Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2409–2423
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and coordination properties of palladium(II) and platinum(II) complexes with phosphonated triphenylphosphine derivatives

Zbyněk Rohlík [a], Petr Holzhauser [a,b], Jan Kotek [a], Jakub Rudovský [a], Ivan Němec [a], Petr Hermann [a,*], Ivan Lukeš [a]

[a] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic
[b] Department of Inorganic Technology, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

Received 9 November 2005; received in revised form 23 December 2005; accepted 11 January 2006
Available online 7 March 2006

Abstract

Two triphenylphosphine derivatives, diethyl [4-(diphenylphosphanyl)benzyl]phosphonate (**3a**) and tetraethyl {[5-(diphenylphosphanyl)-1,3-phenylene]dimethylene}bis(phosphonate) (**3b**), and also the corresponding free acids **4a** and **4b** were prepared. These ligands were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. A full set of their Pd(II) and Pt(II) complexes of the general formula $[MCl_2L_2]$ and one dinuclear complex *trans*-$[Pd_2Cl_4(\mathbf{3a})_2]$ were synthesized and their isomerization behaviour in solution was studied. The complexes were characterized by ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy, mass spectrometry and far-IR spectroscopy. The X-ray structures of all complexes with **3a** or **3b** have usual slightly distorted square-planar geometry on the metal ion. Salts of phosphonic acids **4a** and **4b** and their complexes are freely soluble in aqueous solution; therefore, they can be potentially useful in aqueous or biphasic catalysis.

Keywords: Phosphonato phosphines; Water soluble phosphines; Phosphonate complexes; Palladium complexes; Platinum complexes; Crystal structure determination; Isomerism

1. Introduction

Transition metal-phosphine complexes are of great importance for both industrial- and laboratory-scale catalytic applications. Ambitions to use various "field-proven" homogeneous catalysts under aqueous and biphasic conditions made for the synthesis of a vast amount of phosphines modified by hydrophilic groups such as ammonium and phosphonium (cationic), sulfonate, phosphonate and carboxylate (anionic) or alcohol and polyether chain (neutral) [1]. Phosphines modified by phosphonate moiety [2] have been attracting attention as alternatives to well-established sulfonates [1]; several examples of their use in biphasic catalysis have been mentioned in literature [3–17] (e.g., Pd-catalysed electrochemical reduction of CO_2 [3], Rh-catalysed carbon–carbon double bond hydrogenation or hydroformylation [4,5], Pd-catalysed benzyl halide carbonylation [6] and Suzuki coupling [7]). A great advantage (compared with other hydrophilic moieties) is the possibility to bind the phosphonated ligand to an inert oxide surface (e.g., Al_2O_3) [8], onto activated carbon surface [9] or into a layered framework, e.g., zirconium phosphonate [10,12] or zirconium phosphite/phosphonate hybrid material [13]. Such supported catalysts have been successfully tested in Rh-catalysed alkene hydroformylation [12,14], Rh-catalysed methanol carbonylation [9,15], Ru-catalysed asymmetric β-keto ester hydrogenation [4,11] or Heck reaction [13]. Several tests were also performed in organic solvents under homogeneous conditions (e.g., Pt/Sn-catalysed alkene hydroformylation [11], Rh-catalysed methanol carbonylation [16] and Rh-catalysed styrene hydroformylation [17]).

Here we present the synthesis of triphenylphosphine-based ligands bearing one or two diethyl phosphonomethyl

* Corresponding author. Tel.: +420 22195 1263; fax: +420 22195 1253.
E-mail address: petrh@natur.cuni.cz (P. Hermann).

0022-328X/$ - see front matter © 2006 Elseiver B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.024

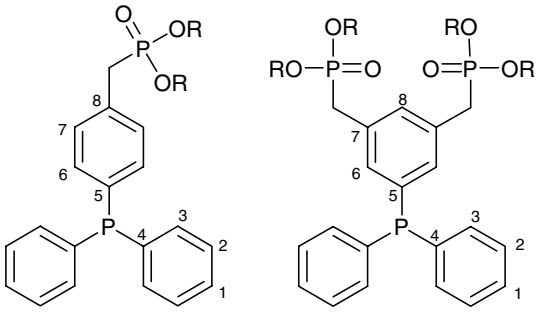
groups (**3a** and **3b**) and corresponding acids (**4a** and **4b**) (Fig. 1) as well as a study of their Pd(II) and Pt(II) complexes. The ligand design promises similar coordination behaviour and catalytic activity as is known for triphenylphosphine, good solubility in water and flexible strong attachment to a solid surface. The *ortho* and *meta* isomers of **3a** and **4a** (and their disodium salts) were already reported by Liek et al. [7] having been used as catalysts in Pd-catalysed Suzuki coupling under biphasic conditions with satisfactory results. Later, also the *para* isomer has been mentioned [14] in a set of phosphanyl-phosphonates (including **4a** and its disodium salt) and experiments on Rh-catalyzed hydroformylation were performed, but no details on characterization of the complexes were mentioned and no attention to Pd(II) and Pt(II) chemistry was paid. To our knowledge, ligands **3b** and **4b** have not been reported yet.

2. Results and discussion

2.1. Ligands

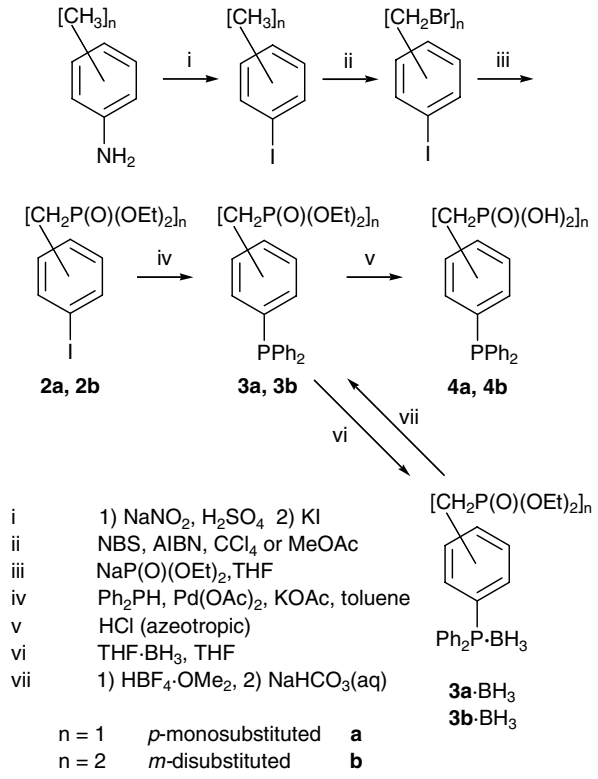
2.1.1. Synthesis

Ligands **3a**, **3b** and **4a**, **4b** were synthesized according to Scheme 1. For the synthesis of iodoaryl phosphonates, standard methods of organic and organophosphorus synthesis were used (Sandmeyer reaction, radical bromination and Michaelis–Becker reaction [18]). The last reaction required at least two-fold molar excess of $NaP(O)(OEt)_2$ for complete substitution; the residual reagent was then removed by extraction with 2% (w/w) aqueous NaOH solution. Out of a variety of reactions introducing the phosphanyl group into the molecule [18] we chose a mild Pd-catalyzed P–C cross-coupling reaction employing the reaction conditions similar to those already used [7,19]. In this reaction diphenylphosphine is used; we have summarized the synthetic methods for its preparation [20] and proposed a simplified procedure, in which we reduced the volume of solvents, avoided unnecessary drying and deoxy-



	R
3a, 3b	Et
4a, 4b	H

Fig. 1. Structure of **3a**, **3b**, **4a** and **4b**.



Scheme 1. Synthesis of the ligands **3a**, **3b**, **4a** and **4b**.

genation procedures and minimized the number of extraction and washing steps [21]. For details, see Section 4.

After several unsuccessful experiments with bromoaryl derivatives as starting materials we used more reactive aryl iodides, which were treated with diphenylphosphine in the presence of 0.2 mol% of $Pd(OAc)_2$ as catalyst and anhydrous KOAc as base. Under the reaction conditions used (toluene, 70–90 °C, 12–36 h), the ^{31}P NMR signal of Ph_2PH disappeared and a new signal assigned to the desired product appeared. A small excess (2 mol%) of Ph_2PH was used to ensure total conversion.

After work-up of the reaction mixture, compounds **3a** and **3b** were obtained as yellowish oils well soluble in organic solvents and in strongly acidic aqueous solutions. Purity of the samples varied between 93% and 97% (^{31}P NMR spectroscopy), which was acceptable for most purposes. In order to prepare samples of higher purity and also to enable the recovery of the ligands from partially oxidized samples, the standard borane protection method was employed [23]. The synthesis of borane adducts of **3a** and **3b** was performed by the reaction with excess of commercial $THF \cdot BH_3$ solution and standard work-up of the reaction mixture [24]. The **3a** · BH_3 was purified by column chromatography and then obtained as colourless crystalline powder upon recrystallization from THF/hexanes (purity 98+% ^{31}P NMR). We failed to crystallize **3b** · BH_3 before as well as after chromatographic purification; it was obtained with purity 96% (^{31}P NMR).

The adducts were deprotected after the purification. The use of secondary amines as the deprotection agent was not

suitable for our purpose because of possible interaction with the phosphonate group and, also, a rather inconvenient separation of the amine-borane adduct from the deprotected ligand (filtration through alumina column [24] or vacuum sublimation [7]). Both general methods reported in literature (deprotection with a mixture of 4 Å molecular sieve, aliphatic alcohol and cyclic ether [25] and deprotection using $HBF_4 \cdot OMe_2$ in dichloromethane [26]) were successful and we chose the later one for its simplicity. The ligands were obtained as colourless turbid oils of purity corresponding to the purity of the borane adducts.

For the preparation of free acids **4a** and **4b** hydrolysis in 20% aqueous HCl was the method of choice. This concentration of the acid was sufficient for dissolution of the ester ligands. Compounds **4a** and **4b** were obtained as white solid foams soluble in methanol, ethanol, strongly acidic and alkaline aqueous solutions, but almost insoluble in water in the pH range 2–6. The salts of **4a** and **4b** were not isolated and their solubilities in water were not quantified, but salts of the **4b** are apparently more soluble.

2.1.2. NMR spectroscopy

^1H and ^{13}C NMR spectra of all ligands and their borane adducts are in agreement with expectations. In ^{31}P NMR the chemical shift of the diethoxyphosphoryl group in both ligands is typically around 26 ppm, the chemical shift of the phosphine functionality is around −6 ppm similarly to triphenylphosphine. In the case of the borane adducts, the phosphine signal is shifted to ca. 20 ppm and broadened significantly, which makes impossible to determine the $^1J_{PB}$ coupling constant.

The ^{31}P NMR of **4a** and **4b** in water is highly pH-dependent due to acid–base properties of both phosphorus-containing moieties. The values of δ_P in methanol-d_4, conc. aqueous HCl and NaOH solutions are listed in Table 1.

2.2. Pt(II) and Pd(II) complexes

2.2.1. Synthesis

Synthesis of Pd(II) and Pt(II) complexes of ester ligands **3a** and **3b** was straightforward. It was performed by mixing the dichloromethane solutions of the ligand and of the metal precursor ([$PdCl_2$(cod)] or [$PtCl_2$(cod)]; cod = cycloocta-1,5-diene) in the ligand-to-metal molar ratio 2:1. The isolated complexes have the stoichiometry [MCl_2L_2] with *trans* arrangement for Pd(II) complexes and *cis* for their Pt(II) analogues (vide infra). A small amount of dinuclear palladium(II) complex *trans*-[Pd_2Cl_4(**3a**)$_2$] · $2CHCl_3$ was isolated by work-up of the mother liquor after crystallization of *trans*-[$PdCl_2$(**3a**)$_2$] · $2CHCl_3$; it originates probably in an inaccuracy of the ligand-to-metal ratio in the starting reaction mixture (Scheme 2).

Table 1
$^{31}P\{H\}$ NMR chemical shifts of **4a** and **4b** (ppm) in various solvents

Solvent	**4a**		**4b**	
	$\delta_{P(V)}$	$\delta_{P(III)}$	$\delta_{P(V)}$	$\delta_{P(III)}$
MeOD	26.8	−3.4	25.7	−4.0
32% HCl	28.5	+4.7[a]	28.5	+4.6[b]
1 M NaOH	20.3	−7.6	20.5	−6.0

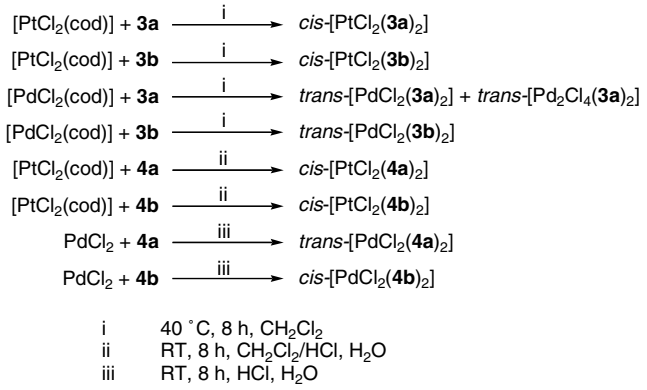
[a] In non-decoupled ^{31}P NMR doublet, $^1J_{PH} = 523$ Hz (phosphonium salt).
[b] In non-decoupled ^{31}P NMR doublet, $^1J_{PH} = 505$ Hz (phosphonium salt).

Various synthetic methods were reported for preparation of complexes with polar acid-modified phosphines. Experimental conditions depend on the solubility of the ligand and the metal-containing compound [1,6,27–31]. Reactions in water are further limited by the pH value because of decomposition and deposition of the precious metal in alkaline solutions. Synthesis of Pd(II) complexes of **4a** and **4b** by a simple biphasic reaction between ligand solution in 20% aqueous HCl and [$PdCl_2$(cod)] solution in CH_2Cl_2 (ligand-to-metal ratio = 2:1) failed. The required complexes were formed upon treatment of solid $PdCl_2$ with ligand solution in ethanol, but their purity was not satisfactory. Finally, the reaction of ligand solution in 20% aqueous HCl with freshly prepared slurry of $PdCl_2$ in the same solvent was successful (Scheme 2). The isolated yellow complexes are soluble in common organic solvents but only slightly soluble in water (pH 6). The low complex solubility is probably caused by polymerization through hydrogen bond network in the solid state (such polymeric structure is proposed for a Pd(II) complex of a similar phosphanyl-phosphonate [13]). The complexes are well soluble in aqueous alkaline solutions (pH > 7).

In the case of Pt(II) complexes, a biphasic reaction of the ligand solution in 20% aqueous HCl with a dichloromethane solution of [$PtCl_2$(cod)] (ligand-to-metal ratio 2:1) was successful. The products were isolated as white powders, hardly soluble in water and common organic solvents. The solubility in aqueous alkaline solutions is similar to the Pd(II) complexes (vide supra).

2.2.2. NMR spectroscopy

In the ^{31}P NMR spectra of the Pd(II) complexes, the phosphonate group chemical shift remains almost the same (around 24 ppm), but the phosphine functionality is shifted significantly. In ^{31}P NMR spectra of [$PdCl_2$(**3a**)$_2$] in $CDCl_3$



Scheme 2. Synthesis of Pd(II) and Pt(II) complexes of **3a**, **3b**, **4a** and **4b**.

solution, besides the two major signals assigned to phosphonate and phosphine functionalities, a couple of minor signals with 1:1 intensity appeared. The signals did not belong to the oxidized ligand, because after addition of **3a**-oxide (prepared by oxidation of **3a** with 30% aqueous H_2O_2 in ethanol) to the sample, new separate peaks appeared. As Pd(II) phosphine complexes are known to produce an equilibrium mixture of *cis*/*trans* isomers upon dissolution [32], we expected the same behaviour in our case. In order to support this hypothesis and to distinguish and assign the signals of both isomers, we used the linear correlation of the coordination chemical shift with the free phosphine chemical shift (Eq. (1)) [33].

$$\Delta\delta_P = \delta_P(\text{coord.}) - \delta_P(\text{free}) = A \times \delta_P(\text{free}) + B \quad (1)$$

Constants A and B have been estimated for a wide range of metal-phosphine complexes; their values are characteristic of the metal ion and the complex stoichiometry. Moreover, the constants differ significantly for various isomers, which allows to use the correlation for assignment of the isomer signals. The relevant coefficients taken from Ref. [33a] are listed in Table 2 (For the calculations, the change in the ^{31}P chemical shift convention in the 1970s must be taken into account, which makes necessary to change the sign of B extracted from the original articles [33a]; this correction enables to use recent values of chemical shifts.).

On the basis of Eq. (1) we found out that the set of minor signals belongs to *cis* isomer (see Table 3). In addition, we measured ^{31}P NMR spectra of the same complex in toluene, where only two signals were present with chemical shift corresponding to the *trans* isomer, and in methanol, where four signals were found corresponding to a mixture of both isomers (Fig. 2), with higher abundance of *cis* isomer compared with $CDCl_3$ solution. This is in accord with the dependence of the *cis*/*trans* isomer ratio on the solvent polarity reported for various Pd(II) phosphine complexes [32]. Similar behaviour was observed for the complex $[PdCl_2(\mathbf{3b})_2]$ as well. ^{31}P NMR of $[PdCl_2(\mathbf{4a})_2]$ and $[PdCl_2(\mathbf{4b})_2]$ dissolved in slightly alkaline aqueous solution (pH 9) contained only the signals corresponding to *cis* isomer (Table 4). This preference of *cis* isomer formation also corresponds well with the above-mentioned overall trend in the isomerization behaviour of the ester ligand complexes.

In the case of platinum(II) complexes, the chemical shift of the phosphonate group was similar to the value observed for uncoordinated ligand (about 25 ppm for **3a** and **3b** complexes in $CDCl_3$ and 18 ppm for **4a** and **4b** complexes in slightly alkaline aqueous media) and no interaction of phosphoryl group with the metal ion was observed (no $^2J_{PtP}$ was detected). The coordination of the phosphine to the metal ion caused a large shift to ca. 14 ppm in all cases. The values of $^1J_{PtP}$ ca. 3600 Hz were found, which corresponds to the phosphine opposite to chlorine [34], i.e., with *cis* arrangement of the phosphine ligands. The value corresponding to the *trans* isomer should be much lower, ca. 2000–2700 Hz [34]. Only *cis* isomers of all the complexes were present in solutions in various solvents (toluene, $CDCl_3$, and methanol for **3a** and **3b** complexes, alkaline aqueous solution for complexes of **4a** and **4b**) (Tables 3 and 4). In the case of $CDCl_3$ solution of *cis*-$[PtCl_2(\mathbf{3a})_2]$, one of the Pt–P satellites overlapped with the signal of phosphonate group; its presence was revealed either by using methanol as solvent or by the addition of the tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate) europium(III) complex (EuFOD NMR shift agent).

In order to obtain spectral data of *trans* isomers also for Pt(II) complexes, we carried out a simple photochemical isomerization experiment as described by Mastin and Haake [35]. The **3a** and **3b** complexes dissolved in $CDCl_3$ or **4a** and **4b** complexes in $NaOH/D_2O$ were irradiated with an 8 W UV lamp ($\lambda = 366$ nm) at room temperature for 5 h. Before and after the irradiation, $^{31}P\ \{^1H\}$ and ^{195}Pt NMR spectra were measured. In the case of ester complexes, the isomerization occurred indeed, although only to a small extent (ca. 20%, ^{195}Pt NMR spectra). In the ^{195}Pt NMR spectra (Fig. 3b and d), the new isomers manifested themselves by a triplet with $^1J_{PtP}$ characteristic of *trans* arrangement (~2640 Hz, vide supra); in $^{31}P\ \{^1H\}$ NMR spectra (Fig. 3a and c), another set of signals corresponding to the *trans* isomer appeared (Table 3), the signals of coordinated phosphine having ^{195}Pt satellites with the same $^1J_{PtP}$ value as that found in ^{195}Pt NMR spectra. In the spectra of acid ligand complexes, no signals assignable to the isomerization product were found after irradiation. This is in accord with the observation made in the original paper that the photochemical transition state is stabilized only in non-polar solvents [35]. The $^{31}P\ \{^1H\}$ chemical shifts of the prepared platinum-containing complexes were correlated using a relationship analogous to Eq. (1) with appropriate coefficients A and B obtained from literature data (Table 2) [33a]. The observed values are in good agreement with the predicted values (Tables 3 and 4).

Table 2
Coefficients A and B in Eq. (1) for *cis* and *trans* isomers of Pd(II) and Pt(II) complexes of the formula $[MCl_2L_2]$ [33]

Complex		A	B
$[PdCl_2L_2]$	*cis*	-0.315 ± 0.033	-38.11 ± 0.86
	trans	-0.359 ± 0.023	-28.01 ± 0.61
$[PtCl_2L_2]$	*cis*	-0.326 ± 0.070	-18.83 ± 1.82
	trans	-0.481 ± 0.023	-21.41 ± 0.55

2.2.3. IR spectroscopy

Kinetic inertness of Pt(II) complexes usually allows to isolate both *cis* and *trans* isomers in the solid state from the complex solution. On the contrary, palladium(II) complexes are less inert and undergo rapid isomerization upon dissolution. Because of thermodynamic and kinetic effects, the *trans* isomer is generally preferred when a Pd(II) complex is being isolated in the solid state from its solution, even when a pure *cis* isomer solution is used [36]. To determine the stereochemistry of our complexes in the solid state, we employed far-IR spectroscopy. Due to a differ-

Table 3
Phosphine chemical shifts δ_P of the free ligands **3a** and **3b** and their Pd(II) and Pt(II) complexes

Parameter	Solvent	**3a**	**3b**	$[PdCl_2(\mathbf{3a})_2]$		$[PdCl_2(\mathbf{3b})_2]$		$[PtCl_2(\mathbf{3a})_2]$		$[PtCl_2(\mathbf{3b})_2]$	
				cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
δ_P	$CDCl_3$	−5.4	−5.4	32.9	21.2	33.3	24.2	13.8	18.1[a]	14.4	20.7[a]
	Toluene	−6.1	−5.4	–[b]	23.5	–[b]	24.3	14.7	–[b]	15.0	–[b]
	MeOH	−5.8	−5.0	33.9	27.2	34.2	27.2	14.2	–[b]	14.8	–[b]
$\Delta\delta_P$(exp)	$CDCl_3$	–	–	38.3	26.6	38.7	29.6	19.2	23.5	19.8	26.1
	Toluene	–	–	–[b]	29.6	–[b]	29.7	20.8	–[b]	20.4	–[b]
	MeOH	–	–	39.7	33.0	39.2	32.2	20.0	–[b]	19.8	–[b]
$\Delta\delta_P$(calc)	$CDCl_3$	–	–	39.8	29.9	39.8	29.9	20.6	24.0	20.6	24.0
	Toluene	–	–	40.0	30.2	39.8	29.9	20.8	24.3	20.6	24.0
	MeOH	–	–	39.9	30.1	39.7	29.8	20.7	24.2	20.5	23.8

Comparison of experimental ($\Delta\delta_P$(exp)) and calculated ($\Delta\delta_P$(calc)) coordination chemical shifts for their *cis* and *trans* isomers in $CDCl_3$, toluene and methanol.

[a] After irradiation of the *cis* isomer, see text.

[b] Not observed or calculated.

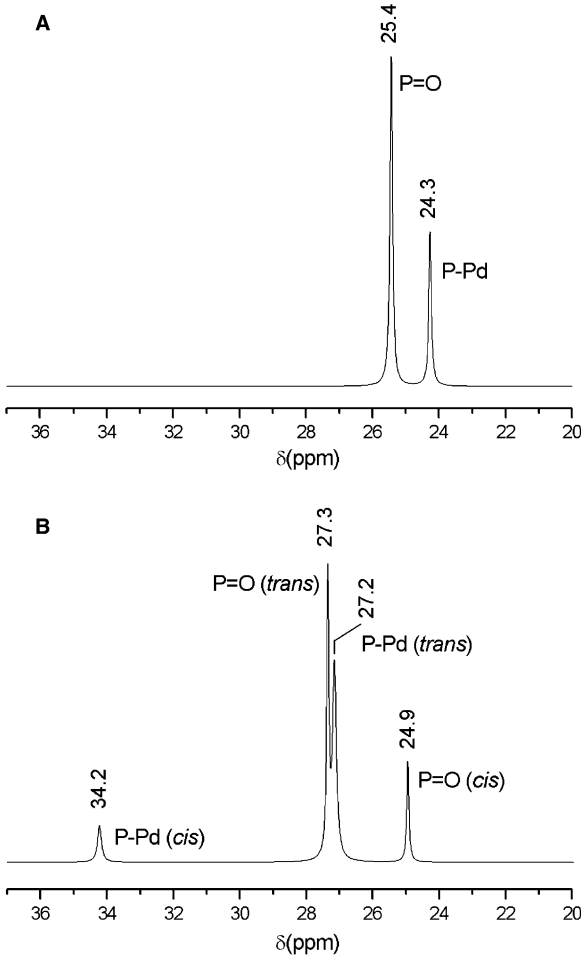


Fig. 2. $^{31}P\{^1H\}$ NMR spectra of $[PdCl_2(\mathbf{3a})_2]$ in toluene (A) and methanol (B) showing solvent-dependent *cis*/*trans* equilibrium.

ence in coordination polyhedron symmetry, the Pd–Cl and Pt–Cl stretching vibrations (at 250–350 cm^{-1} in similar complexes [37]) exhibit two bands in *cis* and only one band in *trans* complexes. In the case of dinuclear complexes, the spectrum is more complicated due to the difference between $Pd–Cl_{terminal}$ and $Pd–Cl_{bridging}$ vibrations [38]. For comparison, we measured both ester ligands and acid ligands complexes, configurations of the former being independently determined by X-ray single crystal analysis (vide infra). Data are summarized in Table 5. All four platinum(II) complexes showed *cis* arrangement, as was expected from the NMR spectroscopy of their solutions. Three palladium(II) complexes were found to be *trans* and $[PdCl_2(\mathbf{4b})_2]$ was found to be *cis* in the solid state. The *cis* stereochemistry is probably a result of intramolecular interaction via hydrogen bonds of phosphonic acid groups. Unfortunately, the distinction between intra- and intermolecular hydrogen bonding investigated by infrared spectroscopy may not be straightforward; this hypothesis could be therefore confirmed only by crystallography. However, our attempts to grow a single crystal of this complex were unsuccessful.

2.2.4. X-ray crystallography

The stereochemistry of **3a** and **3b** complex species was confirmed by X-ray crystallography. Table 6 shows selected interatomic distances and angles. Relevant experimental parameters are listed in Table 7.

The two phosphine ligands in both mononuclear Pd(II) complexes have a mutual *trans* arrangement (Figs. 4 and 5). Both complexes are centrosymmetric with palladium atom in the centre of symmetry. The coordination sphere is square-planar, with small distortion of bond angles P–Pd–Cl (84.6° and 94.4° for *trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$ and 87.5° and 92.5° for *trans*-$[PdCl_2(\mathbf{3b})_2]\cdot 2H_2O$). The coordination bond lengths are in the expected range as observed for similar complexes [39] (Pd–Cl 2.38 and Pd–P 2.33 Å for *trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$ and Pd–Cl 2.30 Å and Pd–P 2.33 Å for *trans*-$[PdCl_2(\mathbf{3b})_2]\cdot 2H_2O$).

Contrary to the palladium(II) compounds, both platinum(II) complexes have a slightly distorted square-planar coordination sphere with two phosphine ligands in mutually *cis* positions (Figs. 6 and 7). The bond angles P–Pt–P are 96.3° for *cis*-$[PtCl_2(\mathbf{3a})_2]\cdot 0.5CHCl_3$ and 98.8° for *cis*-$[PtCl_2(\mathbf{3b})_2]\cdot H_2O\cdot PhMe$ thus showing larger distortion

Table 4
Phosphine chemical shifts δ_P of the free ligands **4a** and **4b** and their Pd(II) and Pt(II) complexes

Parameter	Solvent	**4a**	**4b**	$[PdCl_2(\mathbf{4a})_2]$		$[PdCl_2(\mathbf{4b})_2]$		$[PtCl_2(\mathbf{4a})_2]$		$[PtCl_2(\mathbf{4b})_2]$	
				cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
δ_P	NaOH solution in D_2O (pH 9)	−7.7	−6.7	34.0	–[a]	35.2	–[a]	11.2	–[a]	11.7	–[a]
$\Delta\delta_P$(exp)		–	–	41.7	–[a]	41.9	–[a]	18.9	–[a]	18.4	–[a]
$\Delta\delta_P$(calc)		–	–	40.5	30.8	40.2	30.4	21.3	25.1	21.0	24.6

Comparison of experimental ($\Delta\delta_P$(exp)) and calculated ($\Delta\delta_P$(calc)) coordination chemical shifts for their *cis* and *trans* isomers in alkaline D_2O solution.
[a] Not observed or calculated.

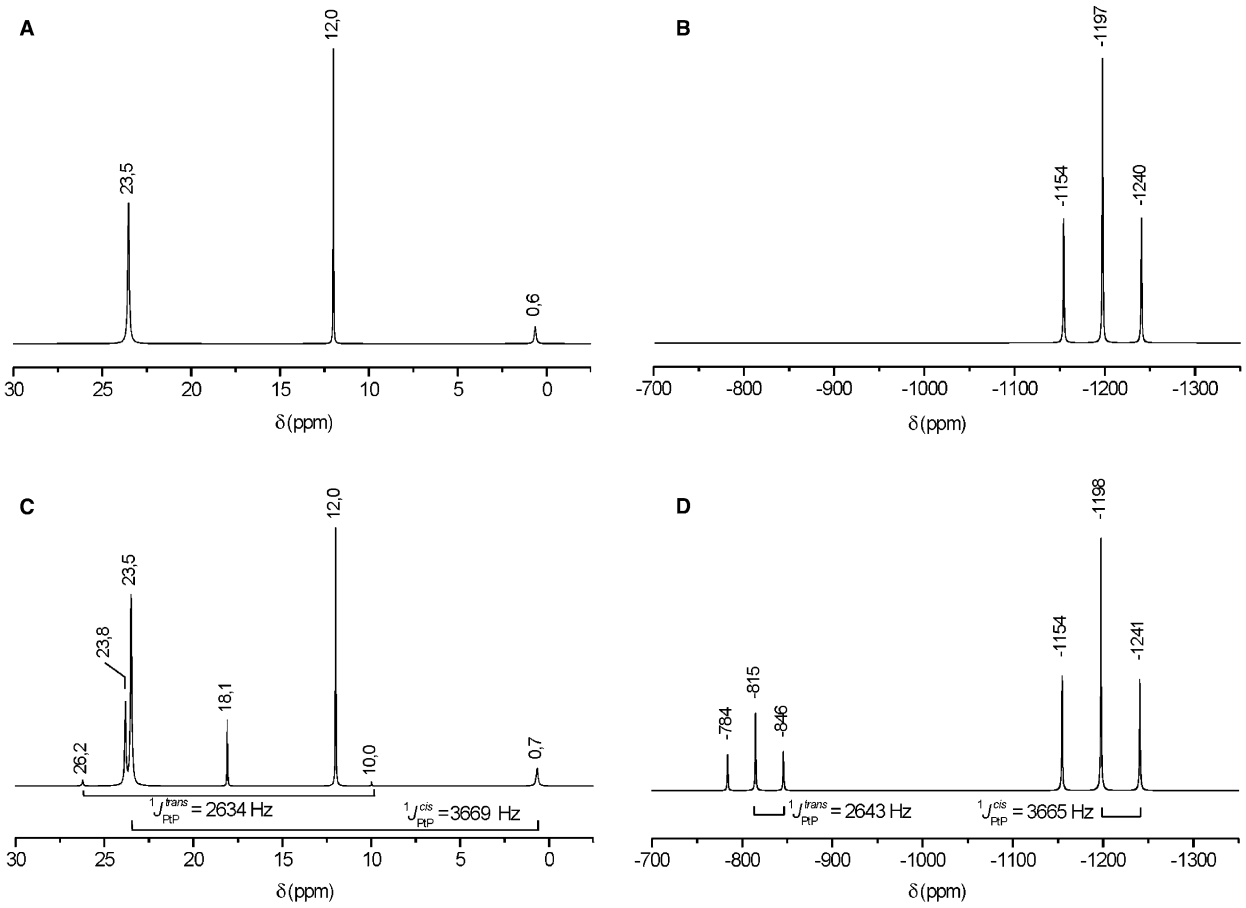


Fig. 3. Photochemical isomerization of *cis*-$[PtCl_2(\mathbf{3a})_2]$: ^{31}P NMR before (A) and after (C) and ^{195}Pt NMR before (B) and after (D) UV-irradiation.

of the regular square-planar geometry in the case of more sterically demanding ligand **3b**. The lengths of coordination bonds are in the expected range for this type of compounds [39] (Pt–Cl 2.33 and 2.36 Å, Pt–P 2.25 and 2.27 Å for *cis*-$[PdCl_2(\mathbf{3a})_2]\cdot 0.5CHCl_3$ and Pt–Cl 2.35 and 2.34 Å, Pt–P 2.26 and 2.27 Å for *cis*-$[PdCl_2(\mathbf{3b})_2]\cdot H_2O\cdot$ PhMe).

In mother liquor after crystallization of *trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$, several red crystals appeared after standing in refrigerator for several months. The X-ray crystallographic study revealed the dinuclear complex of the formula *trans*-$[Pd_2Cl_4(\mathbf{3a})_2]\cdot 2CHCl_3$ (Fig. 8). The molecule has a centre of symmetry on half-way between palladium atoms, with phosphine ligands in *trans* positions. The Pd–Cl distances to the terminal chloride anions are shorter (2.28 Å) than those to the bridging chloride anions; bond length to chloro ligand positioned *trans* to phosphorus atom is longer (2.41 Å) than that *trans* to the terminal chloride anion (2.32 Å).

3. Conclusion

We have synthesized triphenylphosphine derivatives containing phosphonomethyl groups and studied their coordination behaviour towards Pd(II) and Pt(II). The phosphonic acid derivatives and their complexes are well soluble in water after neutralization of the acids; therefore, their use in aqueous or biphasic catalysis is possible,

Table 5
Stretching Pd–Cl or Pt–Cl vibration in Pd(II) and Pt(II) complexes of **3a**, **3b**, **4a** and **4b**

Complex	Wavenumber (cm^{-1})[a]	Stereochemistry	
		IR	X-ray
$[PtCl_2(\mathbf{3a})_2]$	293s, 318s	*cis*	*cis*
$[PtCl_2(\mathbf{3b})_2]$	294s, 317s	*cis*	*cis*
$[PtCl_2(\mathbf{4a})_2]$	287s, 311s	*cis*	–
$[PtCl_2(\mathbf{4b})_2]$	291s, 312s	*cis*	–
$[PdCl_2(\mathbf{3a})_2]$	356s	*trans*	*trans*
$[PdCl_2(\mathbf{3b})_2]$	357s	*trans*	*trans*
$[PdCl_2(\mathbf{4a})_2]$	358s	*trans*	–
$[PdCl_2(\mathbf{4b})_2]$	289s, 307s	*cis*	–
$[Pd_2Cl_4(\mathbf{3a})_2]$	259s, 299m, 313m, 359s	Dinuclear	Dinuclear

Comparison of stereochemistry deduced from far-IR spectroscopy with results of X-ray diffraction analysis.
[a] m – medium, s – strong.

generally under the conditions and in the catalytic reactions already described for triphenylphosphine and its hydrophilic derivatives [1,2].

4. Experimental

4.1. General

All manipulations involving air-sensitive compounds were performed under an atmosphere of argon (5.6, Linde) using standard Schlenk techniques. Solvents were obtained and purified as follows: diethyl ether (Lachema, distilled from Na), dichloromethane (Lachema, distilled from P_2O_5 under Ar), *N*,*N*-dimethylacetamide (Fluka, vacuum-distilled from BaO under Ar), tetrahydrofurane (Lachema, distilled from Na,K/benzophenone under Ar), toluene (Lachema, distilled from Na,K/benzophenone under Ar), methyl acetate (Fluka, used as received), ethyl acetate, hexane, chloroform and methanol (Lachema, used as received), 35% aqueous HCl (Lachema, distilled under Ar), D_2O (99%), $CDCl_3$ (Chemotrade, used as received) and CD_3OD (Deutero GmbH, used as received).

Reagents and chemicals were obtained as follows: 4-methylaniline (Lachema, vacuum-distilled), 3,5-dimethylaniline (Aldrich), charcoal (Fluka), α,α′-azobis(isobutyronitrile) (AIBN, Fluka), diethyl phosphite (Fluka), $PtCl_2$ and $PdCl_2$ (Strem), anhydrous $MgSO_4$ (Acrōs), triphenylphosphine (Acrōs), anhydrous Na_2SO_4 (Lachema), *N*-bromosuccinimide (Fluka), tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate)europium(III) complex (EuFOD, Lachema), $THF \cdot BH_3$ (Fluka), $HBF_4 \cdot OMe_2$ (Aldrich), MS 4 Å (Fluka), anhydrous KOAc (Acrōs).

Chemicals prepared according to literature procedures: 1-iodo-3,5-dimethylbenzene and 3,5-bis(bromomethyl)-1-iodobenzene [40], 4-iodotoluene and 4-bromomethyl-1-iodobenzene (prepared analogously to the *m*-xylene derivatives), palladium(II) acetate [41], $[PdCl_2(cod)]$ and $[PtCl_2(cod)]$ [42].

^1H (399.95 MHz, TMS (internal) $\delta = 0.00$ ppm; CHD_2OD (internal) $\delta = 3.31$ ppm), ^{11}B (128.32 MHz, $BF_3 \cdot OEt_2$ (external) $\delta = 0.00$ ppm), ^{13}C (100.6 MHz, TMS (internal) $\delta = 0.0$ ppm; $CHCl_3$ (internal) $\delta = 77.0$ ppm), ^{31}P (161.9 MHz, 85% H_3PO_4 (external) $\delta = 0.0$ ppm) and ^{195}Pt (85.6 MHz, K_2PtCl_4, saturated solution in D_2O (external) $\delta = 1620$ ppm) NMR spectra were recorded on Varian ^{UNITY}INOVA 400 spectrometer at 25 °C. Multiplicity of the signals is indicated as follows: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad. Values of chemical shifts are in ppm, the values of coupling constants in Hz. For assignment of ^1H and ^{13}C NMR signals of **3a**, **3b**, **4a** and **4b**, HSQC and HMBC pulse

Table 6
Selected interatomic distances (Å) and angles (°) in crystal structures of the complexes *cis*-$[PtCl_2(\mathbf{3a})_2] \cdot 0.5CH_2Cl_2$, *cis*-$[PtCl_2(\mathbf{3b})_2] \cdot H_2O \cdot PhMe$, *trans*-$[PdCl_2(\mathbf{3a})_2] \cdot 2CHCl_3$, *trans*-$[PdCl_2(\mathbf{3b})_2] \cdot 2H_2O$ and *trans*-$[Pd_2Cl_4(\mathbf{3a})_2] \cdot 2CHCl_3$

Parameter	*cis*-$[PtCl_2(\mathbf{3a})_2] \cdot 0.5CH_2Cl_2$	*cis*-$[PtCl_2(\mathbf{3b})_2] \cdot H_2O \cdot PhMe$	*trans*-$[PdCl_2(\mathbf{3a})_2] \cdot 2CHCl_3$[a]	*trans*-$[PdCl_2(\mathbf{3b})_2] \cdot 2H_2O$[a]	*trans*-$[Pd_2Cl_4(\mathbf{3a})_2] \cdot 2CHCl_3$[b]	
Distance (Å)						
M–P1	2.2545(11)	2.2572(9)	2.3318(5)	2.3261(10)	M–P1	2.2340(8)
M–P2	2.2701(12)	2.2682(9)	–	–	$M–Cl_t$[c]	2.2794(8)
M–Cl1	2.3331(14)	2.3396(9)	2.3044(5)	2.3014(10)	$M–Cl_\mu$[d]	2.3202(8)
M–Cl2	2.3548(12)	2.3543(9)	–	–	$M–Cl'_\mu$	2.4143(8)
					Pd–Pd′	3.4761(8)
Angle (°)						
P1–M–P2	96.32(4)	98.83(3)	180	180	$P1–M–Cl_t$	89.40(3)
P1–M–Cl1	89.47(5)	89.51(3)	94.39(2)	92.46(4)	$P1–M–Cl_\mu$	95.58(3)
P1–M–Cl2	175.96(5)	176.35(3)	85.61(2)	87.54(4)	$P1–M–Cl'_\mu$	177.72(3)
P2–M–Cl1	173.56(4)	171.25(3)	–	–	$Cl_t–M–Cl_\mu$	173.35(3)
P2–M–Cl2	86.95(5)	84.59(3)	–	–	$Cl_t–M–Cl'_\mu$	89.34(3)
Cl1–M–Cl2	87.38(5)	87.14(3)	180	180	$Cl_\mu–M–Cl'_\mu$	85.54(3)

[a] Centrosymmetric structures with an inversion centre on Pd atom.
[b] Centrosymmetric structure with an inversion centre between Pd atoms in the dinuclear complex; inversion-associated atom is labelled by an apostrophe.
[c] Terminal chlorine atom.
[d] Bridging chlorine atom.

Table 7
Crystal data for the complexes *cis*-$[PtCl_2(\mathbf{3a})_2]\cdot 0.5CH_2Cl_2$, *cis*-$[PtCl_2(\mathbf{3b})_2]\cdot H_2O\cdot PhMe$, *trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$, *trans*-$[PdCl_2(\mathbf{3b})_2]\cdot 2H_2O$ and *trans*-$[Pd_2Cl_4(\mathbf{3a})_2]\cdot 2CHCl_3$

Parameter	*cis*-$[PtCl_2(\mathbf{3a})_2]\cdot 0.5CH_2Cl_2$	*cis*-$[PtCl_2(\mathbf{3b})_2]\cdot H_2O\cdot PhMe$	*trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$	*trans*-$[PdCl_2(\mathbf{3b})_2]\cdot 2H_2O$	*trans*-$[Pd_2Cl_4(\mathbf{3a})_2]\cdot 2CHCl_3$
Formula	$C_{46.5}H_{53}Cl_3O_6P_4Pt$	$C_{63}H_{84}Cl_2O_{13}P_6Pt$	$C_{48}H_{54}Cl_8O_6P_4Pd$	$C_{56}H_{78}Cl_2O_{14}P_6Pd$	$C_{48}H_{54}Cl_{10}O_6P_4Pd_2$
M	1133.21	1501.11	1240.80	1338.30	1418.10
Crystal colour	Colourless	Colourless	Yellow	Yellow	Red
Crystal shape	Plate	Rod	Prism	Needle	Irregular
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
a (Å)	10.2008(2)	14.1892(3)	10.5661(1)	8.8757(4)	9.6361(2)
b (Å)	16.6091(3)	15.2810(3)	25.1416(2)	11.3631(5)	13.2749(3)
c (Å)	16.6894(3)	16.6641(3)	10.6636(1)	16.1874(8)	13.6129(3)
α (°)	65.5852(8)	67.1336(11)	90	93.889(2)	96.8988(14)
β (°)	79.8597(8)	87.8977(11)	107.0962(5)	102.764(2)	110.1794(13)
γ (°)	79.0313(9)	86.6652(10)	90	98.082(3)	107.4107(12)
U (Å^3)	2512.68(8)	3323.22(11)	2707.60(4)	1568.14(13)	1510.30(6)
T (K)	294	150	150	150	150
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Z	2	2	2	1	1
μ (mm^{-1})	3.123	2.396	0.902	0.595	1.187
Reflections (measured/unique)	11462/10420	15190/13020	6212/5456	7197/4517	6909/6345
R_1[a]	0.0456	0.0366	0.0324	0.0589	0.0439
wR_2[b]	0.1286	0.0918	0.0858	0.1409	0.1281

[a] $R = \sum|F_o - F_c|/\sum|F_c|$.
[b] $wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sum^2(F_o^2) + (A\times P)^2 + B\times P]$; where $P = (F_o^2 + 2F_c^2)/3$.

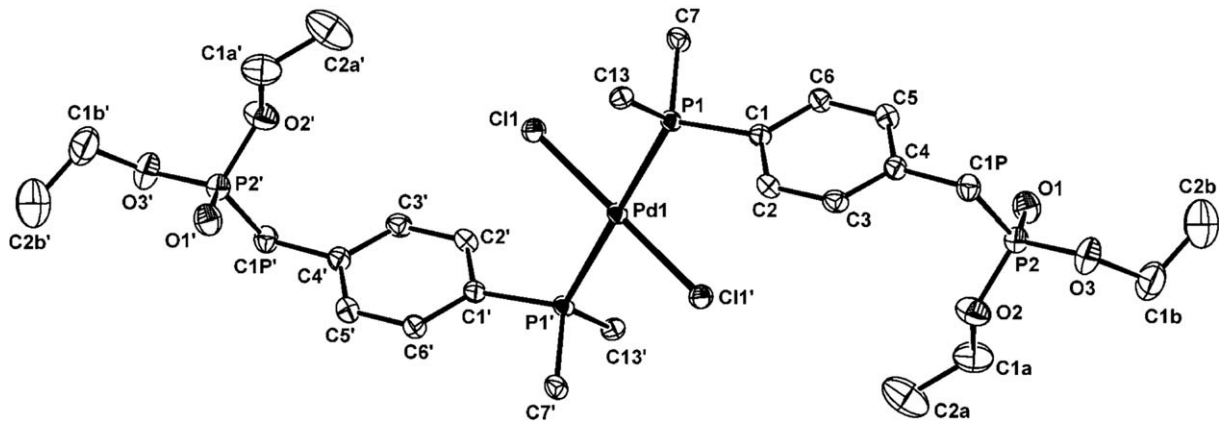


Fig. 4. Molecular structure of *trans*-$[PdCl_2(\mathbf{3a})_2]$ in *trans*-$[PdCl_2(\mathbf{3a})_2]\cdot 2CHCl_3$. Phenyl rings are omitted for clarity, only pivot atoms C7 and C13 are shown.

sequences were employed. The carbon aromatic frame of the molecules is numbered (see Fig. 1). NMR spectra presented in figures were obtained by deconvolution of experimental data using program MESTRE-C 4.1.7.0 [43].

MS spectra were recorded on a Bruker Esquire 3000 spectrometer equipped with electro-spray ion source and ion trap in positive and/or negative mode. For simplicity, the oxidized form (phosphine oxide) of the ligand is denoted as M^{ox}. The positive or negative mode of measurement is distinguished by a superscript attached to the parentheses describing the fragmentation.

Far-IR spectra were measured on a FTIR spectrometer Magna 760 (Nicolet) in polyethylene pellets in the range 100–600 cm^{-1} with resolution 4 cm^{-1} at 25 °C in an atmosphere of dry air. The relative intensity of the signals is described as m – medium or s – strong.

All air-stable organic compounds gave satisfactory elemental analyses; however, the oily nature and tendency to oxidize did not allow obtaining reliable elemental data for phosphines. In the case of metal complexes, microanalyses are not reported because of variable and non-stoichiometric solvation and general problems with combustion. The yields of Pd(II) and Pt(II) complexes are not optimized.

4.2. Syntheses

4.2.1. Diphenylphosphine (**1**) [21]

Under a stream of argon, lithium metal sheets (3.0 g, 0.43 mol) were added into a stirred slurry of triphenylphosphine (50 g, 0.19 mol) in THF (400 mL) in a 2-L Schlenk vessel on cooling (ice-bath). Lithium dissolved within 5 h

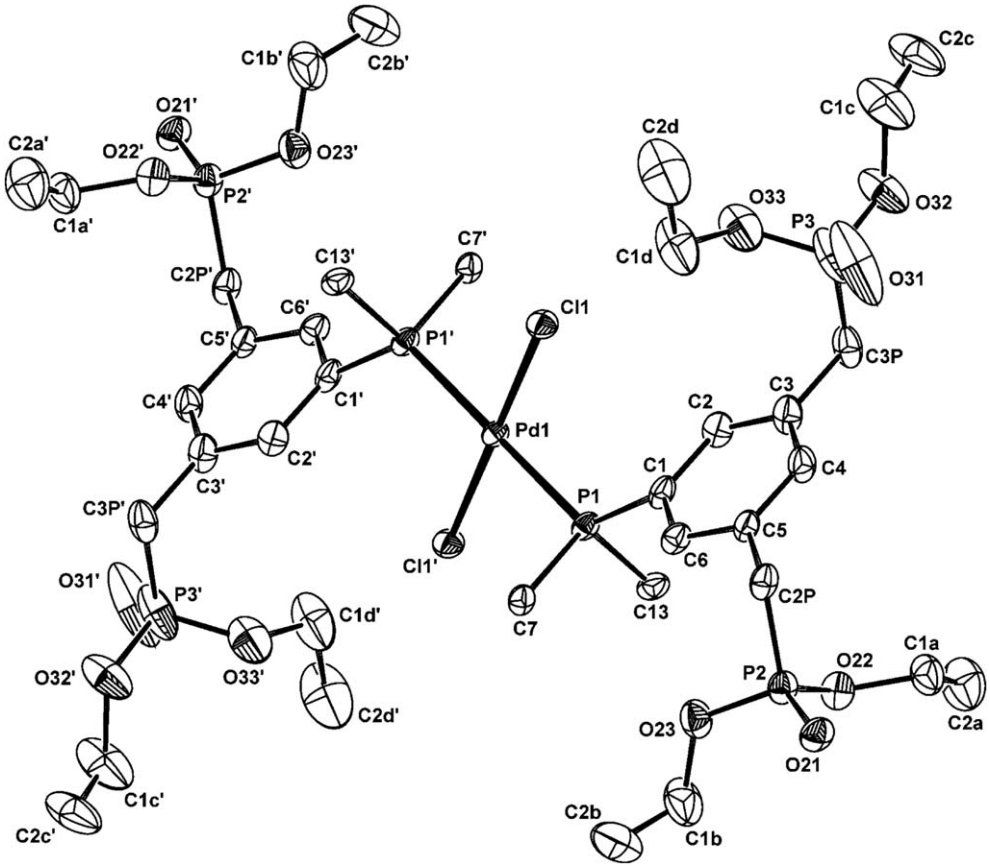


Fig. 5. Molecular structure of *trans*-[$PdCl_2$(**3b**)$_2$] in *trans*-[$PdCl_2$(**3b**)$_2$] · $2H_2O$. Phenyl rings are omitted for clarity, only pivot atoms C7 and C13 are shown.

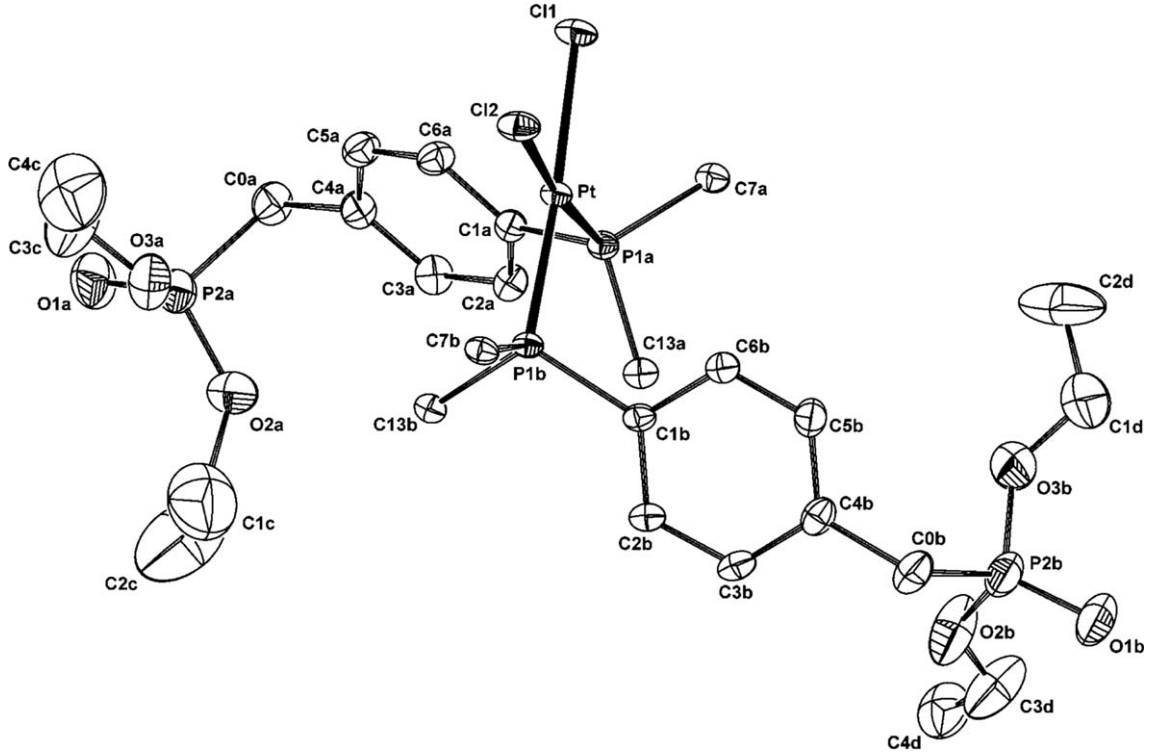


Fig. 6. Molecular structure of *cis*-[$PtCl_2$(**3a**)$_2$] in *cis*-[$PtCl_2$(**3a**)$_2$] · $0.5CH_2Cl_2$. Phenyl rings are omitted for clarity, only pivot atoms C7 and C13 are shown.

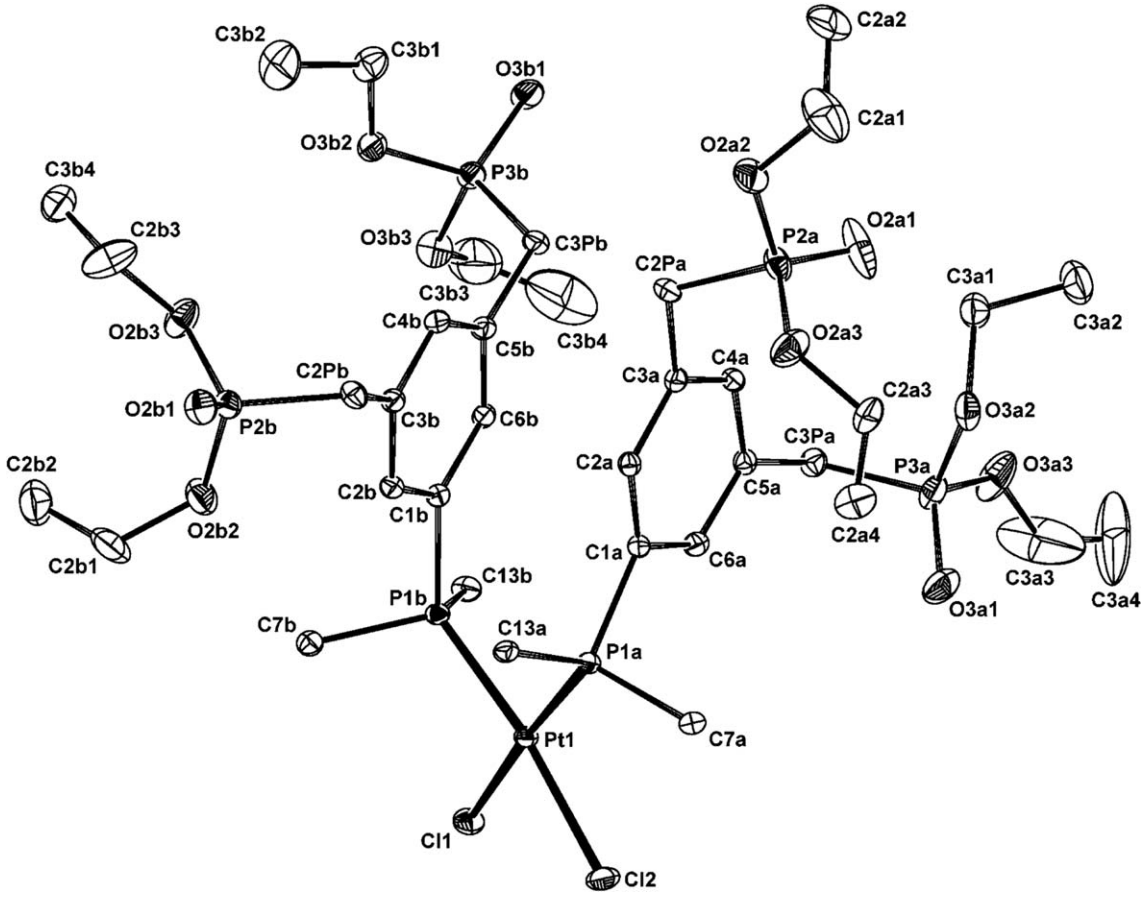


Fig. 7. Molecular structure of *cis*-$[PtCl_2(\mathbf{3b})_2]$ in *cis*-$[PtCl_2(\mathbf{3b})_2] \cdot H_2O \cdot PhMe$. Phenyl rings are omitted for clarity, only pivot atoms C7 and C13 are shown.

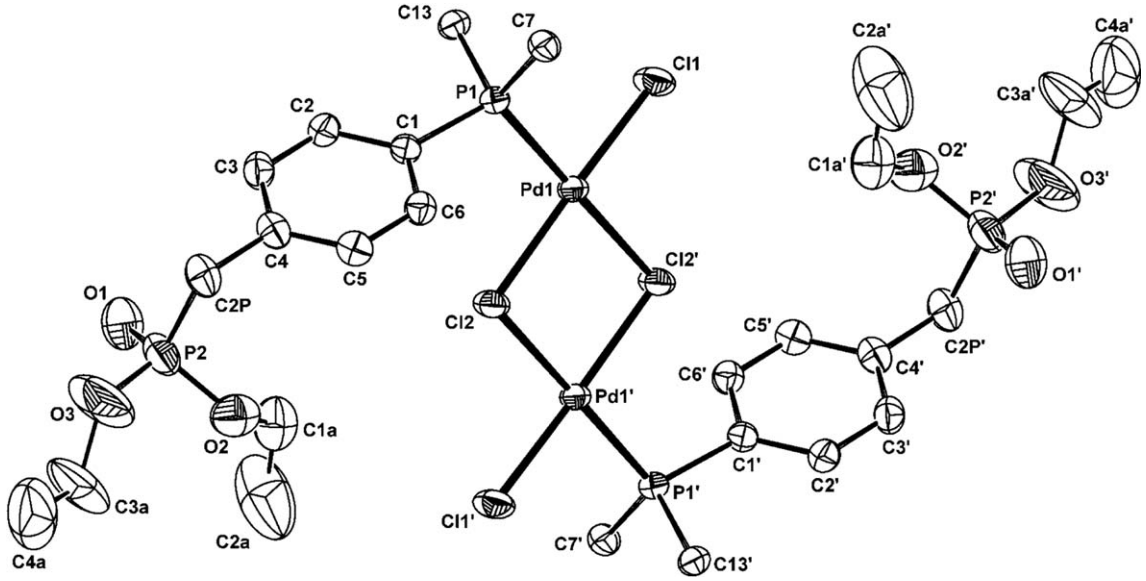


Fig. 8. Molecular structure of *trans*-$[Pd_2Cl_4(\mathbf{3a})_2]$ in *trans*-$[Pd_2Cl_4(\mathbf{3a})_2] \cdot 2CHCl_3$. Phenyl rings are omitted for clarity, only pivot atoms C7 and C13 are shown.

to a deep red solution. Water (150 mL) was added (50 mL dropwise, 100 mL in one portion) on cooling (ice-bath). Deoxygenated diethyl ether (200 mL) was added and the mixture was stirred vigorously. The organic phase was separated and washed with diluted HCl (200 mL, 1:15) and twice with water (200 mL). The organic phase was dried

over anhydrous Na_2SO_4. After filtration, all volatiles were removed under reduced pressure. The residual oil was then distilled in vacuo (85 °C, 54 Pa). Purity according to ^{31}P NMR 98+%.

1 (26 g, 73% based on PPh_3) NMR ($CDCl_3$): ^1H δ 3.83 (P–H, 1H, d, $^1J_{PH} = 217$); 5.87–5.90 (ArH, 6H, m); 6.04–6.08 (ArH, 4H, m); $^{13}C\{^1H\}$ δ 128.4 (*p*-CH, 2C, s); 128.5 (*m*-CH, 4C, d, $^3J_{PC} = 6.4$); 133.9 (*o*-CH, 4C, d, $^2J_{PC} = 6.8$); 134.6 (C–P, 2C, d, $^1J_{PC} = 9.9$); ^{31}P NMR δ −42.1 (d, $^1J_{PH} = 216$); $^{31}P\{^1H\}$ δ −42.1 (s).

4.2.2. Diethyl (4-iodobenzyl)phosphonate (**2a**) and tetraethyl [(5-iodo-1,3-phenylene)dimethylene]-bis(phosphonate) (**2b**)

A 100 mL Schlenk flask equipped with a reflux condenser was charged with sodium wire (1.90 g, 83.0 mmol) and dry THF (17 mL). Diethyl phosphite (11.3 g, 82.0 mmol) was added by means of a syringe under argon atmosphere. The mixture was stirred overnight in water/ice-bath under a gentle argon stream. A solution of 4-bromomethyl-1-iodobenzene (11.9 g, 40.0 mmol) or 3,5-bis(bromomethyl)-1-iodobenzene (8.00 g, 21.0 mmol) in dry THF (15 mL) was added dropwise at RT within 30 min. The reaction was completed by a short reflux and checked by TLC (silica gel, hexane, no reactant detectable at $R_f = 0.2$ or 0.5). Following manipulations were done under air. The white precipitate (NaBr) was removed by centrifugation and washed with a small volume of THF. Supernatants were collected and evaporated on a rotary evaporator. The oily residue was dissolved in ethyl acetate (50 mL) and washed with 2% aqueous NaOH (3 × 30 mL). Organic phase was dried with anhydrous $MgSO_4$ and filtered. After treatment with charcoal and filtration, all volatiles were evaporated. The product was dried by heating at 70 °C in vacuo for 8 h. Ester **2b** can be recrystallized from hexanes.

2a (12.7 g, 89%) Elemental analysis: found C, 33.4; H, 4.25; I, 32.3; $C_{11}H_{16}IO_3P$ requires C, 37.3; H, 4.55; I, 35.8% NMR ($CDCl_3$): ^1H δ 1.25 (CH_3, 6H, t, $^3J_{HH} = 7.2$); 3.14 (CH_2–P, 2H, d, $^2J_{PH} = 22.0$); 4.06 (O–CH_2, 4H, m); 7.32 (Ar–H, 4H, m); $^{13}C\{^1H\}$ δ 16.3 (CH_3, 2C, d, $^3J_{PC} = 6.1$); 33.3 (CH_2–P, 1C, d, $^1J_{PC} = 138$); 62.2 (O–CH_2, 2C, d, $^2J_{PC} = 6.5$); 92.2 (C–I, 1C, d, $^5J_{PC} = 6.6$); 131.3 (*C*–CH_2, 1C, d, $^2J_{PC} = 9.2$); 131.6 (C–H, 2C, d, $^3J_{PC} = 6.6$); 137.5 (C–H, 2C, d, $^2J_{PC} = 3.1$); $^{31}P\{^1H\}$ δ 23.7 (s); MS: *m*/*z* 377.0 $(M + Na)^+$; 355.1 $(M + H)^+$.

2b (8.80 g, 85%) Elemental analysis: found C, 37.3; H, 5.40; I, 24.6; $C_{16}H_{27}IO_6P_2$ requires C, 38.1; H, 5.40; I, 25.2% NMR ($CDCl_3$): ^1H δ 1.27 (CH_3, 12H, t, $^3J_{HH} = 7.2$); 3.06 (CH_2–P, 4H, d, $^2J_{PH} = 21.6$); 4.04 (O–CH_2, 8H, m); 7.20 (Ar–H, 1H, m); 7.55 (Ar–H, 2H, m); $^{13}C\{^1H\}$ δ 16.4 (CH_3, 4C, d, $^3J_{PC} = 6.1$); 33.1 (CH_2–P, 2C, d, $^1J_{PC} = 138$); 62.3 (O–CH_2, 4C, d, $^2J_{PC} = 6.8$); 94.1 (C–I, 1C, s); 130.6 (C–H, 1C, m, $^3J_{PC} = 6.4$); 134.1 (*C*–CH_2, 2C, m, $^2J_{PC} = 6.1$); 137.1 (C–H, 2C, m); $^{31}P\{^1H\}$ δ 25.9 (s); MS: *m*/*z* 527.1 $(M + Na)^+$; 505.0 $(M + H)^+$.

4.2.3. Diethyl [4-(diphenylphosphanyl)benzyl]phosphonate (**3a**) and tetraethyl {[5-(diphenylphosphanyl)-1,3-phenylene]dimethylene}bis(phosphonate) (**3b**)

A 50 mL Schlenk flask was charged with **2a** (2.48 g, 7.00 mmol) or **2b** (3.53 g, 7.00 mmol), dry deoxygenated toluene (25 mL), anhydrous KOAc (0.8 g, 8.0 mmol) and diphenylphosphine (**1**) (1.35 g, 7.18 mmol). The reaction was started by injection of a solution of $Pd(OAc)_2$ (3.5 mg, 0.2 mol%) in dry *N*,*N*-dimethylacetamide (2 mL). The flask was stoppered and the reaction mixture was heated to 90 °C in an oil bath and periodically checked by ^{31}P NMR. After 12–24 h (**3a**) or 24–36 h (**3b**), the mixture was cooled to RT and deoxygenated water (25 mL) was added. After several minutes of vigorous stirring the emulsion was left standing to separate. Organic layer was transferred by means of a syringe into a 50 mL Schlenk flask containing anhydrous Na_2SO_4. The mixture was filtered and the drying agent was washed with a small volume of dry toluene. Volatiles were removed in vacuo and the oily residue was dried by prolonged heating in vacuo at 80 °C. Resulting oils contained 93–97% of the target compounds (^{31}P NMR).

3a (2.40 g, 83%) NMR ($CDCl_3$): ^1H δ 1.23 (CH_3, 6H, t, $^3J_{HH} = 6.8$); 3.14 (CH_2–P, 2H, d, $^2J_{PH} = 21.6$); 4.01 (O–CH_2, 4H, m); 7.27–7.33 (ArH, 14H, m); $^{13}C\{^1H\}$ δ 16.3 (CH_3, 2C, d, $^3J_{PC} = 5.7$); 33.6 (CH_2–P, 1C, d, $^1J_{PC} = 138$); 62.1 (O–CH_2, 2C, d, $^2J_{PC} = 6.8$); 128.4 (C2, 4C, d, $^3J_{PC} = 6.8$); 128.7 (C1, 2C, s); 129.9 (C7, 2C, t, $^3J_{PC} = 6.8$); 132.3 (C5, 1C, d, $^2J_{PC} = 9.2$); 133.6 (C3, 4C, d, $^2J_{PC} = 19.4$); 133.8 (C6, 2C, dd, $^2J_{PC} = 19.8$, $^4J_{PC} = 2.7$); 135.6 (C8, 1C, dd, $^2J_{PC} = 9.2$, $^4J_{PC} = 3.2$); 137.0 (C4, 2C, d, $^1J_{PC} = 10.7$); $^{31}P\{^1H\}$ δ −5.4 (P, 1P, s); 26.9 (P=O, 1P, br); MS: *m*/*z* 451.2 $(M^{ox} + H)^+$; 435.2 $(M + Na)^+$; *m*/*z* 427.1 $(M^{ox} - H)^-$.

3b (3.40 g, 86%) NMR ($CDCl_3$): ^1H δ 1.11 (CH_3, 12H, t, $^3J_{HH} = 7.2$); 3.01 (CH_2–P, 4H, d, $^2J_{PH} = 21.6$); 4.89 (O–CH_2, 8H, m); 7.03 (ArH, 2H, m); 7.16 (ArH, 1H, m); 7.23 (ArH, 10H, m); $^{13}C\{^1H\}$ δ 16.3 (CH_3, 4C, d, $^3J_{PC} = 6.1$); 33.5 (CH_2–P, 2C, d, $^1J_{PC} = 138$); 62.0 (O–CH_2, 4C, d, $^2J_{PC} = 6.8$); 128.4 (C2, 4C, d, $^3J_{PC} = 6.9$); 128.8 (C1, 2C, s); 131.6 (C8, 1C, t, $^3J_{PC} = 6.5$); 132.3 (C7, 2C, m); 133.4 (C6, 2C, dt, $^2J_{PC} = 19.8$, $^3J_{PC} = 4.9$); 133.7 (C3, 4C, d, $^2J_{PC} = 19.4$); 136.7 (C4, 2C, d, $^1J_{PC} = 10.7$); 137.8 (C5, 1C, dt, $^1J_{PC} = 12.3$, $^4J_{PC} = 2.9$); $^{31}P\{^1H\}$ δ −5.4 (P, 1P, s); 26.0 (P=O, 2P, br); MS: 585.3 $(M + Na)^+$; 563.1 $(M + H)^+$; 561.1 $(M - H)^-$.

4.2.4. Borane adducts of diethyl [4-(diphenylphosphanyl)benzyl]phosphonate (**3a** · BH_3) and tetraethyl {[5-(diphenylphosphanyl)-1,3-phenylene]dimethylene}bis(phosphonate) (**3b** · BH_3)

The adducts were prepared from the impure ligand samples by treatment with ca. threefold molar excess of a 1 M THF · BH_3 solution upon cooling in an ice-bath. After 2 h stirring solvents were evaporated in vacuo and the products were purified by column chromatography (silica gel, EtOAc) and crystallization from THF/hexanes (**3a** · BH_3)

or by column chromatography (silica gel, THF/Et_2O/H_2O 10:3:1) (**3b** · BH_3). The purified products had purity 98+% (**3a** · BH_3) and 96+% (**3b** · BH_3) (^{31}P NMR).

3a · BH_3 NMR ($CDCl_3$): ^{1}H δ 1.25 (CH_3, 6H, t, $^3J_{HH} = 7.0$); 1.3 (BH_3, 3H, br); 3.18 (CH_2–P, 2H, d, $^2J_{PH} = 22.0$); 4.04 (O–CH_2, 4H, m); 7.36–7.59 (ArH, 14H, m); ^{11}B δ −38.03 (P–BH_3, br s) ^{13}C{^{1}H} δ 11.2 (CH_3, 2C, d, $^3J_{PC} = 5.7$); 28.6 (CH_2–P, 1C, d, $^1J_{PC} = 138$); 57.1 (O–CH_2, 2C, d, $^2J_{PC} = 6.5$); 122.4 (C5, 1C, dd, $^2J_{PC} = 9.2$, $^5J_{PC} = 3.4$); 123.6 (C2, 4C, d, $^3J_{PC} = 10.0$); 123.9 (C4, 2C, d, $^1J_{PC} = 55.0$); 125.0 (C7, 2C, dd, $^3J_{PC} = 10.3$ and 6.5); 126.0 (C1, 2C, d, $^4J_{PC} = 1.9$); 127.9 (C3, 4C, d, $^2J_{PC} = 9.56$); 128.1 (C6, 2C, dd, $^2J_{PC} = 9.86$, $^4J_{PC} = 2.7$); 130.2 (C8, 1C, dd, $^4J_{PC} = 2.2$, $^2J_{PC} = 9.2$); ^{31}P{^{1}H} δ 20.5 (P–BH_3, 1P, br); 25.4 (P=O, 1P, s); MS: *m/z* 449.2 $(M + Na)^+$; 435.1 $(M - BH_3 + Na)^+$; *m/z* 413.2 $(M - BH_3 + H)^+$.

3b · BH_3 NMR ($CDCl_3$): ^{1}H δ 1.12 (CH_3, 12H, t, $^3J_{HH} = 7.2$); 1.3 (BH_3, 3H, br); 3.05 (CH_2–P, 4H, d, $^2J_{PH} = 22.0$); 3.90 (O–CH_2, 8H, m); 7.30–7.52 (ArH, 13H, m); ^{11}B δ −38.13 (P–BH_3, br s) ^{13}C{^{1}H} δ 16.3 (CH_3, 4C, d, $^3J_{PC} = 6.1$); 33.5 (CH_2–P, 2C, d, $^1J_{PC} = 138$); 62.0 (O–CH_2, 4C, d, $^2J_{PC} = 6.8$); 128.8 (C3, 4C, d, $^2J_{PC} = 10.2$); 128.8 (C4, 2C, d, $^1J_{PC} = 57.9$); 129.7 (C5, 1C, dt, $^2J_{PC} = 56.8$, $^3J_{PC} = 3.0$); 131.3 (C1, 2C, d, $^4J_{PC} = 2.3$); 132.7–133.2 (C6 + C7, 4C, m); 133.1 (C2, 4C, d, $^3J_{PC} = 9.9$); 134.3 (C8, 1C, td, $^3J_{PC} = 6.5$, $^4J_{PC} = 2.3$); ^{31}P{^{1}H} δ 20.5 (P–BH_3, 1P, br); 25.2 (P=O, 2P, s); MS: 599.3 $(M + Na)^+$; 585.2 $(M - BH_3 + Na)^+$; 563.1 $(M - BH_3 + H)^+$.

4.2.5. Deprotection of **3a** · BH_3 and **3b** · BH_3 [26]

After deprotection, the spectral characteristics of the products corresponded to those mentioned above; the purity remained unchanged.

4.2.6. [4-(Diphenylphosphanyl)benzyl]phosphonic acid (**4a**) and {[5-(diphenylphosphanyl)-1,3-phenylene]-dimethylene}bis(phosphonic) acid (**4b**)

In a closed Schlenk flask, the phosphonic acid ester (0.5 g) was heated with 30 mL of 20% aqueous HCl to 100 °C for 24 h in the case of **4a** or 48 h for **4b**. After cooling to RT, the mixture was filtered and all volatiles were evaporated in vacuo. The residue was dissolved in 15 mL of deoxygenated ethanol, stirred for 15 min and evaporated again. The glassy product was dried for 3 h in vacuo. Purity of the products was 98+% (**4a**) and 97+% (**4b**).

4a (0.41 g, 95%) NMR (d_4-methanol): ^{1}H δ 3.14 (CH_2–P, 2H, d, $^2J_{PH} = 22.0$); 7.22–7.34 (ArH, 14H, m); ^{13}C{^{1}H} δ 35.6 (CH_2–P, 1C, d, $^1J_{PC} = 134.4$); 129.7 (C2, 4C, d, $^3J_{PC} = 6.8$); 130.1 (C1, 2C, s); 133.8 (C7, 2C, t, $^3J_{PC} = 6.8$); 134.7 (C3, 4C, d, $^2J_{PC} = 19.1$); 135.0 (C6, 2C, dd, $^2J_{PC} = 19.8$, $^4J_{PC} = 2.3$); 135.6 (C5, 1C, m); 137.7 (C4, 2C, m); ^{31}P{^{1}H} δ −3.4 (P, 1P, s); 26.8 (P=O, 1P, br); MS: 395.0 $(M^{ox} + Na)^+$; 379.3 $(M + Na)^+$; 372.1 $(M^{ox})^+$; 357.1 $(M + H)^+$; 355.2 $(M - H)^-$.

4b (0.38 g, 95%) NMR (d_4-methanol): ^{1}H δ 3.10 (CH_2–P, 4H, d, $^2J_{PH} = 22.0$); 7.21 (CH, 2H, m); 7.30 (C–C*H*–C, 1H, m); 7.30–7.39 (ArH, 10H, m); ^{13}C{^{1}H} δ 35.4 (CH_2–P, 2C, d, $^1J_{PC} = 134.3$); 129.7 (C2, 4C, d, $^3J_{PC} = 4.2$); 130.3 (C1, 2C, s); 133.2 (C8, 1C, m); 134.3–134.9 (C6 and C7, 4C, m); 134.8 (C3, 4C, d, $^2J_{PC} = 19.0$); 137.2 (C4, 2C, d, $^1J_{PC} = 5.3$); 138.0 (C5, 1C, m); ^{31}P{^{1}H} δ −4.0 (P, 1P, s); 25.7 (P=O, 2P, s); MS: 489.1 $(M^{ox} + Na)^+$; 473.1 $(M + Na)^+$; 451.1 $(M + H)^+$; 449.2 $(M - H)^-$.

4.2.7. cis-[$PtCl_2$(**3a**)$_2$], trans-[$PdCl_2$(**3a**)$_2$] and trans-[Pd_2Cl_4(**3a**)$_2$]

A solution of **3a** (480 mg, 1160 μmol) in dichloromethane (5 mL) in a 25 mL Schlenk flask was treated with a solution of [$PtCl_2$(cod)] (217 mg, 570 μmol) or [$PdCl_2$(cod)] (163 mg, 570 μmol) in 5 mL of the same solvent. The flask was stoppered and the reaction mixture was stirred overnight at 35 °C in an oil bath. Following manipulations were done under air. Volatiles were removed in vacuo, the residue was dissolved in 1 mL of dichloromethane and precipitated by slow addition of hexane. The products were collected by centrifugation, washed with hexane (3 × 5 mL) and dried in vacuo.

From the mother liquors after crystallization of *trans*-[$PdCl_2$(**3a**)$_2$] · $2CHCl_3$ left in refrigerator at −20 °C for several months, red crystalline *trans*-[Pd_2Cl_4(**3a**)$_2$] · $2CHCl_3$ was isolated by filtration and dried in vacuo.

cis-[$PtCl_2$(**3a**)$_2$] (420 mg, 66%) NMR ($CDCl_3$): ^{1}H δ 1.23 (CH_3, 6H, t, $^3J_{HH} = 6.8$); 3.13 (CH_2–P, 2H, d, $^2J_{PH} = 22.0$); 4.00 (O–CH_2, 4H, m); 7.14–7.48 (Ar, 14H, m); ^{31}P{^{1}H} δ 13.8 (Pt–P, 1P, s + d, $^1J_{PtP} = 3672$); 25.3 (P=O, 1P, s); ^{195}Pt δ −1192 (t, $^1J_{PtP} = 3666$); MS: 1113.1 $(M + Na)^+$; 1078.8 $(M - Cl + Na)^+$; far-IR: ν_{Pt-Cl}/cm^{-1} 293s, 318s.

trans-[$PdCl_2$(**3a**)$_2$] · $2CHCl_3$ (366 mg, 64%) NMR ($CDCl_3$): ^{1}H δ 1.22 (CH_3, 6H, t, $^3J_{HH} = 7.2$); 3.16 (CH_2–P, 2H, d, $^2J_{PH} = 22.0$); 3.99 (O–CH_2, 4H, m); 7.31–7.44 (Ar, 10H, m), 7.60–7.73 (Ar, 4H, m); ^{31}P{^{1}H} δ 21.2 (Pd–P, 1P, s); 23.7 (P=O, 1P, s); MS: 1025.1 $(M + Na)^+$; 965.2 $(M - Cl)^+$; 624.9 $(M - L + Cl)^-$; far-IR ν_{Pd-Cl}/cm^{-1} 356s.

trans-[Pd_2Cl_4(**3a**)$_2$] · $2CHCl_3$ (40.0 mg) NMR ($CDCl_3$): ^{1}H δ 1.24 (CH_3, 12H, t, $^3J_{HH} = 7.2$); 3.17 (P–CH_2, 4H, d, $^2J_{PH} = 22.0$); 4.01 (O–CH_2, 8H, m); 7.35 (ArH, 4H, m); 7.42 (ArH, 8H, m); 7.52 (ArH, 4H, m); 7.63 (ArH, 4H, m); 7.73 (ArH, 8H, m); ^{31}P{^{1}H} δ 23.1 (P=O, 1P, s); 30.7 (Pd–P, 1P, s); MS: 1202.9 $(M + Na)^+$; 625.0 ([$PdCl_3$(**3a**)])$^-$; far-IR ν_{Pd-Cl}/cm^{-1} 259s, 299m, 313m, 359s.

4.2.8. cis-[$PtCl_2$(**3b**)$_2$] and trans-[$PdCl_2$(**3b**)$_2$]

A solution of **3b** (240 mg, 430 μmol) in dichloromethane (5 mL) in a 25 mL Schlenk flask was treated with a solution of [$PtCl_2$(cod)] (77.0 mg, 205 μmol) or [$PdCl_2$(cod)] (58.5 mg, 205 μmol) in 5 mL of the same solvent. The flask was stoppered and the reaction mixture was stirred overnight at 35 °C in an oil bath. Following manipulations were

done under air atmosphere. Volatiles were evaporated under reduced pressure and residual cycloocta-1,5-diene was removed by evaporation of the residue with 5 mL of dichloromethane. Remaining yellowish oils were dried in vacuo.

cis-[$PtCl_2$(**3b**)$_2$] (230 mg, 80%) NMR ($CDCl_3$): ^{1}H δ 1.21 (CH_3, 12H, t, $^3J_{HH} = 6.8$); 3.01 (CH_2–P, 4H, d, $^2J_{PH} = 22.0$); 3.97 (O–CH_2, 8H, m); 7.16–7.46 (ArH, 13H, m); ^{31}P{^{1}H} δ 14.3 (Pt–P, 1P, s + d, $^1J_{PtP} = 3666$); 25.1 (P=O, 2P, s); ^{195}Pt δ −1198 (t, $^1J_{PtP} = 3662$); MS: 1413.1 $(M + Na - H)^+$; 1425.5 $(M + Cl - H)^-$; far-IR ν_{Pt-Cl}/cm^{-1} 294s, 317s.

trans-[$PdCl_2$(**3b**)$_2$] (219 mg, 82%) NMR ($CDCl_3$): ^{1}H δ 1.15 (CH_3, 12H, t, $^3J_{HH} = 7.2$); 3.11 (CH_2–P, 4H, d, $^2J_{PH} = 22.0$); 3.93 (O–CH_2, 8H, m); 7.35–7.53 (Ar, 10H, m), 7.65–7.70 (Ar, 3H, m); ^{31}P{^{1}H} δ 24.2 (Pd–P, 1P, s); 26.0 (P=O, 2P, s); MS: 1325.1 $(M + Na)^+$; 773.5 $(M - L + Cl)^-$; far-IR ν_{Pd-Cl}/cm^{-1} 357s.

4.2.9. *cis*-[$PtCl_2$(**4a**)$_2$] and *cis*-[$PtCl_2$(**4b**)$_2$]

A solution of **4a** (190 mg, 423 μmol) or **4b** (151 mg, 423 μmol) in 20% aqueous HCl (5 mL) in a 25 mL Schlenk flask was treated with a solution of [$PtCl_2$(cod)] (81.0 mg, 216 μmol) in 5 mL of dichloromethane. The reaction mixture was stirred vigorously overnight at RT. Aqueous phase was removed by means of a syringe and the organic layer containing a white precipitate was evaporated to dryness. The residue was evaporated to dryness with methanol (3 × 5 mL) and washed with hexane (3 × 5 mL). The residue was stirred in dichloromethane (10 ml) overnight, separated by centrifugation, washed with dichloromethane (5 mL) and dried in vacuo.

cis-[$PtCl_2$(**4a**)$_2$] (176 mg, 84%) NMR (D_2O + NaOD, pH 9): ^{1}H δ 2.88 (CH_2–P, 2H, d, $^2J_{PH} = 22.4$); 6.92–7.22 (ArH, 14H, m); ^{31}P{^{1}H} δ 11.0 (Pt–P, 1P, s + d, $^1J_{PtP} = 3709$); 17.4 (P=O, 1P, s); ^{195}Pt δ −1185 (Pt–P, t, $^1J_{PtP} = 3705$); MS: 943.1 $(M - Cl)^+$; 977.2 $(M - H)^-$; far-IR ν_{Pt-Cl}/cm^{-1} 287s, 311s.

cis-[$PtCl_2$(**4b**)$_2$] (137 mg, 56%) NMR (D_2O + NaOD, pH 9): ^{1}H δ 2.55 (CH_2–P, 4H, d, $^2J_{PH} = 20.0$); 7.05 (CH, 2H, d, $^2J_{PH} = 10.4$); 7.13 (CH, 4H, m); 7.23 (CH, 1H, s); 7.28 (CH, 2H, m); 7.42 (CH, 4H, m); ^{31}P{^{1}H} δ 11.7 (Pt–P, 1P, s + d, $^1J_{PtP} = 3560$); 20.5 (P=O, 2P, s); ^{195}Pt δ −875 (Pt–P, t, $^1J_{PtP} = 3580$); MS: 1165.5 $(M - H)^-$; far-IR ν_{Pt-Cl}/cm^{-1} 291s, 312s.

4.2.10. *trans*-[$PdCl_2$(**4a**)$_2$] and *cis*-[$PdCl_2$(**4b**)$_2$]

A freshly prepared slurry of $PdCl_2$ (22.3 mg, 126 μmol) in 20% aqueous HCl (2 mL) was added to a solution of **4a** (95.0 mg, 265 μmol) or **4b** (120 mg, 265 μmol) in 20% aqueous HCl (3 mL) in a 25 mL Schlenk flask. The slurry was stirred overnight at RT. The yellow product was separated by centrifugation, washed with 20% aqueous HCl (2 mL) and dried in a desiccator (over NaOH).

trans-[$PdCl_2$(**4a**)$_2$] (84.0 mg, 73%) NMR (D_2O + NaOD, pH 9): ^{1}H δ 2.56 (CH_2–P, 2H, d, $^2J_{PH} = 8.2$); 6.99–7.63 (ArH, 14H, m); ^{31}P{^{1}H} δ 16.4 (P=O, 1P, s); 34.0 (Pd–P, 1P, s); MS: 854.1 $(M - Cl)^+$; 889.0 $(M - H)^-$; far-IR ν_{Pd-Cl}/cm^{-1} 358s.

cis-[$PdCl_2$(**4b**)$_2$] (88.0 mg, 62%) NMR (D_2O + NaOD, pH 9): ^{1}H δ 2.31 (CH_2–P, 4H, d, $^2J_{PH} = 8.4$); 6.78–7.73 (ArH, 13H, m); ^{31}P{^{1}H} δ 18.4 (P=O, 1P, s); 35.1 (Pd–P, 1P, s); MS: 1076.9 $(M - H)^-$; 1040.9 $(M - 2H - Cl)^-$; far-IR ν_{Pd-Cl}/cm^{-1} 289s, 307s.

4.2.11. Photochemical isomerization of Pt(II) complexes

cis-[$PtCl_2$(**3a**)$_2$] and *cis*-[$PtCl_2$(**3b**)$_2$]: 20 mg of the complex was dissolved in 0.7 ml of $CDCl_3$ in a quartz NMR tube. The sample was irradiated for 5 h with an 8 W UV lamp ($\lambda = 366$ nm).

cis-[$PtCl_2$(**4a**)$_2$] and *cis*-[$PtCl_2$(**4b**)$_2$]: A 20 mg sample of the complex was suspended in 0.2 ml of D_2O and a 0.3 M NaOD in D_2O was added dropwise until the solid dissolved. The volume of the sample was adjusted to 0.7 ml with D_2O. After transfer into a quartz NMR tube, the sample was irradiated as described above.

cis- and *trans*-[$PtCl_2$(**3a**)$_2$] NMR ($CDCl_3$, *after irradiation*): ^{31}P{^{1}H} δ 12.0 (P–Pt *cis*, s + d, $^1J_{PtP} = 3669$ Hz); 18.1 (P–Pt *trans*, s + d, $^1J_{PtP} = 2634$ Hz); 23.5 (P=O *cis*, s); 23.8 (P=O *trans*, s); ^{195}Pt δ −1196 (*cis*, t, $^1J_{PtP} = 3665$ Hz); −814 (*trans*, t, $^1J_{PtP} = 2643$ Hz).

cis- and *trans*-[$PtCl_2$(**3b**)$_2$] NMR ($CDCl_3$, *after irradiation*): ^{31}P{^{1}H} δ 14.4 (P–Pt *cis*, s + d, $^1J_{PtP} = 3667$ Hz); 20.7 (P–Pt *trans*, s + d, $^1J_{PtP} = 2643$ Hz); 25.4 (P=O *cis*, s); 25.6 (P=O *trans*, s); ^{195}Pt δ −1199 (*cis*, t, $^1J_{PtP} = 3663$ Hz); −823 (*trans*, t, $^1J_{PtP} = 2645$ Hz).

4.3. X-ray crystallography

The single crystals of compound *cis*-[$PtCl_2$(**3a**)$_2$] · 0.5CH_2Cl_2 were prepared from its dichloromethane solution by slow diffusion of hexane. The crystals of *cis*-[$PtCl_2$(**3b**)$_2$] · PhMe · H_2O were prepared by slow diffusion of hexane to a solution of the complex in chloroform/toluene. *Trans*-[$PdCl_2$(**3a**)$_2$] · 2$CHCl_3$ crystallized from hexane/ethanol/chloroform mixture on cooling to −18 °C, *trans*-[$PdCl_2$(**3b**)$_2$] · 2H_2O crystallized from its oil upon standing. Dinuclear complex *trans*-[Pd_2Cl_4(**3a**)$_2$] · 2$CHCl_3$ crystallized on prolonged standing of mother liquor after crystallization of *trans*-[$PdCl_2$(**3a**)$_2$] · 2$CHCl_3$.

The selected crystals were mounted in random orientations onto a glass fibre using nujol or epoxy glue. The data were collected on Nonius Kappa CCD diffractometer (Enraf-Nonius) at 294 K (*cis*-[$PtCl_2$(**3a**)$_2$] · 0.5CH_2Cl_2) or 150 K (Cryostream Cooler Oxford Cryosystem) (all other complexes). Data were analyzed using the HKL DENZO program package [44].

All crystal structures were solved by direct methods (SIR92 [45]). Positions of heavy metal, phosphorus, oxygen and some carbon atoms were determined from direct solution, other non-hydrogen atoms were found as maxima in the difference map of the electron density. All structures were refined by least-squares technique (SHELXL97 [46]). Pictures were processed by PLATON98 [47]. In general, the

hydrogen atoms of the phosphine moieties were fixed in theoretical positions using a riding model, with their isotropic thermal factors restrained to 1.2 multiple of *U*-value of corresponding carbon atoms. The hydrogen atoms of ester groups were restrained in the same way, using isotropic thermal factors of 1.2 for methylene and 1.5 for methyl groups.

The structure of *cis*-$[PtCl_2(\mathbf{3a})_2]$ contains a disordered molecule of dichloromethane. This disorder was preferably described by the presence of half-occupied solvent molecule with one of the chlorine atoms equally distributed over two positions, so the compound is therefore formulated as *cis*-$[PtCl_2(\mathbf{3a})_2] \cdot 0.5CH_2Cl_2$. In the crystal structure of *cis*-$[PtCl_2(\mathbf{3b})_2] \cdot PhMe \cdot H_2O$, rather unusual combination of toluene and water solvate molecules was found. Both *trans* palladium(II) complexes are centrosymmetric, having chloroform (*trans*-$[PdCl_2(\mathbf{3a})_2] \cdot 2CHCl_3$) or water (*trans*-$[PdCl_2(\mathbf{3b})_2] \cdot 2H_2O$) as solvates. The dinuclear complex shows also a centre of symmetry, possessing one half of the molecule as crystallographically independent unit, and chloroform solvate, giving the formula *trans*-$[Pd_2Cl_4(\mathbf{3a})_2] \cdot 2CHCl_3$.

The experimental and refinement data are listed in Table 7. All data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre as CCDC reference numbers 281318–281322.

Acknowledgements

This project was supported by the Grant Agency of the Charles University (grant No. 321/2005/B-CH/PrF). We also wish to thank V. Kubíček for MS measurements and K. Teubner and Dr. I. Císařová for X-ray data collection.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.024.

References

[1] (a) N. Pinault, D.W. Bruce, Coordin. Chem. Rev. 241 (2003) 1;
(b) B. Cornils, W.A. Herrmann, Aqueous-Phase Organometallic Catalysis, Wiley-VCH, 1998;
(c) F.R. Hartley, Supported Metal Complexes – A New Generation of Catalysts, D. Riedel Publishing Company, 1985.
[2] T.L. Schull, D.A. Knight, Coordin. Chem. Rev. 249 (2005) 1269.
[3] A.M. Herring, B.D. Steffey, A. Miedaner, S.A. Wander, D.L. Dubois, Inorg. Chem. 34 (1995) 1100.
[4] T.L. Schull, L.R. Olano, D.A. Knight, Tetrahedron 56 (2000) 7093.
[5] S. Lelievre, F. Mercier, F. Mathey, J. Org. Chem. 61 (1996) 3531.
[6] T.L. Schull, J.C. Fettinger, D.A. Knight, Inorg. Chem. 35 (1996) 6717.
[7] C. Liek, P. Machnitzki, T. Nickel, S. Schenk, M. Tepfer, O. Stelzer, Z. Naturforsch., B: Chem. Sci. 54 (1999) 1532.
[8] B.A. Harper, D.A. Knight, C. George, S.L. Brandow, W.J. Dressick, C.S. Dalcey, T.L. Schull, Inorg. Chem. 42 (2003) 516.
[9] S. Bischoff, A. Weigt, H. Miessner, B. Lucke, J. Mol. Catal. A 107 (1996) 339.
[10] G. Alberti, U. Costantino, S. Allulli, N. Tomassini, J. Inorg. Nucl. Chem. 40 (1978) 1113.
[11] D.D. Ellis, G. Harrison, A.G. Orpen, H. Phetmung, P.G. Pringle, J.G. deVries, H. Oevering, J. Chem. Soc., Dalton Trans. (2000) 671.
[12] S. Bischoff, A. Weigt, M. Kant, U. Schulke, B. Lucke, Catal. Today 36 (1997) 273.
[13] D. Villemin, P.A. Jaffres, B. Nechab, F. Courivaud, Tetrahedron Lett. 38 (1997) 6581.
[14] S. Bischoff, A. Köckritz, M. Kant, Top. Catal. 13 (2000) 327.
[15] A. Köckritz, A. Weigt, M. Kant, Phosphorus Sulfur Silicon Rel. Elem. 117 (1996) 287.
[16] J. Freiberg, A. Weigt, J. Prakt. Chem. 335 (1993) 337.
[17] I. Le Gall, P. Laurent, E. Soulier, J.Y. Salaun, H. des Abbayes, J. Organomet. Chem. 567 (1998) 13.
[18] G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, second ed., Wiley-Interscience, 1972.
[19] O. Herd, A. Hessler, M. Hingst, M. Tepper, O. Seltzer, J. Organomet. Chem. 522 (1996) 69.
[20] (a) V.D. Bianco, S. Doronzo, Inorg. Synth. 16 (1976) 161;
(b) W. Gee, R.A. Shaw, B.C. Smith, Inorg. Synth. 9 (1967) 19;
(c) G.W. Luther III, G. Beyerle, Inorg. Synth. 17 (1977) 186.
[21] There is no need to deoxygenate water and aqueous HCl, because the loss of Ph_2PH caused by dissolved oxygen is negligible on large scale. A smaller volume of non-dried THF can be used with a positive effect on the rate of Ph_2PLi formation [22]; no vigorous or uncontrolled reaction was observed. All this modifications did not affect the yield and/or purity of the product significantly.
[22] P. Brooks, M.J. Gallagher, A. Sarroff, Aust. J. Chem. 40 (1987) 1341.
[23] (a) for a review see B. Carboni, L. Monnier, Tetrahedron 55 (1999) 1197;
(b) J.M. Brunel, B. Faure, M. Maffei, Coordin. Chem. Rev. 178–180 (1998) 665.
[24] T. Imamoto, T. Oshiki, T. Kusumoto, K. Sato, J. Am. Chem. Soc. 112 (1990) 5244.
[25] M. Schröder, K. Nozaki, T. Hiyama, Bull. Chem. Soc. Jpn. 77 (2004) 1931.
[26] L. McKinstry, T. Livinghouse, Tetrahedron 51 (1995) 7655.
[27] S. Ganguly, J.T. Mague, D.M. Roundhill, Inorg. Chem. 31 (1992) 3500.
[28] T. Hayashi, M. Konishi, M. Kumada, Tetrahedron Lett. 21 (1979) 1871.
[29] F. Joó, Z. Tóth, J. Mol. Catal. 8 (1980) 369.
[30] J.L. Wedgwood, A.P. Hunter, R.A. Kresinski, A.W.G. Platt, B.K. Stein, Inorg. Chim. Acta 290 (1999) 189.
[31] P. Roffia, F. Conti, G. Gregori, Chem. Ind. (Milan) 53 (1971) 361.
[32] D.A. Redfield, J.H. Nelson, Inorg. Chem. 12 (1973) 15.
[33] (a) B.E. Mann, B.L. Masters, R.M. Slade, R.E. Stainbank, Inorg. Nucl. Chem. Lett. 7 (1971) 881;
(b) S. Berger, S. Braun, H.-O. Kalinowski, NMR Spectroscopy of the Non-Metallic Elements, Wiley, 1996, pp. 707–715.
[34] R.V. Parish, NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry, Ellis Horwood, 1990, pp. 61–69.
[35] S.H. Mastin, P. Haake, Chem. Commun. (1970) 202.
[36] G.K. Anderson, R.J. Cross, Chem. Soc. Rev. 9 (1980) 185, and references therein.
[37] (a) S.O. Grim, R.L. Keiter, Inorg. Chim. Acta 4 (1970) 56;
(b) R.D. Gillard, M.F. Pilbrow, J. Chem. Soc., Dalton Trans. (1974) 2320;
(c) D.M. Adams, J. Chatt, J. Gerratt, A.D. Westland, J. Chem. Soc. (1964) 734.
[38] (a) D.M. Adams, P.J. Chandler, J. Chem. Soc. A (1969) 588;
(b) R.J. Goodfellow, P.L. Goggin, L.M. Venanzi, J. Chem. Soc. A (1967) 1897.
[39] A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, 1995.

[40] H.P. Dijkstra, M.D. Meijer, J. Patel, R. Kreiter, G.P.M. van Klink, M. Lutz, A.L. Spek, A.J. Canty, G. van Koten, Organometallics 20 (2001) 3159.
[41] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, J. Chem. Soc. (1965) 3632.
[42] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52.
[43] http://www.mestrec.com.
[44] Z. Otwinowski, W. Minor, HKL DENZO and SCALEPACK Program Package by Nonius BV, Delft, 1997;
Z. Otwinowski, W. Minor, Meth. Enzymol. 276 (1997) 307.
[45] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92, Program for Crystal Structure Solution by Direct Methods;
A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[46] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement from Diffraction Data, Götingen, 1997.
[47] A.L. Spek, PLATON. A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands, 2002. (Available from: <http://www.cryst.chem.uu.nl/platon>).