Complexes of hydrophilic triphenylphosphines modified with *gem*-bis(phosphonate) moiety. An unusual simultaneous *cis* and *trans* arrangements in the Pt(II) dinuclear complex†

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New triphenylphosphines substituted with the *gem*-bis(phosphonate) moiety in the form of ethyl esters, tetraethyl [4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2a**) and octaethyl bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2b**), and the corresponding free acids **3a** and **3b** were prepared by a multi-step synthesis and characterized by multinuclear NMR spectroscopy and mass spectrometry. The ester ligands **2a** and **2b** were conveniently purified through their borane adducts. The X-ray structure of **2b**·$2BH_3$·H_2O was determined. Coordination properties of new ligands towards Rh(I), Pd(II) and Pt(II) ions were studied. ^{1}H, ^{31}P and ^{195}Pt NMR spectroscopy showed that ligands **2a** and **3a** form the expected [RhCl(η^2:η^2-cod)(**L**)] (cod = cycloocta-1,5-diene) and [MCl_2(**L**)$_2$] (M = Pd, Pt) complexes. The compounds **2b** and **3b** behave as bridging bidentate ligands forming dinuclear complexes of the {[RhCl(η^2:η^2-cod)]$_2$(μ-**L**-κ^2*P,P′*)} and [M_2Cl_4(μ-**L**-κ^2*P,P′*)$_2$] (M = Pd, Pt) type. These findings are consistent with mass spectrometry and far-IR and Raman spectroscopy results. X-Ray structures of *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$] and *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$] were determined; the dinuclear complex exhibits a different arrangement on the Pt(II) centres which was observed for the first time in the solid state. Salts of complexes of the free acid **3a** are highly soluble in water.

Introduction

Platinum group metal complexes, especially those with phosphine ligands, are often used as catalysts in various industrial and laboratory-scale processes. For the application of these catalysts in more sophisticated set-ups (*e.g.* heterogeneous or biphasic catalysis), it is necessary to make the complex soluble in polar solvents or attachable to a solid support. This problem can be solved, more or less easily, by the modification of the phosphine scaffold with an appropriate moiety. There is a number of various suitable functionalities[1] but obviously each such moiety has its advantages and disadvantages. When synthetic availability, acid–base properties and/or hydrophilicity of these moieties are compared, the phosphonate moiety seems to be very suitable.[2] It not only makes the ligands (and its complexes) very water-soluble in a wide pH-range but it can also be used to anchor the molecules to oxide solid supports such as TiO_2, SiO_2, Al_2O_3 or ZrO_2.[3] It can also be bound in a zirconium phosphonate/phosphate three-dimensional framework[4–6] or used for stabilization of metal clusters in aqueous solution.[7,8] The number of phosphonate groups and their mutual position affects strongly all the properties mentioned above, as well as the coordination behaviour.

Thus, to continue our previous work,[9] we have decided to synthesize *gem*-bis(phosphonate)-modified triphenylphosphine-based ligands and study their coordination properties. In the literature, only one phosphine type substituted with a *gem*-bis(phosphonate) group, a derivative of diphenylalkylphosphine,[4,10,11] has been described so far despite the availability of many synthetic routes for the introduction of the bis(phosphonate) moiety due to the enormous interest in bis(phosphonates) for medical utilization.[12] The bis(phoshonate) moiety offers a more polar character and a higher solubility of complexes in aqueous solution as well as stronger interaction with oxide supports compared with other polar groups which have been used for phosphine modification until now.

Results and discussion

Ligand syntheses

The synthesis of ligands is shown in Scheme 1. 4-Bromomethyl-1-iodobenzene (IBnBr) was reacted with tetraethyl methylene-bis(phosphonate) sodium salt (Na^+TMBP^-) in THF.[13] The reaction resulted in a mixture of mono- and disubstituted products **1a** and **1b**, in a ratio dependent on the relative amount of TMBP, NaH and IBnBr in the reaction mixture. The C–H acidity of **1a** is higher than that of the parent TMBP and, therefore, **1a** formed during the reaction reacts with Na^+TMBP^- forming free TMBP and the sodium salt of **1a**. This salt further reacts with IBnBr leading to the compound **1b** which was always present in the product mixture. The best results for production of **1a** were obtained employing the NaH:TMBP:IBnBr ratio of 1.2:1:1. Higher excesses of NaH and IBnBr (typically 3.5:1:2) led to pure **1b**. The reactions were

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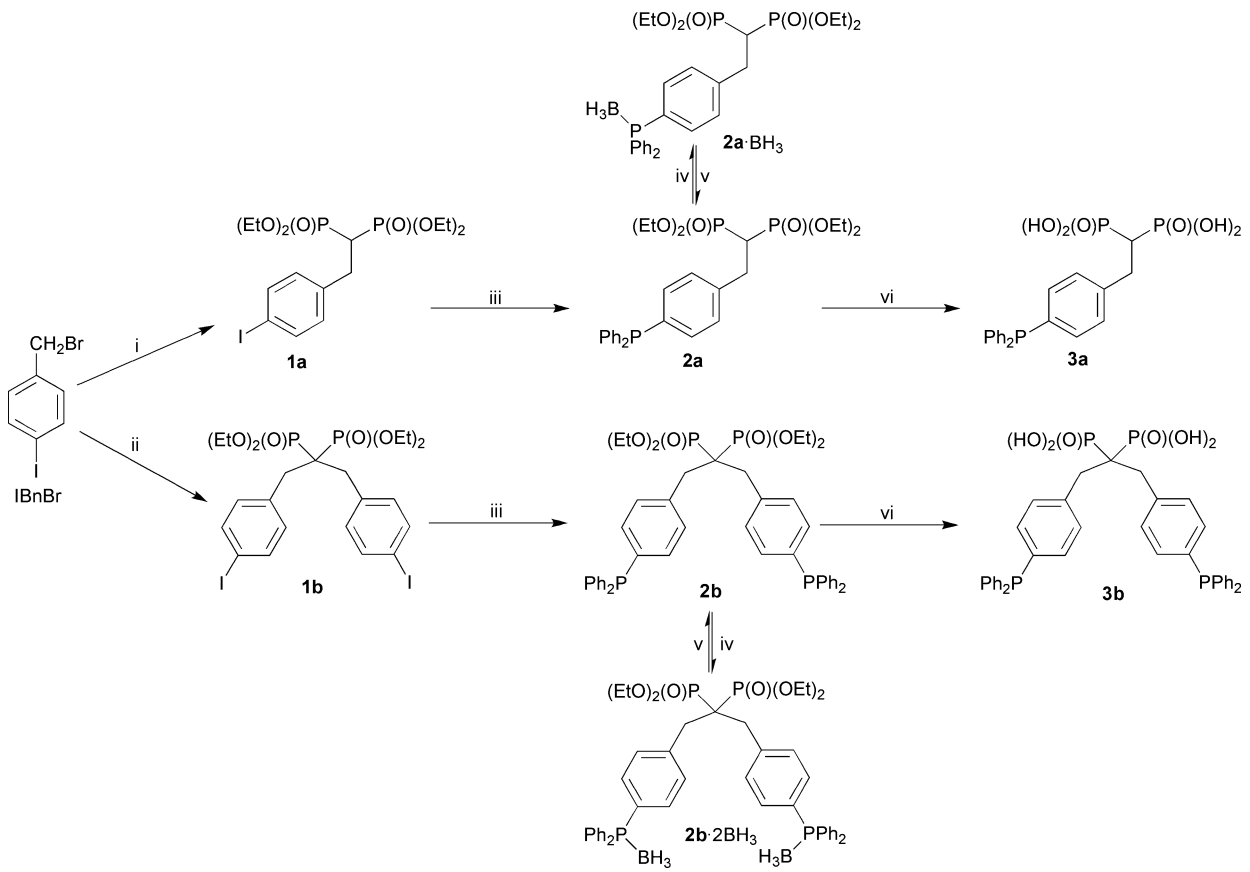
† Electronic supplementary information (ESI) available: δ_P of prepared organic phosphorus-containing compounds, characterization of the **2a** and **2b** complexes, coordination shift of ^{31}P NMR resonances, selected geometric parameters found in the structure of **2b**·$2BH_3$·H_2O, experimental X-ray data and figures of $^{31}P\{^1H\}$ NMR spectra of the complexes. CCDC reference numbers 705469–705471. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b818259k



Scheme 1 Synthesis of the ligands. (i) NaH:TMBP:IBnBr 1.2:1:1, THF; (ii) NaH:TMBP:IBnBr 3.5:1:2, THF; (iii) $HPPh_2$, KOAc, $Pd(OAc)_2$, toluene; (iv) 1.1 eq. BH_3·THF, THF; (v) a) HBF_4·Me_2O, b) sat. aq. $NaHCO_3$; (vi) HCl (6M aq.), 90 °C.

monitored by ^{31}P NMR spectroscopy, as the signals of TMBP, **1a** and **1b** were well separated (19.6, 22.7 and 23.7 ppm, respectively). The products were separated by column chromatography (silica, CH_2Cl_2:THF 2:1).

Introduction of the diphenylphosphanyl moiety was achieved by the palladium-catalyzed P–C coupling analogously as described elsewhere.[9,14] The reaction mixtures were kept at ~70 °C; at higher temperatures some degradation occurred. The crude products were contaminated mainly by the unreacted $HPPh_2$ and, in order to remove the impurity, the products were purified through borane adducts by the standard borane-protection/purification/deprotection procedure.[15] This procedure completely removed any trivalent phosphorus impurities; impurities still present (according to the ^{31}P NMR data) contained only pentavalent phosphorus and not one exceeded <1.5%. Single crystals of bis(borane)adduct of **2b** suitable for X-ray diffraction analysis were obtained (*vide infra*).

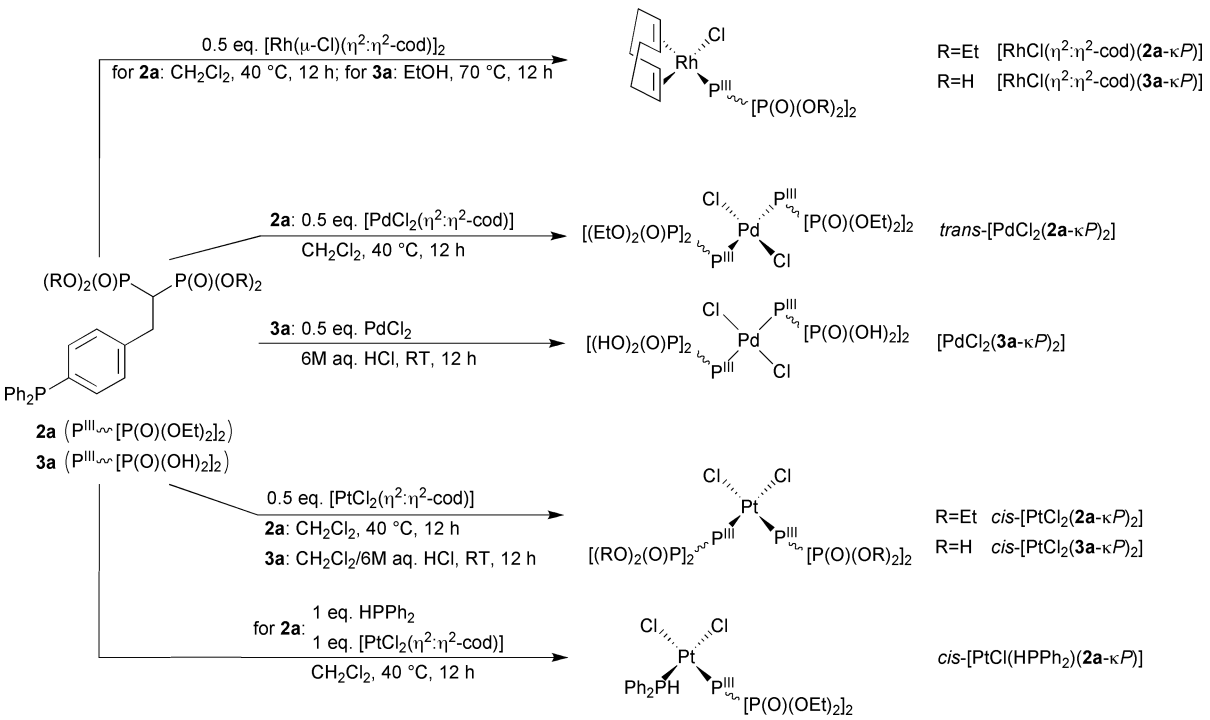
Free acids **3a** and **3b** were prepared by hydrolysis of the esters **2a** and **2b** in 6M aq. HCl (90 °C, 2 d).[9] A higher purity of the prepared acids, if compared to the initial esters, was caused by a precipitation of impurities during the hydrolytic procedure.

Synthesis of complexes

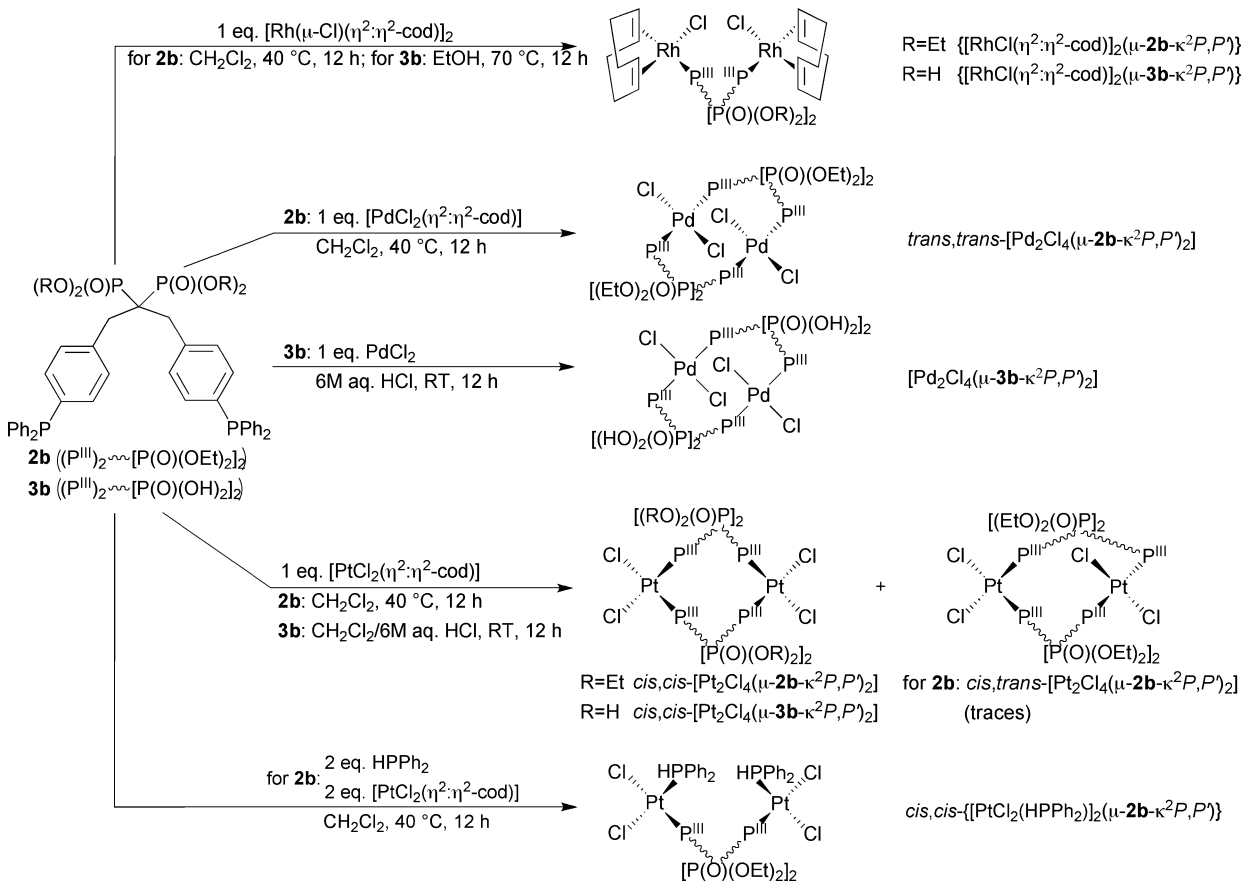
In order to characterize the coordination behaviour of **2a**, **2b**, **3a** and **3b**, we have prepared and studied their Rh(I), Pd(II) and Pt(II) complexes.

The Rh(I) complexes of **2a** and **2b** (Schemes 2 and 3) were prepared in dichloromethane solution at slightly elevated temperature, using $[Rh(\mu\text{-}Cl)(\eta^2\text{:}\eta^2\text{-cod})]_2$ as the source of the metal ion. The (metal atom):(phosphine atom) ratio was 1:1, because the phosphine only breaks the dimeric precursor without substitution of the olefin. The Pd(II) and Pt(II) complexes of **2a** and **2b** (Schemes 2 and 3) were prepared similarly with the ligands, metal precursors $[MCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ and products being well soluble in dichloromethane; the used (metal atom):(phosphine atom) ratio was 1:2. After work-up, the complexes of **2a** were further purified by column chromatography, but the final product still contained trace amounts of the starting 1,5-cod complex. All resulting complexes of ester ligands **2a** and **2b** are well soluble in polar solvents (THF, $CHCl_3$, CH_2Cl_2), slightly soluble in toluene and insoluble in other hydrocarbons.

When impure ligands obtained directly from the coupling reaction were used for preparation of the Pt(II) complexes, the ^{31}P NMR spectrum of the product contained additional signals with a rather complex coupling pattern. It suggested that these signals belong to the mixed diphenylphosphine-**L** complexes, *cis*-$[PtCl_2(\mathbf{2a}\text{-}\kappa P)(HPPh_2)]$ and *cis,cis*-$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')(HPPh_2)_2]$ formed because of the presence of a small amount of the unreacted $HPPh_2$. A literature search showed, surprisingly, that only a very limited number of platinum(II) complexes containing the intact diphenylphosphine (*i.e.* not in the form of a phosphide anion) and another phosphine have been described.[16,17] To confirm the



Scheme 2 Synthesis of complexes of the monophosphine ligands **2a** and **3a**.



Scheme 3 Synthesis of complexes of the bis(phosphine) ligands **2b** and **3b**.

nature of these by-products and to gain more data on such mixed $HPPh_2$–phosphine complexes we decided to synthesize them by targeted preparation from the equimolar mixture of $HPPh_2$, the appropriate phosphine ligand and the metal precursor in the same way as described above for the other phosphine complexes (Schemes 2 and 3). The *cis,cis*-[Pt_2Cl_4(μ-**2b**-κ^2P,P')($HPPh_2$)$_2$] complex is the only known dinuclear complex containing $HPPh_2$ where diphenylphosphine is present as a non-bridging ligand.

Rh(I) complexes of **3a** and **3b** were obtained by mixing an ethanolic suspension of [Rh(μ-Cl)(η^2:η^2-cod)]$_2$ with the appropriate phosphine ligand in ethanol and heating overnight at 70 °C. The Pd(II) complexes of **3a** and **3b** were prepared by treating the suspension of $PdCl_2$ in 6M aq. HCl with the phosphine ligand dissolved in the same solvent; the yellow product precipitated immediately. The Pt(II) complexes of **3a** and **3b** were prepared by vigorous stirring of [$PtCl_2$(η^2:η^2-cod)] dichloromethane solution with the phosphine ligand dissolved in aq. 6M HCl. The products precipitated in the dichloromethane phase. The complex syntheses are compiled in Schemes 2 and 3.

NMR spectroscopy

NMR spectroscopy of ligands. For **1a–3a**, the ^{1}H NMR spectra contain a characteristic pattern of the ethylidene group (α and β hydrogen atoms) due to phosphorus–hydrogen and hydrogen–hydrogen coupling (α: triplet of triplets, $^2J_{PH}$ ~24 Hz, $^3J_{HH}$ ~6.5 Hz; β: triplet of doublets, $^3J_{PH}$ ~16.5 Hz, $^3J_{HH}$ ~6.5 Hz). On the contrary, **1b–3b** have the β hydrogen atoms only (triplet, $^3J_{PH}$ ~16.5 Hz). However, the aromatic region of the ^{1}H NMR spectra is unresolved.

In the ^{13}C{^{1}H} NMR spectra, the phosphorus–carbon coupling was well resolved in both bis(phosphonate) and phosphine parts of the ligand molecule. In the phosphonate part, the ethylidene carbon atoms signals were found at δ_C ~40 ppm (α: triplet, $^1J_{PC}$ ~132 Hz) and δ_C ~30 ppm (β: multiplet). In addition, the signal of quarternary aromatic carbon atom was found at δ_C ~138 ppm (multiplet). In the phosphine part of the molecule, the doublets with $^1J_{PC}$ ~10 Hz, $^2J_{PC}$ ~20 Hz and $^3J_{PC}$ ~7 Hz were found for the aromatic carbon signals. However, the interpretation of aromatic region is difficult because of a long-range coupling of the aromatic carbon atoms with both sets of non-equivalent phosphorus atoms. The significantly higher values of P^{III}–C coupling constants on the benzene ring bridging the phosphine and bis(phosphonate) parts than on the other rings were observed. The detailed assessment of the ^{13}C spectra was based on the results reported for analogous compounds.[9]

The ^{31}P NMR spectra contain the signals of the phosphine moiety at δ_P ~(−6) ppm (similar to the value for triphenylphosphine itself, −4.7 ppm)[18] and bis(phosphonate) with δ_P in range of 20.2–22.8 for **1a–3a** and 23.7–24.8 for **1b–3b**. The chemical shifts are pH- and solvent-dependent, but in general follow the trend δ(tetraethyl ester) ≥ δ(acid) > δ(salt).[19] Further chemical modifications of the phosphine phosphorus atom (protonation to phosphonium, adduct formation with borane) affect the chemical shifts as indicated in Table S1.†

NMR spectroscopy of complexes. The ^{1}H NMR spectra of Rh(I), Pd(II) and Pt(II) complexes of **2a**, **2b**, **3a** and **3b** were similar to those of the free ligands. The ^{31}P chemical shifts of the *gem*-bis(phosphonate) moiety were always close to those of the corresponding free ligands with no sign of phosphoryl–metal interaction. Therefore, mostly ^{31}P (phosphine signals) and ^{195}Pt (measured where possible) NMR spectra are discussed below.

The ^{1}H NMR spectra of the Rh(I) complexes contained signals of the phosphine ligands (virtually unaffected by the coordination) and the coordinated cod (its δ_H coordination shift confirms the presence of chloride and phosphine ligands in the complexes[20]). In ^{31}P NMR spectra, the phosphine signals (~30 ppm) were split into a doublet with $^1J_{RhP}$ ~150 Hz. A very minor signal of the ligand phosphinoxide was often present due to the oxidation of the ligand excess during work-up. There were no signs of *P,O*-hemilabile behaviour of the ligands. The NMR spectra fully support the suggested structure of the complexes as [RhCl(η^2:η^2-cod)(**L**-κ*P*)] (ligands **2a** and **3a**) and {[RhCl(η^2:η^2-cod)]$_2$(μ-**L**-κ^2P,P')} (ligands **2b** and **3b**).

In the ^{31}P NMR spectra of palladium(II) complexes of **2a** and **2b**, the phosphine signal is slightly overlapping with the phosphonate signal. Stereochemical information was obtained from the ^{31}P-coordination chemical shift ($\Delta\delta_P = \delta_P$(coord.) − δ_P(free))[21] and confirmed by the analysis of *cis*/*trans* isomerisation of the complexes in three solvents with different polarity (chloroform, toluene, methanol). *Cis*/*trans* isomerism of many similar Pd(II) complexes in different solvents has been well documented[21] and our data correlate well with those for known complexes (Table S2†). D_2O solutions of Pd(II) complexes with **3a** and **3b** were prepared by careful addition of ~0.2M NaOD/D_2O until complete dissolution. These solutions were moderately stable up to pH 9; a long standing or higher pH value led to their degradation. From the comparison of the calculated and observed values of $\Delta\delta_P$ (Table S3†), it can be concluded that the complexes have predominantly the *cis*-arrangement; the *cis* arrangement is expected to be preferred with increasing polarity of solvent. Despite a number of attempts to obtain single crystals suitable for X-ray diffraction analysis and to confirm the geometry, only crystals of *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$] were successfully obtained (*vide infra*).

Analysis of ^{31}P-coordination chemical shift ($\Delta\delta_P$),[21] and ^{195}Pt–^{31}P coupling interaction ($^1J_{PtP}$)[9] in both ^{195}Pt (a triplet) and ^{31}P NMR (a quasi-triplet; a central line with satellites in the ratio 1:4:1) spectra confirmed the expected[22] stoichiometry (generally [$PtCl_2$(P(III))$_2$]) and *cis*-stereochemistry ($^1J_{PtP}$ ~3700 Hz) of the prepared Pt(II) complexes (Tables S2 and S3†). To have a complete set of data, the *trans*-isomers were prepared *in situ* by photochemical isomerisation.[23] After irradiation, a new set of signals appeared in the ^{31}P and ^{195}Pt NMR spectra, which apparently belongs to the *trans*-complex ($^1J_{PtP}$ about ~2600 Hz, $\Delta\delta_P$ close to the expected values; Table S2†). All attempts at preparation of single crystals for X-ray diffraction analysis failed except one. A few single crystals of the *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2P,P')$_2$] complex crystallized from the mother liquor after removal of the precipitated *cis,cis*-[Pt_2Cl_4(μ-**2b**-κ^2P,P')$_2$] complex. The very unusual arrangement was definitely confirmed by X-ray diffraction study. The ^{31}P NMR spectrum of this compound showing two different phosphine signals (13.8 and 20.0 ppm) with different $^1J_{PtP}$ (3679 and 2639 Hz) as well as infrared spectra (see below) are in accord with the presence of the *cis*- and *trans*-arrangements on the metal centres. Spectra of the mixed $HPPh_2$-**L** complexes are more complex. Both phosphine signals in

the $^{31}P\{^{1}H\}$ NMR spectrum are shifted downfield unequally and split into a doublet of 1:4:1-quasi-triplets due to the mutual P–P interaction ($^{2}J_{PP}$ ~15 Hz) and the interaction with platinum (with a similar $^{1}J_{PtP}$ for $HPPh_2$ and **2a** or **2b**, ~3580 Hz) (Fig. 1A). It points to the *cis*-arrangement of the phosphines and to the stoichiometry [$PtCl_2$(**L**)(**L′**)]. In proton-coupled ^{31}P NMR spectrum, the diphenylphosphine signal is further split into a doublet due to the P–H bond ($^{1}J_{PH}$ ~400 Hz, Fig. 1B). The ^{195}Pt NMR confirms the structural motif obtained from the ^{31}P NMR measurement (triplet with $^{1}J_{PtP}$ ~3580 Hz; the coupling constants of **2a** or **2b** and $HPPh_2$ had the same value). It should be noted that, surprisingly, these data are the only published NMR data for mixed $HPPh_2$-phosphine platinum(II) complexes except for a complex of the $HPPh_2$-$^{n}Bu_3P$[17a] and the $HP(Mes)_2$-PPh_3[17b] pairs. In the case of complexes with **3a** and **3b**, the coordination chemical shift is lower than expected. The δ_P of bis(phosphonate) is shifted to ~20 ppm as an effect of pH (see Experimental). Data for *trans*-isomers were not accessible, because the photochemical isomerization did not proceed in polar (aqueous) solutions.[9,23] No crystals suitable for X-ray diffraction study were prepared in the case of the **3a** and **3b** complexes.

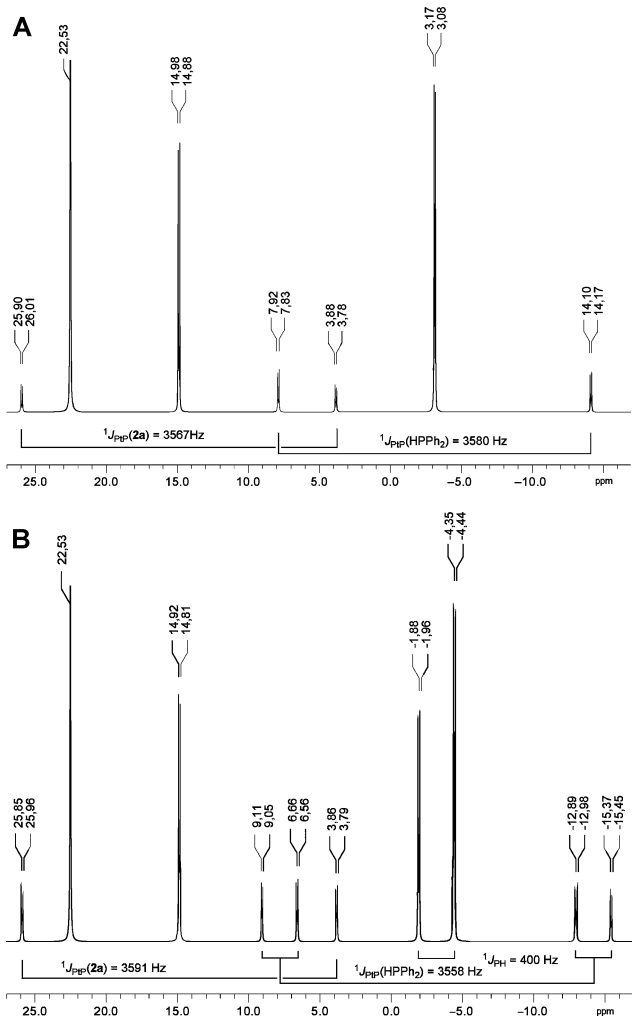


Fig. 1 $^{31}P\{^{1}H\}$ (A) and ^{31}P NMR (B) spectra of the *cis*-[$PtCl_2$(**2a**-κ*P*)($HPPh_2$)] complex.

Crystal structures

Crystal structure of 2b·2BH$_3$·H$_2$O‡. Crystals suitable for X-ray diffraction study were prepared by vapour diffusion of hexane into THF solution of **2b**·2BH_3 at +5 °C. The independent unit contains one molecule of the phosphine–BH_3 adduct together with the water solvate. The geometries around the phosphine phosphorus atoms are roughly tetrahedral (angles 105–113°), with P–C distances around 1.81–1.82 Å and a P–B coordination bond of 1.91 Å. Geometry of the phosphonate groups is also tetrahedral (101–116°), with a phosphoryl bond length of 1.47 Å, P–O(ester) distances of 1.57 Å, and a P–C bond length of 1.84 Å. The P1A–C1–P1B angle is 110°. All other bond lengths and angles also fall into the expected ranges.[24] Crystal solvated water forms medium-to-strong (2.8–2.9 Å) hydrogen bonds to phosphoryl oxygen atoms of the bis(phosphonate) unit. The molecular structure of **2b**·2BH_3 is depicted in Fig. 2 and selected structural parameters are given in Table S4.†

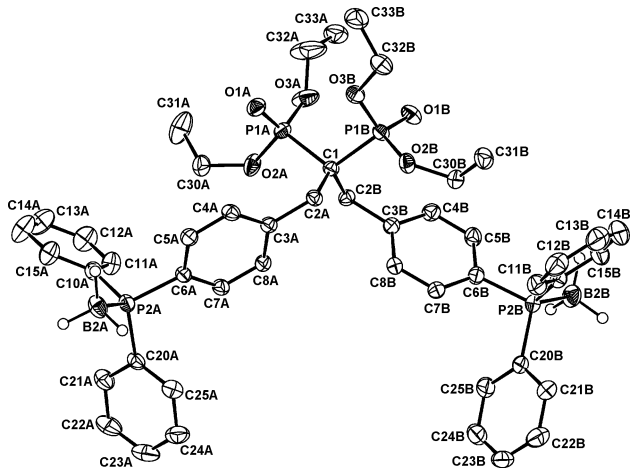


Fig. 2 The molecular structure of the **2b**·2BH_3 adduct found in the structure of **2b**·2BH_3·H_2O. Hydrogen atoms (except the boran bound) were omitted for clarity; the thermal ellipsoids are drawn with 50% probability.

Crystal structure of *trans*-[$PdCl_2$(2a-κ*P*)$_2$]·2$CHCl_3$‡. The Pd(II) coordination sphere is planar and centrosymmetric, with a small distortion of the bond angles P–Pd–Cl 87.0° and 93.0°. The Pd(II) ion is located on the crystallographic centre of symmetry

‡ Selected experimental crystallographic data: Crystal data for **2b**·2BH_3·H_2O. $C_{47}H_{60}B_2O_7P_4$, M = 882.45, monoclinic, a = 23.2795(2), b = 14.6939(1), c = 14.2210(3) Å, β = 105.9901(6)°, U = 4676.32(10) Å^3, T = 150 K, space group $P2_1/c$ (no. 14), Z = 4, 69 921 reflections measured, 10 721 unique (R_{int} = 0.040) which were used in all calculations. The final $wR(F^2)$ was 0.1190 (all data).Crystal data for *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$. $C_{58}H_{76}Cl_8O_{12}P_6Pd$, M = 1541.01, triclinic, a = 8.2868(3), b = 10.5786(3), c = 21.4686(7) Å, α = 103.009(2), β = 92.235(2), γ = 107.821(2)°, U = 1733.86(10) Å^3, T = 150 K, space group P-1 (no. 2), Z = 1, 31622 reflections measured, 7631 unique (R_{int} = 0.077) which were used in all calculations. The final $wR(F^2)$ was 0.1202 (all data).Crystal data for *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]·7CH_2Cl_2. $C_{101}H_{118}Cl_{18}O_{12}P_8Pt_2$, M = 2799.98, triclinic, a = 17.5897(2), b = 18.3345(3), c = 20.9857(3) Å, α = 84.3179(7), β = 68.7386(9), γ = 69.7078(9)°, U = 5913.0(2) Å^3, T = 150 K, space group P-1 (no. 2), Z = 2, 109563 reflections measured, 26 966 unique (R_{int} = 0.040) which were used in all calculations. The final $wR(F^2)$ was 0.1515 (all data).

(Fig. 3). The lengths of coordination bonds are 2.33 Å for Pd–P and 2.30 Å for Pd–Cl that is in the typical range of atom distances for such types of Pd(II) complexes.[24] Selected geometrical parameters are compiled in Table 1.

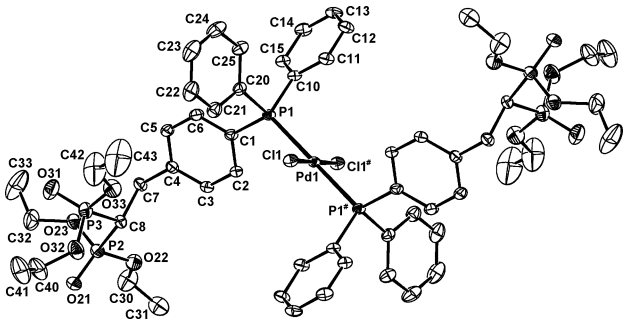


Fig. 3 The molecular structure of the *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$] complex found in the structure of *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$. Hydrogen atoms were omitted for clarity; the thermal ellipsoids are drawn with 30% probability.

Crystal structure of *cis,trans*-[Pt_2Cl_4(μ-2b-κ^2*P,P′*)$_2$]·7CH_2Cl_2‡. The crystals appeared as a very minor product from the mother solution after precipitation of the *cis,cis* isomer; the compound was hardly detectable by NMR spectroscopy even in this mother solution (see also above). In the structure of this Pt(II) complex, a very unusual feature appeared—one of the platinum atoms (Pt1) has a *cis*- and the other one (Pt2) a *trans*-arrangement of the coordination sphere (Fig. 4). This coordination mode in dinuclear complexes has been observed for the first time. Surroundings of both metal centres are slightly distorted from the ideal square planar arrangement. The sphere of Pt1 is tetrahedrally distorted and that of Pt2 has tetragonal-pyramidal distortion. The large distortion from the regular square-planar geometry caused by the sterically demanding ligand **2b** can be seen from the bond angle P1A–Pt1–P2C 97.0° in the *cis*-Pt1 unit. The

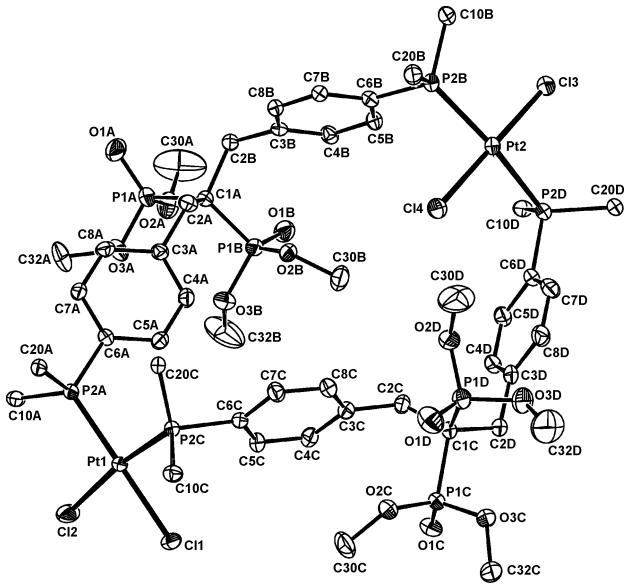


Fig. 4 The molecular structure of the *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$] complex found in the structure of *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]·7CH_2Cl_2. Hydrogen atoms are omitted and only pivot atoms of phenyl groups are shown for clarity. The methyl groups of ethyl esters were omitted as well. The thermal ellipsoids are drawn with 40% probability.

value is significantly higher than the Cl1–Pt1–Cl2 angle (86.1°). The Pt1–P bonds (2.25 and 2.27 Å, respectively) are noticably shorter than the Pt1–Cl bonds (2.34 and 2.37 Å, respectively). Contrary to the coordination sphere of Pt1, parameters of the coordination sphere of the *trans*-Pt2 centre are more regular, with P–Pt2–Cl angles in the range of 87.2–93.2°, and Pt2–Cl and Pt2–P bond distances in the range of 2.31–2.33 Å. Selected geometrical parameters are compiled in Table 1. This structure suggests that the ligand **2b** is prone to serve as a bridge in the binuclear complexes. The presence of the *cis*- and *trans*-isomers in one molecule is enabled by a flexible (and rather long)

Table 1 Selected interatomic distances (Å) and bond angles (°) found in the crystal structures of the *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$ and *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]·7CH_2Cl_2 complexes

trans-[$PdCl_2$(**2a**-κ*P*)$_2$]		*cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]			
		cis		*trans*	
Distances (Å)					
Pd1–P1	2.3276(8)	Pt1–P2A	2.247(1)	Pt2–P2B	2.309(2)
Pd1–Cl1	2.3023(8)	Pt1–P2C	2.266(2)	Pt2–P2D	2.307(2)
		Pt1–Cl1	2.365(1)	Pt2–Cl3	2.329(2)
		Pt1–Cl2	2.340(2)	Pt2–Cl4	2.315(2)
Angles (°)					
P1–Pd1–P1ª	180	P2A–Pt1–P2C	96.95(5)	P2B–Pt2–P2D	168.65(5)
P1–Pd1–Cl1	92.99(3)	P2A–Pt1–Cl1	176.12(6)	P2B–Pt2–Cl3	93.21(5)
P1–Pd1–Cl1ª	87.01(3)	P2A–Pt1–Cl2	91.23(5)	P2B–Pt2–Cl4	88.08(5)
Cl1–Pd1–Cl1ª	180	P2C–Pt1–Cl1	85.97(5)	P2D–Pt2–Cl3	87.16(5)
		P2C–Pt1–Cl2	170.55(6)	P2D–Pt2–Cl4	90.69(5)
		Cl1–Pt1–Cl2	86.07(6)	Cl3–Pt2–Cl4	175.27(6)

ª Centrosymmetrically related atom.

Table 2 Values of valence vibrations ν_{M-Cl} of the Pd(II) and Pt(II) complexes in Raman and Far-IR spectra and the corresponding stereochemistry of the complexes

Complex	IR ν_{M-Cl} (cm^{-1})[a]	Raman ν_{M-Cl} (cm^{-1})[a]	Geometry
$[PdCl_2(\mathbf{2a}\text{-}\kappa P)_2]$	361s	307s	*trans*
$[Pd_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$	357s	303s	*trans*
$[PdCl_2(\mathbf{3a}\text{-}\kappa P)_2]$	284m, 305m	306br m	*cis,trans*[c]
$[Pd_2Cl_4(\mu\text{-}\mathbf{3b}\text{-}\kappa^2 P,P')_2]$	(290, 314)m, 355m	–[b]	*cis,trans*[c]
$[PtCl_2(\mathbf{2a}\text{-}\kappa P)_2]$	296s, 320s	298s, 320s	*cis*
$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$	296s, 320s	297s, 321s	*cis*
$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$[d]	298s, 319s, 343s	—	*cis,trans*
$[PtCl_2(\mathbf{3a}\text{-}\kappa P)_2]$	287s, 316s	287m, 316s	*cis*
$[Pt_2Cl_4(\mu\text{-}\mathbf{3b}\text{-}\kappa^2 P,P')_2]$	293s, 319s	294m, 319s	*cis*
$[PtCl_2(\mathbf{2a}\text{-}\kappa P)(HPPh_2)]$	293s, 317s	–[b]	*cis*
$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')(HPPh_2)_2]$	294s, 319s	–[b]	*cis*

[a] s = strong, m = medium, br = broad. [b] Decomposed under laser irradiation. [c] Obtained as a mixture of isomers. [d] Minor by-product characterized by X-ray diffraction as the *cis,trans*-$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$ complex (*vide supra*).

C_3-chain connecting the two triphenylphosphine units in the *para* position.

This simultaneous *cis*/*trans* coordination arrangement has been only very recently observed in dinuclear Pd(II) complexes with ligands derived from [2-(pyridin-2-yl)ethyl]diphenylphosphine.[25] Depending on the steric demands of other substituents on the ligand skeleton, *cis*/*trans* or *trans*/*trans* configurations were found. It was explained by the presence of a rather flexible three-atom chain between pyridine nitrogen and phoshine phosphorus donor atoms. Two *cis* and one *trans* configuration was also observed in a trinuclear Pd(II) complex with 2,6-bis(diphenylphosphanyl)pyridine.[26]

Far-infrared and Raman spectroscopy

Stereochemistry of the prepared complexes in the solid phase was studied by Far-IR and Raman spectroscopies. The number of valence vibration bands (~300 cm^{-1}) is determined by the coordination polyhedron symmetry and, in the case of square-planar complexes $[MX_2(\mathbf{L})_2]$, it can be used to distinguish between the more symmetrical *trans* (one band) and less symmetrical *cis* isomers (two bands).[27] The wave numbers of the M–Cl valence vibrations observed for the prepared complexes are compiled in Table 2.

From the data in Table 2, it can be assumed that all isolated Pt(II) complexes (except one) have *cis* configuration and the $[PdCl_2(\mathbf{2a}\text{-}\kappa P)_2]$ and $[Pd_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$ complexes have *trans* configuration in the solid state. For the $[PdCl_2(\mathbf{2a}\text{-}\kappa P)_2]$ complex, the *trans*-configuration was also confirmed by the single crystal diffraction. In the case of the $[PdCl_2(\mathbf{3a}\text{-}\kappa P)_2]$ and $[Pd_2Cl_4(\mu\text{-}\mathbf{3b}\text{-}\kappa^2 P,P')_2]$ complexes, two or three bands appeared, probably due to the presence of both *cis*- and *trans*-species. The results are in good agreement with data obtained previously for complexes with similar ligands; the *cis* configuration of Pd(II) complexes with **3a** and **3b** can be caused by the inter- or intramolecular hydrogen bond system involving the *gem*-bis(phosphonic) moiety.[9,28]

Mass spectrometry

The mass spectra of the complexes with **2a** and **2b** were recorded (complexes with the acid ligands **3a** and **3b** could not be measured due to their large charge). The ions formed by an addition of H^+ or Na^+ or by an elimination of Cl^- to form $[MCl(\mathbf{2a})_2]^+$ or $[M_2Cl_3(\mathbf{2b})_2]^+$ were observed in the positive mode. In the negative mode, mostly the ions formed by the ethyl group elimination were found. The *m*/*z* values of the molecular ions correspond well to the theoretical M_r for mononuclear $[MCl_2(\mathbf{2a})_2]$ and binuclear $[M_2Cl_4(\mathbf{2b})_2]$ complexes (see Experimental part).

Experimental

General

All manipulations involving air-sensitive compounds were performed under an atmosphere of argon (5.6, Linde) using standard Schlenk techniques. Dry solvents were prepared by standard purification procedures,[29] distilled under argon and stored over 4 Å molecular sieves in an argon atmosphere: Et_2O (Lachema, distilled from Na), CH_2Cl_2 (Lachema, distilled from P_2O_5), *N*,*N*-dimethylacetamide (Fluka, vacuum-distilled from BaO), THF (Lachema, distilled from Na,K/benzophenone), toluene (Lachema, distilled from Na,K/benzophenone), ethyl acetate, hexane, chloroform and methanol (Lachema, used as received), 35% aq. HCl (Lachema, distilled under Ar). Anhydrous KOAc (Acrōs) and $Pd(OAc)_2$ (Strem) were dried by prolonged heating at 90 °C *in vacuo*.

Diphenylphosphine, 4-iodotoluene and 4-bromomethyl-1-iodobenzene,[9] tetraethyl methylene-bis(phosphonate),[30] $[PdCl_2(\eta^2\text{:}\eta^2\text{-cod})]$,[31] $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$[32] and $[Rh(\mu\text{-Cl})(\eta^2\text{:}\eta^2\text{-cod})]_2$ [33] were prepared by literature procedures. Other chemicals were obtained from commercial sources and used without further purification.

NMR spectra: ^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) $\delta = 0.00$ ppm; $CHCl_3$ (internal) $\delta = 77.00$ ppm], ^{31}P [161.9 MHz, 85% H_3PO_4 (external) $\delta = 0.00$ ppm] and ^{195}Pt [85.6 MHz, K_2PtCl_4, saturated solution in D_2O (external) $\delta = 1620$ ppm] were recorded on a 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. Deuterated solvents, D_2O (99.9% D), $CDCl_3$ (99.8% D) and CD_3OD (99.8% D) from Chemtrade, were used as received. The atom numbering scheme of the compounds is given in Fig. 5. The NMR spectra presented in Fig. 1 were obtained by deconvolution of the experimental data in program Mestre-C 4.9.9.6.[34]

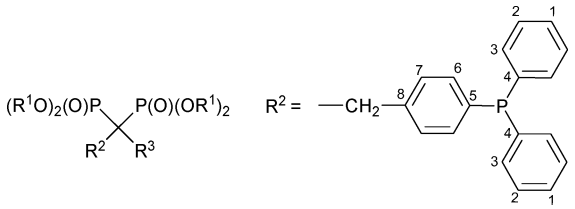


Fig. 5 Structures and numbering scheme of the prepared ligands: **2a** (R^1 = Et, R^3 = H), **2b** (R^1 = Et, $R^3 = R^2$), **3a** ($R^1 = R^3$ = H) and **3b** (R^1 = H, $R^3 = R^2$).

Mass spectra were measured on a Bruker spectrometer ESQUIRE 3000 equipped with an electrospray ion source and ion trap in positive/negative mode. Far-IR spectra (50–600 cm^{-1}) were obtained on the MAGNA 760 (Nicolet). Samples were measured at 25 °C in polyethylene pellets under dry air. Raman spectra (100–600 cm^{-1}) were recorded on the same device with the NEXUS NICOLET Raman module (Nd-YVO_4 laser, λ = 1064 nm). For thin layer chromatography, Merck aluminium foils with silica gel 60 F254 or aluminium oxide 60 F254 impregnated with fluorescent dye were used. Elemental analyses were performed at the Institute of Macromolecular Chemistry (Prague). However, analyses of phosphonic acid metal complexes are generally incorrect due to an incomplete combustion of the samples as a consequence of formation of metal phosphates (holding undecomposed organic matter) as a final product; so, elemental analyses of the metal complexes were not recorded.

Tetraethyl (4-iodobenzyl)methylene-bis(phosphonate) (1a). The compound was prepared analogously to the reported procedure.[13a,c] To a stirred suspension of NaH (0.88 g, 20.2 mmol, 1.2 eq.; 55% in mineral oil) in THF (10 mg) in a 100-ml Schlenk flask with a rubber septum, the solution of TMBP (4.85 g, 16.8 mmol) in THF (10 ml) was added dropwise by means of a syringe under ice-cooling. The resulting mixture was stirred for 2 h at room temperature. Then, the solution of IBnBr (5.00 g, 16.8 mmol) in THF (10 ml) was added in one portion by means of a syringe. The resulting white slurry was stirred overnight at RT and checked by TLC (SiO_2; CH_2Cl_2:THF 2:1; UV detection; R_f = 0.5). The following manipulations were performed in air. The reaction was carefully quenched by water (20 ml), stirred for 5 min and the mixture was extracted with dichloromethane (4 × 25 ml). Combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated. The product was purified by column chromatography (SiO_2, CH_2Cl_2:THF 2:1, R_f = 0.5) and dried *in vacuo* by 60 °C to obtain a yellowish oil (3.96 g, 46% based on IBnBz; purity 98+% according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.21 (CH_3, 12H, td, $^3J_{HH}$ = 7.1 Hz, $^4J_{PH}$ = 3.8 Hz); 2.50 (CH–P, 1H, tt, $^2J_{PH}$ = 23.8 Hz, $^3J_{HH}$ = 6.4 Hz); 3.11 (CH_2, 2H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.4 Hz); 4.03 (O–CH_2, 8H, m); 7.25 (CH, 4H, AA′BB′); ^{13}C{^{1}H} δ 16.1 (CH_3, 4C, m); 30.6 (CH_2, 1C, t, $^2J_{PC}$ = 4.8 Hz); 38.7 (CH–P, 1C, t, $^1J_{PC}$ = 132.8 Hz); 62.4 (O–CH_2, 4C, m); 91.4 (C–I, 1C, s); 130.8 (CH, 2C, s); 137.0 (CH, 2C, s); 139.1 (C–CH_2, 1C, t, $^3J_{PC}$ = 7.6 Hz); ^{31}P{^{1}H} δ 22.7 (s); ^{31}P δ 22.7 (m); MS: *m/z* (+) 527.0 (M + Na)$^+$; (–) 502.8 (M – H)$^-$; elemental analysis for $C_{16}H_{27}O_6P_2I$, M_r = 504.24; found (calculated) C 39.00 (38.11); H 5.20 (5.40); I 27.42 (25.17).

Octaethyl bis(4-iodobenzyl)methylene-bis(phosphonate) (1b). The synthetic procedure for **1a** was repeated using NaH (1.28 g, 29.3 mmol, 3.5 eq., 55% in mineral oil), TMBP (2.42 g, 8.4 mmol) and IBnBr (5.00 g, 16.8 mmol). Crude product was recrystallized from hexane, filtered and dried *in vacuo* at 60 °C. Pure **1b** was obtained as a white solid (4.33 g, 71% based on IBnBz; purity 99+% according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.16 (CH_3, 12H, t, $^3J_{HH}$ = 7.0 Hz); 3.22 (CH_2, 4H, t, $^3J_{PH}$ = 16.4 Hz); 4.02 (O–CH_2, 8H, m); 7.36 (CH, 8H, AA′BB′); ^{13}C{^{1}H} δ 16.0 (CH_3, 4C, m); 37.5 (CH_2, 2C, t, $^2J_{PC}$ = 4.6 Hz); 48.2 (C–P, 1C, t,$^1J_{PC}$ = 131.4 Hz); 62.3 (O–CH_2, 4C, m); 92.1 (C–I, 2C, s); 133.6 (CH, 4C, s); 136.0 (C–CH_2, 2C, t, $^3J_{PC}$ = 6.3 Hz); 136.3 (CH, 4C, s); ^{31}P{^{1}H} δ 23.7 (s); ^{31}P δ 23.7 (m); MS: *m/z* (+) 743.0 (M + Na)$^+$; (–) 690.7 (M – Et)$^-$; TLC (SiO_2; CH_2Cl_2:THF 2:1; UV) R_f = 0.7; elemental analysis for $C_{23}H_{32}O_6P_2I_2$, M_r = 720.26; found (calculated) C 38.57 (38.35); H 4.31 (4.48); I 35.24 (34.53).

Tetraethyl [4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (2a). The compound was prepared analogously to the reported procedure.[9,14] Compound **1a** (2.98 g, 5.8 mmol), anhydrous potassium acetate (1.02 g, 6.5 mmol) and diphenylphosphine (1.0 ml, 5.9 mmol) in dry toluene (20 ml) in a 100-ml Schlenk flask fitted with a rubber septum were treated with a solution of $Pd(OAc)_2$ (2.6 mg, 12 µmol, 2 mol‰) in dry *N,N*-dimethylacetamide (1.5 ml). The reaction mixture was heated at 70 °C for 24 h. The progress of the reaction was followed by ^{31}P NMR. After cooling to RT, the mixture was stirred vigorously with deoxygenated water (25 ml) for 2 h. The emulsion was left standing to separate. The organic layer was separated and dried with anhydrous Na_2SO_4. The solvents were removed *in vacuo* to give a red oil (1.91 g, 59% based on **1a**; 89% **2a** and 11% $HPPh_2$ according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.18 (CH_3, 12C, m); 2.57 (CH–P, 1H, tt, $^2J_{PH}$ = 23.8 Hz, $^3J_{HH}$ = 6.4 Hz); 3.17 (CH_2, 2H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.4 Hz); 4.02 (O–CH_2, 8H, m); 7.14–7.26 (CH, 14H, m); ^{13}C{^{1}H} δ 16.2 (CH_3, 4C, m); 31.0 (CH_2, 1C, m); 38.8 (CH–P, 1C, t, $^1J_{PC}$ = 132.8 Hz); 62.5 (O–CH_2, 4C, m); 128.4 (C2, 4C, d, $^3J_{PC}$ = 6.8 Hz); 128.6 (C1, 2C, s); 129.1 (C7, 2C, d, $^3J_{PC}$ = 7.3 Hz); 133.5 (C3, 4C, d, $^2J_{PC}$ = 18.3 Hz); 133.7 (C6, 2C, d, $^2J_{PC}$ = 20.2 Hz); 135.0 (C5, 1C, d, $^1J_{PC}$ = 10.3 Hz); 137.2 (C4, 2C, d, $^1J_{PC}$ = 10.8 Hz); 140.4 (C8, 1C, m); ^{31}P{^{1}H} δ –6.1 (P–C, 1P, s); 22.8 (P–O, 2P, s); ^{31}P δ –6.1 (P–C, 1P, s); 22.8 (P–O, 2P, m); MS: *m/z* (+) 585.2 (M + Na)$^+$; 601.2 (M^{ox} + Na)$^+$; (–) 533.1 (M – Et)$^-$; 561.1 (M – H)$^-$.

Octaethyl bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (2b). The synthetic procedure as for **2a** was repeated using **1b** (4.33 g, 6.0 mmol), KOAc (2.1 g, 13.2 mmol), $HPPh_2$ (2.1 ml, 12.3 mmol, 1.02 eq.) and $Pd(OAc)_2$ (6.0 mg, 24 µmol, 2 mol ‰) in DMAA (3.4 ml). The product was obtained as a reddish oil (3.76 g, 73% based on **1b**; 88% **2b** and 12% $HPPh_2$ according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.03 (CH_3, 12H, t, $^3J_{HH}$ = 7.1 Hz); 3.24 (CH_2, 4H, t, $^3J_{PH}$ = 16.2 Hz); 3.90 (O–CH_2, 8H, m); 7.11–7.33 (CH, 28H, m); ^{13}C{^{1}H} δ 16.1 (CH_3, 4C, m); 37.8 (CH_2, 2C, m); 48.6 (C–P(O), 1C, t, $^1J_{PC}$ = 131.6 Hz); 62.3 (O–CH_2, 4C, m); 128.4 (C2, 8C, d, $^3J_{PC}$ = 6.8 Hz); 128.5 (C1, 4C, s); 131.8 (C7, 4C, d, $^3J_{PC}$ = 7.2 Hz); 132.9 (C6, 4C, d, $^2J_{PC}$ = 19.7 Hz); 133.5 (C3, 8C, d, $^2J_{PC}$ = 19.3 Hz); 135.1 (C5, 2C, d, $^1J_{PC}$ = 10.3 Hz); 137.3 (C4, 4C, d, $^1J_{PC}$ = 10.5 Hz); 137.4 (C8, 2C, m); ^{31}P{^{1}H} δ –6.1 (P–C, 2P, s); 24.0 (P–O, 2P, s); ^{31}P δ –6.1 (P–C, 2P, bs); 24.0 (P–O, 2P,

m); MS: *m/z* (+) 859.4 $(M + Na)^+$; 875.3 $(M^{ox} + Na)^+$; (–) 807.2 $(M - Et)^-$.

Borane adduct of tetraethyl [4-(diphenylphosphanyl)benzyl]-methylene-bis(phosphonate) (2a·BH$_3$). The compound was prepared analogously to the reported procedure.[15] The crude red oil containing **2a** (1.91 g, 3.26 mmol of **2a** + 0.4 mmol of $HPPh_2$) was dissolved in dry THF (10 ml) in a 100-ml Schlenk flask. The 1M solution of BH_3·THF in THF (3.7 ml, 3.7 mmol) was added dropwise under ice-cooling. The mixture was stirred for about 5 h at RT. After removal of the solvents, the residue was purified by SiO_2 chromatography with CH_2Cl_2:THF 2:1 as eluent (TLC: SiO_2, CH_2Cl_2:THF 2:1, UV detection, $R_f = 0.6$). The desired borane adduct was obtained as a light yellow oil (1.30 g, 39% based on **1a**; purity 100% according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.26 (CH_3, 12H, m); 2.64 (CH–P, 1H, tt, $^2J_{PH} = 24.0$ Hz, $^3J_{HH} = 6.4$ Hz); 3.28 (CH_2, 2H, td, $^3J_{PH} = 16.4$ Hz, $^3J_{HH} = 6.4$ Hz); 4.10 (O–CH_2, 8H, m); 7.28–7.59 (CH, 14H, m); ^{13}C{^{1}H} δ 16.2 (CH_3, 4C, m); 31.1 (CH_2, 1C, m); 38.7 (CH–P, 1C, t, $^1J_{PC} = 133.0$ Hz); 62.6 (O–CH_2, 4C, m); 127.1 (C5, 1C, d, $^1J_{PC} = 58.7$ Hz); 128.7 (C2, 4C, d, $^3J_{PC} = 10.3$ Hz); 129.2 (C4, 2C, d, $^1J_{PC} = 57.9$ Hz); 129.4 (C7, 2C, d, $^3J_{PC} = 10.7$ Hz); 131.2 (C1, 2C, d, $^4J_{PC} = 2.2$ Hz); 133.0 (C3, 4C, d, $^2J_{PC} = 9.6$ Hz); 133.1 (C6, 2C, d, $^2J_{PC} = 9.3$ Hz); 143.2 (C8, 1C, td, $^3J_{PC} = 7.6$ Hz, $^4J_{PC} = 2.3$ Hz); ^{31}P{^{1}H} δ 20.1 (P–B, 1P, bs); 22.5 (P–O, 2P, s); ^{31}P δ 20.1 (P–B, 1P, bs); 22.5 (P–O, 2P, bs); MS: *m/z* (+) 599.2 $(M + Na)^+$; 563.2 $(M + H)^+$ $M_r = 576.36$; elemental analysis for $C_{28}H_{40}O_6P_3B·1.5H_2O$, found (calculated) C 55.64 (55.69); H 6.72 (7.13).

Bis(borane) adduct of octaethyl bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) monohydrate (2b·2BH$_3$·H$_2$O). The synthetic procedure for **2a**·BH_3 was repeated using crude **2b** (3.24 g, 3.65 mmol of **2b** + 1.0 mmol of $HPPh_2$) and 1M BH_3·THF in THF (8.5 ml, 8.5 mmol, 1.1 eq.). The residue after silica gel column chromatography with CH_2Cl_2/THF 2:1 (TLC: SiO_2, CH_2Cl_2:THF 2:1, UV detection, $R_f = 0.7$) was dissolved in THF (20 ml) and the crystalline product was obtained by vapour diffusion of hexane at 5 °C (1.04 g, 23% based on **1b**; purity 100% according to ^{31}P NMR).

NMR ($CDCl_3$): ^{1}H δ 1.11 (CH_3, 12H, t, $^3J_{HH} = 7.0$ Hz); 3.34 (CH_2, 4H, t, $^3J_{PH} = 16.4$ Hz); 4.00 (O–CH_2, 8H, m); 7.40–7.60 (CH, 28H, m); ^{13}C{^{1}H} δ 16.0 (CH_3, 4C, m); 38.2 (CH_2, 2C, m); 48.5 (C–P(O), 1C, t, $^1J_{PC} = 131.8$ Hz); 62.5 (O–CH_2, 4C, m); 127.3 (C5, 2C, d, $^1J_{PC} = 58.7$ Hz); 128.7 (C2, 8C, d, $^3J_{PC} = 9.9$ Hz); 129.2 (C4, 4C, d, $^1J_{PC} = 57.9$ Hz); 131.1 (C1, 4C, d, $^4J_{PC} = 2.3$ Hz); 132.0 (C6, 4C, d, $^2J_{PC} = 10.7$ Hz); 132.2 (C7, 4C, d, $^3J_{PC} = 9.9$ Hz); 133.0 (C3, 8C, d, $^2J_{PC} = 9.5$ Hz); 140.1 (C8, 2C, m); ^{31}P{^{1}H} δ 20.0 (P–B, 2P, bs); 23.4 (P–O, 2P, s); ^{31}P δ 20.0 (P–B, 2P, bs); 23.4 (P–O, 2P, bs); MS: *m/z* (+) 888.2 $(M + Na)^+$; (–) 835.2 $(M - Et)^-$, $M_r = 864.50$; elemental analysis for $C_{47}H_{60}O_7P_4B_2·H_2O·THF$, found (calculated) C 63.94 (64.11); H 6.84 (7.12); P 12.14 (12.99).

Deprotection of borane adducts 2a·BH$_3$ and 2b·2BH$_3$·H$_2$O. The deprotection was performed according to the reported procedure.[15] The borane adduct **2a**·BH_3 (1.18 g, 2.05 mmol) or **2b**·2BH_3·H_2O (0.90 g, 1.04 mmol) was dissolved in dry CH_2Cl_2 (20 ml) in a 100-ml Schlenk flask and cooled to –5 °C. HBF_4·Me_2O (2.11 ml, 20.5 mmol, 10 eq. for **2a** or 2.15 ml, 20.8 mmol, 10 eq. for **2b**) was added dropwise and the mixture was stirred at RT for 24–36 h. The solution was diluted with CH_2Cl_2 (10 ml) and deoxygenated saturated aq. $NaHCO_3$ (20 ml) was carefully added. The emulsion was stirred vigorously for 10 min. Et_2O (10 ml) was added, the organic layer was separated and washed with water (10 ml) and dried over anhydrous Na_2SO_4. Volatiles were removed *in vacuo* to give the desired foamy product (1.02 or 0.77 g, 89% or 88%; purity 95+% and 93+% according to ^{31}P NMR; for **2a** and **2b**, respectively). **2a** elemental analysis for $C_{28}H_{37}O_6P_3·2H_2O$, found (calculated) C 56.23 (56.19); H 6.66 (6.90). **2b** elemental analysis for $C_{47}H_{56}O_7P_4·H_2O$, found (calculated) C 65.82 (66.04); H 6.26 (6.37).

[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonic acid) (3a). The compound was prepared analogously to the reported procedure.[9] Compound **2a** (0.76 g, 1.69 mmol) was dissolved in 6M aq. HCl (25 ml) and heated to 90 °C for 2 d in a sealed Schlenk vessel. The reaction mixture was left to cool in a refrigerator overnight and the precipitated impurities were filtered off on a 0.2 μm Teflon syringe filter (Whatman). Volatiles were removed in vacuum and the residue was dissolved in ethanol (5 ml) and evaporated (three times). Free acid **3a** was obtained as a white foam (0.57 g, 95%; purity 100% according to ^{31}P NMR).

NMR (D_2O + NaOD): ^{1}H δ 2.13 (CH–P, 1H, tt, $^2J_{PH} = 22.0$ Hz, $^3J_{HH} = 5.6$ Hz); 3.14 (CH_2, 2H, td, $^3J_{PH} = 15.6$ Hz, $^3J_{HH} = 5.6$ Hz); 7.32–7.78 (CH, 14H, m); ^{31}P{^{1}H} δ –7.8 (P–C, 1P, s); 20.2 (P–O, 2P, s); ^{31}P δ –7.8 (P–C, 1P, bs); 20.2 (P–O, 2P, m); NMR (CD_3OD): ^{13}C{^{1}H} δ 31.0 (CH_2, 1C, m); 40.5 (CH–P, 1C, t, $^1J_{PC} = 127.0$ Hz); 128.5 (C2, 4C, d, $^3J_{PC} = 6.7$ Hz); 128.9 (C1, 2C, s); 129.2 (C7, 2C, d, $^3J_{PC} = 7.3$ Hz); 133.6 (C3, 4C, d, $^2J_{PC} = 18.3$ Hz); 133.8 (C6, 2C, d, $^2J_{PC} = 20.2$ Hz); 135.0 (C5, 1C, d, $^1J_{PC} = 10.3$ Hz); 137.2 (C4, 2C, d, $^1J_{PC} = 10.8$ Hz); 140.4 (C8, 1C, m); MS: *m/z* (–) 464.9 (M + O–H)$^-$, $M_r = 450.31$; elemental analysis for $C_{20}H_{21}O_6P_3·EtOH$, found (calculated) C 53.65 (53.29); H 5.17 (5.44); P 17.47 (18.73).

Bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonic acid) (3b). The procedure for **3a** was repeated using **2b** (0.95 g, 1.31 mmol) and 6M aq. HCl (50 ml). Free acid **3b** was obtained as a white foam (0.80 g, 97%; purity 100% according to ^{31}P NMR).

NMR (D_2O + NaOD): ^{1}H δ 3.24 (CH_2, 4H, m); 7.12–7.88 (CH, 28H, m); ^{31}P{^{1}H} δ –5.6 (P–C, 2P, s); 24.8 (P–O, 2P, s); ^{31}P δ –5.6 (P–C, 2P, bs); 24.8 (P–O, 2P, bs); NMR (CD_3OD): ^{13}C{^{1}H} δ 39.2 (CH_2, 2C, m); 129.6 (C2, 8C, d, $^3J_{PC} = 7.2$ Hz); 130.1 (C1, 4C, s); 133.1 (C7, 4C, m); 133.9 (C6, 4C, d, $^2J_{PC} = 19.4$ Hz); 134.7 (C3, 8C, d, $^2J_{PC} = 19.1$ Hz); 135.4 (C5, 2C, d, $^1J_{PC} = 6.2$ Hz); 137.9 (C4, 4C, d, $^1J_{PC} = 6.4$ Hz); 139.2 (C8, 2C, t, $^3J_{PC} = 5.3$ Hz). Triplet corresponding to the signal of C–P(O) was overlapped with the solvent peak; MS: *m/z* (+) 725.1 $(M + H)^+$, (–) 723.1 $(M - H)^-$, $M_r = 724.61$; elemental analysis for $C_{39}H_{36}O_6P_4·EtOH·H_2O$, found (calculated) C 62.00 (62.39); H 5.13 (5.58); P 15.19 (15.72).

Synthesis of complexes

General procedure for preparation of 2a and 2b complexes. The compounds were prepared analogously to a reported procedure.[9] The solution of **2a** or **2b** (~100 mg) in CH_2Cl_2 (2.5 ml) was treated with a solution of the metal precursor (0.9 eq.) in CH_2Cl_2 (2.5 ml). The flask was sealed and heated to 40 °C overnight. The following manipulations were performed in air. Volatiles were removed *in vacuo*. Rh(I) complexes were dissolved in CH_2Cl_2 (1.0 ml), the same volume of hexane was added to the dichloromethane solution

and volatiles were removed *in vacuo*. Pt(II) and Pd(II) complexes were dissolved in CH_2Cl_2 (1.0 ml), precipitated by addition of an excess of hexane and separated by centrifugation. The procedure was repeated (removal of 1,5-cod). All desired products were dried *in vacuo* (0.02 Torr, RT, overnight). All yields are based on the amount of the precursors, $[Rh_2(\mu\text{-}Cl)_2(\eta^2\text{:}\eta^2\text{-cod})_2]$, $[PdCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ or $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$. All characterizations of the complexes can be found in the ESI.†

*[RhCl(η²:η²-cod)(**3a**-κP)].* Yellow suspension of $[Rh_2(\mu\text{-}Cl)_2(\eta^2\text{:}\eta^2\text{-cod})_2]$ (16.4 mg, 33 μmol) in EtOH (3 ml) in a 25-ml Schlenk flask was treated with a solution of **3a** (30.0 mg, 67 μmol) in the same solvent (3 ml) and the mixture was heated at 70 °C overnight. The following manipulations were performed in air. After cooling down to RT, the solvent was evaporated and the desired orange product was dried *in vacuo* (41.1 mg, 89%).

NMR (CD_3OD + $CDCl_3$): ^1H δ 2.02 (CH_2–1,5-cod, 4H, m); 2.40 (CH_2–1,5-cod, 4H, m); 2.53 (CH–P, 1H, m); 3.20 (CH-1,5-cod *trans* to Cl, 2H, bs); 3.27 (CH_2, 4H, m); 5.44 (CH-1,5-cod *trans* to P, 2H, bs); 7.35–7.79 (CH, 14H, m); $^{31}P\{^1H\}$ δ 22.1 (P–O, 2P, s); 30.4 (Rh–P, 1P, d, $^1J_{PRh}$ = 149.6 Hz); ^{31}P δ 22.1 (P–O, 2P, s); 30.4 (Rh–P, 1P, d, $^1J_{PRh}$ = 149.6 Hz).

*{[RhCl(η²:η²-cod)]₂(μ-**3b**-κ²P,P′)}.* The procedure for [Rh(Cl)(η²:η²-cod)(**3a**-κ*P*)] was repeated using **3b** (45.4 mg, 63 μmol) and $[Rh_2(\mu\text{-}Cl)_2(\eta^2\text{:}\eta^2\text{-cod})_2]$ (30.9 mg, 63 μmol). A yellow powder was obtained (61.8 mg, 81%).

NMR (MeOD + NaOH): ^1H δ 2.38 (CH_2–1,5-cod, 8H, m); 3.14 (CH-1,5-cod *trans* to Cl, 2H, bs); 3.65 (CH_2, 4H, m); 5.67 (CH-1,5-cod *trans* to P, 2H, bs); 7.36–7.78 (CH, 28H, m); $^{31}P\{^1H\}$ δ 23.1 (P–O, 2P, br s); 30.4 (Rh–P, 2P, br s) ^{31}P δ 23.1 (P–O, 2P, br s); 30.4 (Rh–P, 2P, br s).

*[PdCl₂(**3a**-κP)₂].* Compound **3a** (52.4 mg, 116 μmol) in 6M aq. HCl (2,5 ml) in a 25-ml Schlenk flask was treated with a fresh suspension of $PdCl_2$ (10.3 mg, 58 μmol) in 6M aq. HCl (2.5 ml). The yellow suspension was stirred at RT overnight. The precipitate was separated by centrifugation, washed with 6M aq. HCl (2 ml) and centrifuged again. The orange product was dried in a desiccator over KOH (39.0 mg, 62%).

NMR (D_2O + NaOD): ^1H δ 2.11 (CH–P, 1H, m); 3.07 (CH_2, 2H, m); 7.23–7.72 (CH, 14H, m); $^{31}P\{^1H\}$ δ 20.0 (P–O, 2P, s); 22.4 (Pd–P*trans*, 1P, br s); 34.8 (Pd–P*cis*, 1P, m); ^{31}P δ 20.0 (P–O, 2P, m); 22.4 (Pd–P*trans*, 1P, m); 34.8 (Pd–P*cis*, 1P, m); Far-IR: 284*m*, 305*m*; Raman: 306 *br m.*

*[Pd₂Cl₄(μ-**3b**-κ²P,P′)₂].* The procedure for the [PdCl₂(**3a**-κ*P*)₂] complex was repeated using **3b** (43.4 mg, 60 μmol) and $PdCl_2$ (10.6 mg, 60 μmol). A yellow powder was obtained (38.9 mg, 72%).

NMR (D_2O + NaOD): ^1H δ 3.20 (CH_2, 4H, t, $^3J_{PH}$ = 15.6 Hz); 7.41–7.71 (CH, 28H, m); $^{31}P\{^1H\}$ δ 20.6 (P–O, 2P, s); 24.7 (Pd–P*trans*, 2P, s); 37.9 (Pd–P*cis*, 2P, s); ^{31}P δ 20.6 (P–O, 2P, m); 24.7 (Pd–P*trans*, 2P, s); 37.9 (Pd–P*cis*, 2P, m); Far-IR (290, 314)*m*, 355*m.*

cis-*[PtCl₂(**3a**-κP)₂].* Compound **3a** (44.9 mg, 100 μmol) in azeotropic aq. HCl (2.5 ml) in a 25-ml Schlenk flask was treated with a solution of $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ (18.6 mg, 50 μmol) in CH_2Cl_2 (2.5 ml). The suspension was stirred at RT overnight. The following manipulations were performed in air. The organic phase with the precipitate was separated and concentrated. The residue was dissolved in MeOH (5 ml) and evaporated to dryness (three times). The product was washed with hexane (3 × 5 ml) and CH_2Cl_2 (3 × 5 ml). The yellowish oily product was dried *in vacuo* (39.2 mg, 68%).

NMR (D_2O + NaOD): ^1H δ 2.11 (CH–P, 1H, tt, $^2J_{PH}$ = 22.0 Hz, $^3J_{HH}$ = 6.0 Hz); 3.14 (CH_2, 2H, td, $^3J_{PH}$ = 15.6 Hz, $^3J_{HH}$ = 6.0 Hz); 7.26–7.53 (CH, 14H, m); $^{31}P\{^1H\}$ δ 7.8 (Pt–P, 1P, s + d, $^1J_{PtP}$ = 3554 Hz); 20.2 (P–O, 2P, s); ^{31}P δ 7.8 (Pt–P, 1P, s + d, $^1J_{PtP}$ = 3590 Hz); 20.2 (P–O, 2P, m); Far-IR: 287*s*, 316*s*; Raman: 287*m*, 316*s.*

cis,cis-*[Pt₂Cl₄(μ-**3b**-κ²P,P′)₂].* The procedure for *cis*-[PtCl₂(**3a**-κ*P*)₂] was repeated using **3b** (76.3 mg, 105 μmol) and $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ (39.4 mg; 105 μmol). The product was obtained as a white powder (79.9 mg, 92%).

NMR (D_2O + NaOD): ^1H δ 3.14 (CH_2, 4H, m); 6.89–7.82 (CH, 28H, m); $^{31}P\{^1H\}$ δ 7.2 (Pt–P, 2P, br s); 21.4 (P–O, 2P, br m); ^{31}P δ 7.2 (Pt–P, 2P, br m); 21.4 (P–O, 2P, br m; Far-IR: 293*s*, 319*s*; Raman: 294*m*, 319*s.*

cis-*[PtCl₂(**2a**-κP)(HPPh₂)].* Diphenylphosphine (33 μl, 192 μmol) was added *via* a Hamilton syringe to a solution of **2a** (108 mg, 192 μmol) in CH_2Cl_2 (5 ml) in a 25-ml Schlenk flask. The resulting mixture was treated with a solution of $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ (71.8 mg, 192 μmol) in CH_2Cl_2 (10 ml) and heated at 40 °C overnight. The following manipulations were performed in air. After cooling to RT, volatiles were removed *in vacuo*, the residue was dissolved in CH_2Cl_2/hexane and evaporated (three times). The light yellow product was dried *in vacuo* (167 mg, 86%).

NMR ($CDCl_3$): ^1H δ 1.19 (CH_3, 12H, t, $^3J_{HH}$ = 7.2 Hz); 2.55 (CH–P, 1H, tt, $^2J_{PH}$ = 24.0 Hz, $^3J_{HH}$ = 6.4 Hz); 3.20 (CH_2, 2H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.4 Hz); 4.02 (O–CH_2, 8H, m); 4.73 (P–H, 1H, dd, $^1J_{PH}$ = 400.0 Hz, $^3J_{PH}$ = 12.8 Hz); 7.27–7.66 (CH, 24H, m); $^{31}P\{^1H\}$ δ –3.1 (Pt–P–H, 1P, d + dd, $^1J_{PtP}$ = 3567 Hz, $^2J_{PP}$ = 15.2 Hz); 14.9 (Pt–P, 1P, d + dd, $^1J_{PtP}$ = 3580 Hz, $^2J_{PP}$ = 15.2 Hz); 22.5 (P–O, 2P, s); ^{31}P δ –3.1 (Pt–P–H, 1P, dm + ddm, $^1J_{PtP}$ = 3558 Hz, $^1J_{PH}$ = 400.0 Hz); 14.9 (Pt–P, 1P, bs + dm, $^1J_{PtP}$ = 3591 Hz); 22.5 (P–O, 2P, m); ^{195}Pt δ –1278 (t, $^1J_{PtP}$ = 3572 Hz); MS: *m/z* (+) 1036.2 $(M + Na)^+$; (–) 1013.2 $(M - H)^-$; Far-IR: 293*s*, 317*s.*

***cis,cis*-[Pt₂Cl₄(μ-2b-κ²*P,P′*)(HPPh₂)₂].** The procedure for the *cis*-[PtCl₂(**2a**-κ*P*)(HPPh₂)] complex was repeated using **2b** (182 mg, 217 μmol), $HPPh_2$ (76 μl, 434 μmol) and $[PtCl_2(\eta^2\text{:}\eta^2\text{-cod})]$ (162 mg, 434 μmol). Light yellow powder was obtained (345 mg, 92%).

NMR ($CDCl_3$): ^1H δ 1.04 (CH_3, 12H, t, $^3J_{HH}$ = 7.2 Hz); 3.23 (CH_2, 4H, t, $^3J_{PH}$ = 16.4 Hz); 3.91 (O–CH_2, 8H, m); 4.73 (P–H, 2H, dd, $^1J_{PH}$ = 400.3 Hz, *J* = 12.8 Hz); 7.19–7.62 (CH, 38H, m); $^{31}P\{^1H\}$ δ –3.0 (Pt–P–H, 2P, d + dm, $^1J_{PtP}$ = 3572 Hz, $^2J_{PP}$ = 15.2 Hz); 14.9 (Pt–P, 2P, d + dm, $^1J_{PtP}$ = 3587 Hz, $^2J_{PP}$ = 15.2 Hz); 23.4 (P–O, 2P, s); ^{31}P δ –3.0 (Pt–P–H, 1P, dm + ddm, $^1J_{PtP}$ = 3565 Hz, $^1J_{PH}$ = 401.4 Hz); 14.9 (Pt–P, 1P, bs + d, $^1J_{PtP}$ = 3587 Hz); 23.4 (P–O, 2P, m); ^{195}Pt δ –1278 (t, $^1J_{PtP}$ = 3571 Hz); Far-IR: 294*s*, 319*s.*

Photochemical isomerisation of cis-*[PtCl₂(**2a**-κP)₂] and* cis,cis-*[Pt₂Cl₄(μ-**2b**-κ²P,P′)₂].* Photochemical isomerisation was performed as described previously.[23] *cis*-[PtCl₂(**2a**-κ*P*)₂] (77.2 mg) or *cis,cis*-[Pt₂Cl₄(μ-**2b**-κ²*P,P′*)₂] (133 mg) were dissolved in $CDCl_3$ (1 ml) in a quartz NMR tube. Samples were irradiated by a

UV lamp (366 nm, 8 W) for 24 h. ^{31}P and ^{195}Pt NMR spectra were recorded. Conversion to *trans* isomers was 62% or 55%, respectively.

NMR ($CDCl_3$) after irradiation of *cis*-[$PtCl_2$(**2a**-κ*P*)$_2$]: $^{31}P\{^1H\}$ δ 13.6 (Pt–P*cis*, s + d, $^1J_{PtP}$ = 3687 Hz); 19.8 (Pt–P*trans*, s + d, $^1J_{PtP}$ = 2636 Hz); 22.6 (P–O, s); ^{195}Pt δ −817 (Pt–P*trans*, t, $^1J_{PtP}$ = 2625 Hz); −1199 (Pt–P*cis*, t, $^1J_{PtP}$ = 3666 Hz).

NMR ($CDCl_3$) after irradiation of *cis,cis*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$] $^{31}P\{^1H\}$ δ 13.5 (Pt–P*cis*, s + d, $^1J_{PtP}$ = 3680 Hz); 19.8 (Pt–P*trans*, s + d, $^1J_{PtP}$ = 2629 Hz); 23.6 (P–O, s); ^{195}Pt δ −815 (Pt–P*trans*, t, $^1J_{PtP}$ = 2625 Hz); −1199 (Pt–P*cis*, t, $^1J_{Pt}$ = 3664 Hz).

X-Ray crystallography

Single crystals of **2b**·2BH_3·H_2O suitable for X-ray analysis were prepared by slow diffusion of hexane vapour into a THF solution of the compound at 5 °C. The crystals of *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$ were prepared by slow diffusion of hexane vapour into a chloroform solution of the complex at 5 °C. The *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]·7CH_2Cl_2 complex crystallized by slow evaporation (at 5 °C) of the hexane/CH_2Cl_2 mother solution after removal of the precipitate of the *cis,cis*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$] complex.

The selected crystals were mounted in random orientations onto a glass fibre using an epoxy glue. The diffraction data were collected using a Nonius Kappa CCD diffractometer (Enraf-Nonius) at 150(1) K using Mo-Kα radiation (λ = 0.71073 Å) and analysed using the HKL program package.[35] The structures were solved using direct methods and refined by full-matrix least-squares techniques (SIR92[36] and SHELXL97[37]). Scattering factors for neutral atoms were included in the SHELXL97 program.

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. 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 multiples of a *U*-value of the corresponding carbon atoms. The hydrogen atoms of the ester groups were restrained in the same way, using isotropic thermal factors of 1.2 for methylene and 1.5 for methyl groups.

In the crystal structure of **2b**·2BH_3·H_2O, one ligand molecule and one water solvated molecule form the independent (asymmetric) unit. However, the phosphine molecule adopts a roughly (non-crystallographic) C_2 symmetry. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were treated using the riding model, but those attached to boron atoms were refined freely.

In the crystal structure of *trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$, one half of the complex molecule forms the asymmetric unit. The solvate molecules were extremely disordered and form rather a mass of diffraction maxima and, therefore, the disordered electron density was squeezed using PLATON98.[38] It corresponds to 61 electrons per independent unit, *i.e.* roughly to one molecule of the chloroform solvate. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated in theoretical positions. Some of the ethyl ester groups have large thermal parameters; however, trials to refine them disordered in to two positions brought no improvement to the fit. Carbon atoms of several ethyl ester groups were found unrealistically close to each other; therefore, the DFIX command was applied to fix the appropriate C–C bond lengths.

The asymmetric unit in the crystal structure of *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P′*)$_2$]·7CH_2Cl_2 contains a whole molecule of the complex and seven solvate molecules of dichloromethane. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated in theoretical positions. Some of the ethyl ester groups and dichloromethane chlorine atoms have large thermal parameters; however, trials to refine the atom split into two positions led to large uncertainties in the atom positions (due to the increase in the number of the parameters) and some nonrealistic bond distances. Therefore, the final refinement was performed without modulation of the disorder. Similarly as in the previous case, the DFIX command was applied to fix the appropriate C–C bond lengths in several ethyl ester groups as the free refinement led to unrealistically close contacts.

The experimental and refinement data are listed in the ESI† (Table S5).

Conclusions

New bis(phosphonate)-substituted triphenylphosphines were synthesized in the form of ethyl esters **2a** and **2b** and corresponding free acids **3a** and **3b**. The complexation with the most important platinum group metal ions, Rh(I), Pd(II) and Pt(II), was studied. The expected complexes of [RhCl(η^2:η^2-cod)(**L**)] and [MCl_2(**L**)$_2$] (M = Pd, Pt) stoichiometry were prepared for the monodentate ligands, **2a** and **3a**. The bidentate ligands **2b** and **3b** serve as bridging ligands forming the {[RhCl(η^2:η^2-cod)]$_2$(μ-**L**-κ^2*P,P′*)} and [M_2Cl_4(μ-**L**-κ^2*P,P′*)$_2$] (M = Pd, Pt) complexes. Bis(triphenylphosphines) **2b** and **3b**, having a flexible propylene spacer in the *para*-positions not sterically suitable for chelation to the same metal ion, were prepared and studied for the first time. The Pt(II) complexes show a preference for the *cis*-arrangement and they can be rearranged to the *trans* complexes by UV-irradiation. As a consequence of the steric possibilities of ligand **2b**, the dinuclear complex showing both *cis* and *trans* arrangements around the central Pt(II) ions was observed for the first time. In the case of the Pd(II) complexes, a different ratio of *cis*- and *trans*-isomers depending on the solvent was observed. In general, the solubility of **2a** and **3a** (in organic polar solvents and NaOH/H_2O, respectively) and their complexes is higher than that of **2b** and **3b** and their complexes. So, the systems containing **2a** or **3a** are more convenient for use in biphasic or solid-supported catalysis and a supported catalyst with the Rh(I)–**3a** complex anchored on TiO_2 is under investigation in our laboratory.

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Notes and references

1 (*a*) N. Pinault and D. W. Bruce, *Coord. Chem. Rev.*, 2003, **241**, 1–25; (*b*) S. Liu and J. Xiao, *J. Mol. Catal. A: Chem.*, 2007, **270**, 1–43.
2 T. L. Schull and D. A. Knight, *Coord. Chem. Rev.*, 2005, **249**, 1269–1282.
3 (*a*) F. R. Hartley, *Supported Metal Complexes–A New Generation of Catalysts*, D. Riedel, Publishing Company, Dordrecht, 1985; (*b*) J.

Freiberg and A. Weigt, *J. Prakt. Chem.*, 1993, **335**, 337–344; (*c*) S. Bischoff, A. Weigt, M. Kant, U. Schulke and B. Lucke, *Catal. Today*, 1997, **36**, 273–284; (*d*) B. A. Harper, D. A. Knight, C. George, S. L. Brandow, W. J. Dressick, C. S. Dalcey and T. L. Schull, *Inorg. Chem.*, 2003, **42**, 516–524; (*e*) T. L. Schull, L. Henley, J. R. Deschamps, R. J. Butcher, D. P. Maher, C. A. Klug, K. Swider-Lyons, W. J. Dressick, B. Bujoli, A. E. Greenwood, L. K. B. Congiardo and D. A. Knight, *Organometallics*, 2007, **26**, 2272–2276.

4 S. Bischoff, A. Köckritz and M. Kant, *Top. Catal.*, 2000, **13**, 327–334.

5 A. Hu, H. L. Ngo and W. B. Lin, *Angew. Chem., Int. Ed.*, 2003, **42**, 6000–6003.

6 G. Guerrero, P. H. Mutin, E. Framery and A. Vioux, *New J. Chem.*, 2008, **32**, 1519–1525.

7 (*a*) C. N. Kostelansky, J. J. Pietron, M.-S. Chen, W. J. Dressick, K. E. Swider-Lyons, D. E. Ramaker, R. M. Stroud, C. A. Klug, B. S. Zelakiewicz and T. L. Schull, *J. Phys. Chem. B*, 2006, **110**, 21487–21496; (*b*) D. S. Gatewood, T. L. Schull, O. Baturina, J. J. Pietron, Y. Garsany, K. E. Swider-Lyons and D. E. Ramaker, *J. Phys. Chem. C*, 2008, **112**, 4961–4970.

8 J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, H.-H. Strehblow, P. Keller, E. Rentschler and W. Kläui, *Angew. Chem., Int. Ed.*, 2007, **46**, 1164–1167.

9 Z. Rohlík, P. Holzhauser, J. Kotek, J. Rudovský, I. Němec, P. Hermann and I. Lukeš, *J. Organomet. Chem.*, 2006, **691**, 2409–2423.

10 I. Le Gall, P. Laurent, E. Soulier, J. Y. Salaun and H. des Abbayes, *J. Organomet. Chem.*, 1998, **567**, 13–20.

11 L. Delain-Bioton, A. Turner, N. Lejeune, D. Villemin, G. B. Hix and P.-A. Jaffrès, *Tetrahedron*, 2005, **61**, 6602–6609.

12 (*a*) H. Fleisch, *Bisphosphonates in Bone Diseases*, Academic Press, New York, 2000; (*b*) S. Zhang, G. Gangal and H. Uludag, *Chem. Soc. Rev.*, 2007, **36**, 507–531.

13 (*a*) H. R. Hays and T. J. Logan, *J. Org. Chem.*, 1966, **31**, 3391–3394; (*b*) O. T. Quimby, J. D. Curry, D. A. Nicholson, J. B. Prentice and C. H. Roy, *J. Organomet. Chem.*, 1968, **13**, 199–207; (*c*) L. M. Nguyen, E. Niesor and C. L. Bentzen, *J. Med. Chem.*, 1987, **30**, 1426–1433.

14 (*a*) P. Machnitzki, T. Nickel, O. Stelzer and C. Landgrafe, *Eur. J. Inorg. Chem.*, 1998, 1029–1034; (*b*) C. Liek, P. Machnitzki, T. Nickel, S. Schenk, M. Tepper and O. Stelzer, *Z. Naturforsch.*, 1999, **54b**, 1532–1542.

15 (*a*) B. Mohr, D. M. Lynn and R. H. Grubbs, *Organometallics*, 1996, **15**, 4317–4325; (*b*) U. Schmidt, B. Riedl, H. Griesser and C. Fitz, *Synthesis*, 1991, 655–657; (*c*) A. Börner, J. Ward, W. Ruth, J. Holz, A. Kless, D. Keller and H. B. Kagan, *Tetrahedron*, 1994, **50**, 10419–10430; (*d*) D. Enders, T. Berg, G. Raabe and J. Runsink, *Helv. Chim. Acta*, 1996, **79**, 118–122; (*e*) L. McKinstry and T. Livinghouse, *Tetrahedron*, 1995, **51**, 7655–7666; (*f*) Z. Chen, Q. Jinag, G. Zhu, D. Xiao, P. Cao, C. Guo and X. Zhang, *J. Org. Chem.*, 1997, **62**, 4521–4523.

16 J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433–2445.

17 (*a*) F. H. Allen and S. N. Sze, *J. Chem. Soc. A*, 1971, 2054–2056; (*b*) E. M. Pelczar, E. A. Nytko, M. A. Zhuravel, J. M. Smith, D. S. Glueck, R. Sommer, C. D. Incarvito and A. L. Rheingold, *Polyhedron*, 2002, **21**, 2409–2419.

18 J. C. Tebby, *CRC Handbook of Phosphorus-31 NMR Data*, CRC Press, Boca Raton, 1991, p. 160.

19 S. Berger, S. Braun and H. O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, J. Wiley & Sons, Chichester, England, 1996, pp. 707–715.

20 J. Tiburcio, S. Bernés and H. Torrens, *Polyhedron*, 2006, **25**, 1549–1554.

21 (*a*) B. E. Mann, B. L. Masters, R. M. Slade and R. E. Stainbank, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 881–885; (*b*) S. Berger, S. Braun and H. O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, J. Wiley & Sons, Chichester, England, 1996, pp. 835–838.

22 R. V. Parish, *NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, Ellis Horwood Ltd., London, 1990, pp. 64–68.

23 S. H. Mastin and P. Haake, *Chem. Commun.*, 1970, 202–202.

24 *International Tables for Crystallography*, Vol. C, ed. A. J. C. Wilson, Kluwer Academic Publisher, Dordrecht, 1995.

25 J. Flapper, P. Wormald, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, C. J. Elsevier and P. C. J. Kamer, *Eur. J. Inorg. Chem.*, 2008, 4968–4976.

26 H.-B. Song, Z.-Z. Zhang and T. C. W. Mak, *Inorg. Chem. Commun.*, 2002, **5**, 442–445.

27 (*a*) R. D. Gillard and M. F. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1974, 2320–2325; (*b*) D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, 1964, 734–739; (*c*) P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A*, 1966, 1462–1466; (*d*) R. J. Goodfellow, J. G. Evans, P. L. Goggin and D. A. Duddell, *J. Chem. Soc. A*, 1968, 1604–1609; (*e*) F. G. Mann and D. Purdie;, *J. Chem. Soc.*, 1935, 1549–1563; (*f*) S. H. Mastin, *Inorg. Chem.*, 1974, **13**, 1003–1005.

28 S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 1970, **4**, 56–60.

29 D. D. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1988.

30 V. Kubíček, J. Kotek, P. Hermann and I. Lukeš, *Eur. J. Inorg. Chem.*, 2007, 333–344.

31 (*a*) W. A. Hermann and A. Salzer, *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 1, Georg Thieme Verlag, Stuttgart, 1996, p. 163; (*b*) D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52–55.

32 W. A. Hermann and A. Salzer, *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 1, Georg Thieme Verlag, Stuttgart, 1996, p. 168.

33 (*a*) W. A. Hermann and A. Salzer, *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 1, Georg Thieme Verlag, Stuttgart, 1996, p. 150; (*b*) G. Giordano and R. H. Grabtree, *Inorg. Synth.*, 1990, **28**, 88–90.

34 http://www.mestrec.com.

35 (*a*) Z. Otwinowski and W. Minor, *HKL Denzo and Scalepack Program Package*, Nonius BV, Delft, The Netherlands, 1997; (*b*) Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307–326.

36 *SIR92-A Program for Automatic Solution of Crystal Structures by Direct Methods.* See:; A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435–435.

37 (*a*) G. M. Sheldrick, *SHELXL-97-A Computer Program for Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997; (*b*) G. M. Sheldrick and T. R. Schneider, *Methods Enzymol.*, 1997, **277**, 319–343.

38 A. L. Spek, *PLATON–A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2005.