylphenols with different ethoxylation grades.

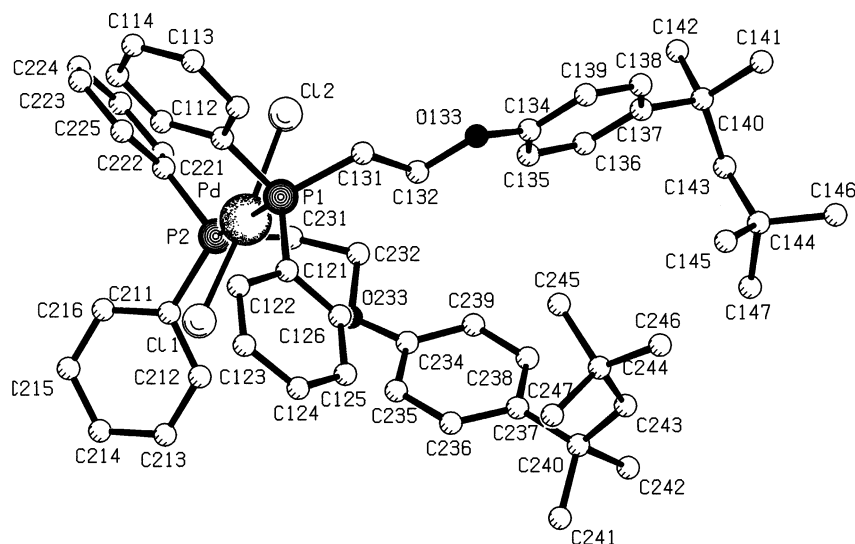
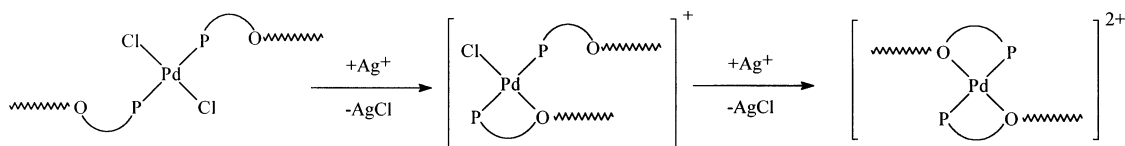


Fig. 1. View of the molecular structure of *trans*-PdCl₂(**1**)₂ together with the atomic numbering scheme.



Scheme 2.

the small value of the C131–P1–P2–C231 torsion angle (24.0(2)°) and it follows that the two *tert*-octylphenoxyethyl chains are close each other. This arrangement could be explained by the trend of the more hydrophobic parts of the molecule to be close together, although other factors should also be considered. Thus, the Cl2 atom is located in a position near the methylene groups bonded to the oxygen atoms. The partial electrophilic character of these hydrogen atoms is shown by their position in the ¹H-NMR spectrum (4.19 ppm) and the existence of a hydrogen bond between the Cl2 atom and the hydrogens of the methylene groups seems realistic². Similarly, the presence of another weak hydrogen bond between one oxygen atom and one phenyl group can be proposed³. In a previous paper [8b], we observed a particular molecular packing of a ruthenium complex with the ligand CH₃(OCH₂CH₂)₃PPhR (R = isopentyl) in such a way that the hydrophobic isopentyl groups were close together. In the crystal structure of *trans*-PdCl₂(**1**)₂, each *tert*-octyl group is close to a *tert*-octyl group of a

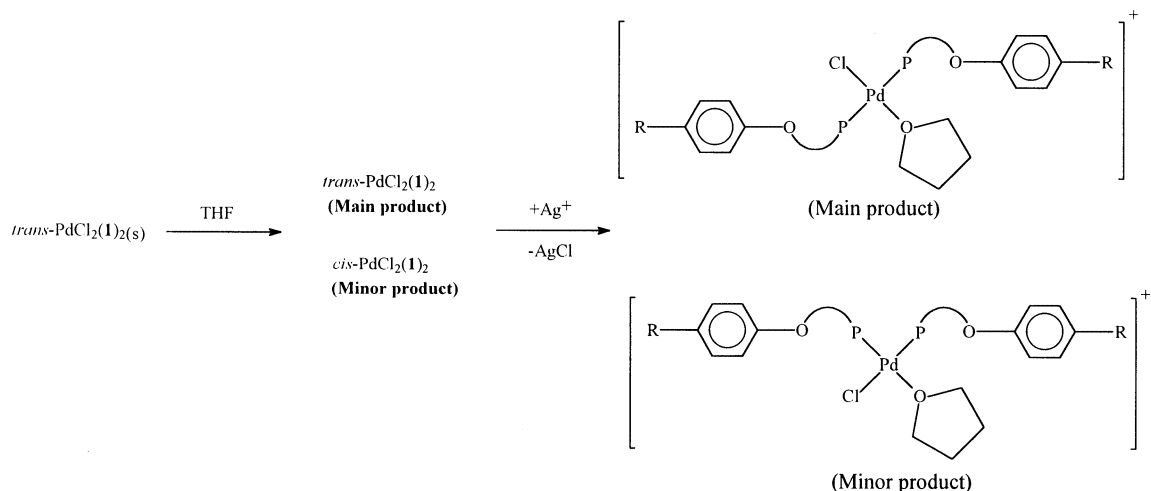
neighboring molecule, and the shortest Me–Me distances are similar to those found in the above ruthenium complex (C–C = 3.9–4.2 Å).

2.3. Reactivity of PdCl₂L₂ complexes toward AgBF₄

The results obtained in the above section are very similar to those previously reported for phosphinoether ligands like Ph₂PCH₂CH₂OCH₃ [11], which react with PdCl₂(COD) to form P-coordinated palladium complexes. Likewise, these previous studies have shown that the *trans*-PdCl₂(P ~ O)₂ complexes (P ~ O = P-coordinated phosphinoether ligand) can lead to chelated complexes [PdCl(P ∩ O)(P ~ O)]⁺ and [Pd(P ∩ O)₂]²⁺ (P ∩ O = chelated phosphinoether ligand) after abstraction of Cl[−] with Ag⁺. In order to find out if the reported palladium complexes display a similar behavior, their reaction with Ag⁺ was studied by ³¹P-NMR. After addition of one equivalent of Ag⁺, PdCl₂L₂ complexes (L = **2**, **3**, **5**, **6** and **7**) displayed a similar behavior, which is consistent with previous work with phosphinoethers. The main signal at 12.4–14.1 ppm of the *trans*-PdCl₂L₂ complex faded and two broad bands around 36 and 54 ppm appeared, which are respectively assigned to the phosphorus atoms of the monodentate and a 5-membered ring chelate ligands [11] (Scheme 2). After addition of another equivalent of Ag⁺, a main signal at 45–51 ppm was observed. This was assigned to the bis(chelate) complex (Scheme 2). Since ligands **8**

² C132–H and C232–H: 0.97 Å (hydrogen atoms placed in calculated positions). C132...Cl2: 3.478(5) Å, H(C132)...Cl2: 2.74 Å, C132–H...Cl2: 133°; C232...Cl2: 3.658(5) Å, H(C232)...Cl2: 2.94 Å, C232–H...Cl2: 131°.

³ C212–H: 0.93 Å (hydrogen atom placed in calculated position). C212...O233: 3.261(6) Å, H...O233: 2.46 Å, C212–H...O233: 144°.



Scheme 3.

and **9** are racemic mixtures, the same reaction with their PdCl_2L_2 complexes led to more complicated ^{31}P -NMR spectra. Nevertheless, after addition of two equivalents of Ag^+ , two main signals in the 40–41 ppm region were observed clearly. These are attributable to the two diastereoisomers of the $[\text{Pd}(\text{P}\cap\text{O})_2]^{2+}$ complexes.

As noted above, ligand **1** is substantially different from the other ligands and shows a particular behavior. Hence, although the ^{31}P -NMR of a tetrahydrofuran solution of $\text{PdCl}_2(\mathbf{1})_2$ is similar to those of the other $trans\text{-PdCl}_2\text{L}_2$ complexes⁴, after addition of one equivalent of Ag^+ , it evolved to a main signal at 12.6 ppm and two small signals at 26.3 and 30.3 ppm with the characteristic shape of an AB system ($J = 6.8$ Hz). After addition of a second equivalent of Ag^+ the spectrum changed to two signals at 23.9 and 34.6 ppm. Since the bidentate coordination of **1** is hindered by electronic and steric effects of the aryl group bonded to the oxygen atom, these facts can be explained by the replacement of a chloride ligand by a molecule of tetrahydrofuran (Scheme 3). The substitution of a Cl^- by a molecule of tetrahydrofuran led to a compound with two equivalent phosphorus atoms in the $trans$ isomer and non-equivalent phosphorus atoms in the cis isomer. Nevertheless, when two equivalents of Ag^+ are added in a less coordinant solvent like dichloromethane only a main signal at 48 ppm is observed, which is concordant with the formation of a bis(chelate) complex $[\text{Pd}(\text{P}\cap\text{O})_2]^{2+}$.

Ligand **4** is a mixture that contains a compound similar to **1**, with the phenolic oxygen as the only oxygen atom. However, this compound coexists with other molecules with short polyether chains which, as

ligands **2**, **3**, **5**, **6** and **7**, can chelate more easily. Consequently, after addition of Ag^+ to $\text{PdCl}_2(\mathbf{4})_2$ signals were observed in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum that were similar to those obtained with **1**, coexisting with peaks observed in the analogous reaction with **2**, **3**, **5**, **6** and **7**.

3. Experimental

3.1. General

All reactions were performed under nitrogen by standard Schlenk tube techniques. The NMR spectra were recorded by the Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona on a Bruker AC250 instrument. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvents for ^1H spectra, to solvent signals for ^{13}C spectra and to external phosphoric acid for ^{31}P spectra.

Compounds **1–9** were prepared by published procedures [8b]. Microanalyses were performed in Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

3.2. Synthesis of $trans\text{-PdCl}_2(\mathbf{1})_2$

A solution of **1** (0.580 g, 1.4 mmol) in dichloromethane (10 ml) was added to a solution of $\text{PdCl}_2(\text{COD})$ (0.200 g, 0.7 mmol) in dichloromethane (10 ml) at room temperature. The orange solution was stirred for 2 h and evaporated to dryness subsequently. The solid residue was recrystallized from acetone–ethanol at -18°C . The yellow crystals were collected, washed in ethanol and dried in vacuo.

⁴ A main signal at 13.0 ppm assigned to $trans\text{-PdCl}_2(\mathbf{1})_2$ is observed with only another small signal at 26.6 ppm assigned to the $cis\text{-PdCl}_2(\mathbf{1})_2$ complex.

Yield of *trans*-PdCl₂(1)₂, 56%. Anal. Calc. for C₅₆H₇₀Cl₂O₂P₂Pd: C, 66.30; H, 6.96. Found: C, 66.21; H, 6.90. ³¹P{¹H}-NMR (CDCl₃): 13.0 (s, *trans*-PdCl₂(1)₂), 26.6 (s, *cis*-PdCl₂(1)₂). ¹H-NMR (CDCl₃; except phenyl resonances): 0.65 (s, (CH₃)₃), 1.26 (s, (CH₃)₂), 1.62 (s, CH₂, *tert*-octyl), 2.95 (m, CH₂-P), 4.19 (m, CH₂O). ¹³C{¹H}-NMR (CDCl₃; except phenyl resonances): 26.5 (t, *J* = 14.4 Hz, CH₂P), 31.5 (s, CH₃), 31.7 (s, CH₃), 32.2 (s, CMe₃), 37.8 (s, CMe₂), 56.8 (s, CH₂, *tert*-octyl), 63.3 (b, CH₂O).

3.3. Reactivity of 2–9 with PdCl₂(COD)

In a representative procedure, a solution of ligand (1.4 mmol) in dichloromethane (10 ml) was added to a solution of PdCl₂(COD) (0.200 g, 0.7 mmol) in dichloromethane (10 ml) at room temperature. The orange solution was stirred for 2 h and evaporated to dryness yielding an orange oil. The ³¹P-NMR was measured with a portion of this final oil.

Significant ³¹P{¹H} (CDCl₃) data:

- 2: {12.5 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 24.8 (s, *cis*-PdCl₂(P ~ O)₂)}
- 3: {12.7 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 24.8 (s, *cis*-PdCl₂(P ~ O)₂)}
- 4: {13.8 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 25.0–25.2 (m, *cis*-PdCl₂(P ~ O)₂)}
- 5: {12.6 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 25.0–25.3 (m, *cis*-PdCl₂(P ~ O)₂)}
- 6: {12.5 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 24.8–26.3 (m, *cis*-PdCl₂(P ~ O)₂)}
- 7: {12.6 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 24.8 (s, *cis*-PdCl₂(P ~ O)₂)}
- 8: {10.0 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 18.9 (s, *cis*-PdCl₂(P ~ O)₂), 19.2 (s, *cis*-PdCl₂(P ~ O)₂)}
- 9: {9.3 (s, main signal, *trans*-PdCl₂(P ~ O)₂), 17.6 (s, *cis*-PdCl₂(P ~ O)₂), 18.1 (s, *cis*-PdCl₂(P ~ O)₂)}

3.4. X-ray structure determination of *trans*-PdCl₂(1)₂

3.4.1. Crystal data

Suitable single crystals of the titled complex were obtained by recrystallization in acetone–ethanol. C₅₆H₇₀Cl₂O₂P₂Pd, *M_r* = 1014.36. Triclinic; *a* = 10.020(3) Å, *b* = 16.180(9) Å, *c* = 17.015(6) Å, α = 77.39(4)°, β = 78.39(3)°, γ = 82.66(4)°, *V* = 2626.8(19) Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), space group *P* $\bar{1}$ (no. 2), *Z* = 2, *D_{calc}* = 1.282 g cm^{−3}. Yellow, air-stable crystals, μ (Mo–Kα) = 0.56 mm^{−1}.

3.4.2. Data collection and processing

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a ω–2θ scan, ω scan width = 0.80 + 0.35 tan θ, ω scan

speed 1.3–5.5°. Reflection ranges for the data collection were 1 < θ < 25°, −11 ≤ *h* ≤ 11, −18 ≤ *k* ≤ 19, 0 ≤ *l* ≤ 20. Lp and empirical absorption corrections [14] were applied, *T_{min}* = 0.922, *T_{max}* = 1.000. Unique reflections, 9244; 7483 with *I* > 2σ(*I*).

3.4.3. Structure solution and refinement

The structure was solved by direct methods (SHELXS-86) [15] and refined by full-matrix least-squares procedures on *F*² for all reflections (SHELXL-97) [16]. One *tert*-octyl group showed structural disorder and it was split. Final site occupation factors were 0.52/0.48. Disordered carbons were refined isotropically and geometrical restraints were applied. The rest of non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with isotropic displacement factors 1.5 (methyl H) or 1.2 (the rest) times the *U_{eq}* values of corresponding carbons. A total of 250 parameters were refined. The final weighting scheme was *w* = 1/[σ²(*F_o*²) + (0.0845*P*)² + 0.1521*P*] where *P* = [max(*F_o*², 0) + 2*F_c*²]/3. Final *R*(*F*) and *R_w*(*F*²) values were 0.040 and 0.117 for reflections with *I* > 2σ(*I*).

3.5. Reactivity of PdCl₂L₂ (L = 1–9) complexes toward AgBF₄

In a representative procedure, two aliquot parts of a solution (0.5 ml) of the complex PdCl₂L₂ in tetrahydrofuran (0.02 M) were placed in two NMR tubes. Next, one equivalent of a AgBF₄ solution in tetrahydrofuran (0.43 M) was added to the first tube and two equivalents to the second tube. The solid silver chloride was allowed to sediment and the ³¹P{¹H}-NMR of the tetrahydrofuran solutions were recorded with an insert tube of acetone-*d*₆.

Significant ³¹P{¹H}-NMR data:

1. After adding one equivalent of Ag⁺:
 - 1: {12.6 (s); *trans*-PdCl(thf)(P ~ O)₂}, {26.3 (d, ²*J_{PP}* = 6.8 Hz), 30.3 (d, ²*J_{PP}* = 6.8 Hz); *cis*-PdCl(thf)(P ~ O)₂}.
 - 1 (spectrum recorded in CH₂Cl₂ with an insert of acetone-*d*₆): {33.3 (b, P ~ O), 44.2 (b, P ⊂ O)}
 - 2: {36.0 (b, P ~ O), 54.0 (b, P ⊂ O)}
 - 3: {36.0 (b, P ~ O), 54.3 (b, P ⊂ O)}
 - 4: {12.6 (s, P ~ O), 35.2 (b, P ~ O), 54.7 (b, P ⊂ O)}
 - 5: {36.0 (b, P ~ O), 51.0 (b, P ⊂ O)}
 - 6: {36.5 (b, P ~ O), 54.5 (b, P ⊂ O)}
 - 7: {37.5 (b, P ~ O), 55.0 (b, P ⊂ O)}
2. After adding two equivalents of Ag⁺:
 - 1: {23.9 (s, *trans*-Pd(thf)₂(P ~ O)₂), 34.6 (b, *cis*-Pd(thf)₂(P ~ O)₂)}
 - 1 (spectrum recorded in CH₂Cl₂ with an insert of acetone-*d*₆): {48.0 (s, P ⊂ O)}
 - 2: {46.5 (b, P ⊂ O)}
 - 3: {46.6 (b, P ⊂ O)}

- 4: {18–22 (m, P ~ O), 33.0 (s, P ~ O), 55.1 (s, P ~ O)}
 5: {35.9 (s, P ~ O, minor signal), 51.6 (b, P ~ O, main signal)}
 6: {36.0 (s, P ~ O, minor signal), 51.4 (b, P ~ O, main signal)}
 7: {50.8 (s, P ~ O)}
 8: {40.9 (s, P ~ O), 41.4 (s, P ~ O)}
 9: {40.2 (s, P ~ O), 40.3 (s, P ~ O)}

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151792 for compound *trans*-PdCl₂(1)₂. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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