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Synthesis and structure of Pd^{II} and Pt^{II} complexes containing chiral diphosphazane ligands

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Abstract

The reaction of the dichloro derivatives *cis*-[$Cl_2M(S$-peap)] [M = Pd **1**, Pt **2**; *S*-peap = *S*-$(Ph_2P)_2NC(H)(Me)(Ph)$] with $AgClO_4$ (1:1 molar ratio) results in the formation of the corresponding cationic dinuclear chlorine-bridge complexes [$M(\mu$-Cl)(*S*-peap)]$_2(ClO_4)_2$ (M = Pd **5**, Pt **6**) which, by further treatment with Tl(acac) give the acac-*O*,*O*′ derivatives [M(acac-*O*,*O*′)(*S*-peap)](ClO_4) (M = Pd **7**, Pt **8**). Complex **8** reacts in refluxing acetone with an excess of α-amino acids, such as glycine, L-alanine and D-alanine, to give the α-amino acidato complexes [Pt(Aa)(*S*-peap)](ClO_4) (Aa = gly **9**, L-ala **10**, D-ala **11**). When an equimolecular mixture of L- and D-alanine was allowed to react with **8**, an equimolecular mixture of **10** and **11** was obtained, showing that the chiral centre present in the diphosphazane ligand does not promote an stereoselective induction in the coordination of the amino acids. On the other hand, the reaction of *cis*-[$Cl_2Pt(S$-diphos)] [*S*-diphos = *S*-peap **2**, *S*-plap **4**; *S*-plap = *S*-$(Ph_2P)_2NC(H)(CH_2Ph)(CO_2Me)$] with an excess of N_2CH_2 results in the formation of the neutral bis(chloromethyl) complexes [$Pt(CH_2Cl)_2(S$-diphos)] (*S*-diphos = *S*-peap **12**, *S*-plap **13**). However, the reaction of **2** or **4** with $N_2C(H)CO_2Et$ (1:1.5 molar ratio) results in the insertion of the $C(H)CO_2Et$ fragment in only one of the two Pt–Cl bonds, giving the corresponding chloro(chloroalkyl) complexes [$PtCl(CHClCO_2Et)(S$-diphos)] (*S*-diphos = *S*-peap **14**, *S*-plap **15**) as a mixture of the two diastereoisomers (*RS*/*SS*). Once again, the chiral centre present in the diphosphazane ligand does not promote an stereoselective insertion reaction. Several concomitant factors could probably account for this lack of stereoselectivity: the remote location of the chiral centre from the reaction site, the free rotation of the C(H)(R)(R′) fragment around the C–N bond and the *exo* position of the chiral centre relative to the four-membered ring of the coordinated diphosphazane.

Keywords: Palladium; Platinum; Diphosphazane; Chiral; Amino acid; Diazo compounds

1. Introduction

During the past few years we have been interested in palladium complexes containing chiral ligands (L-chiral), and we have studied the behaviour of different 'Pd(L-chiral)' fragments in stereoselective coordination processes [1–3], catalytic reactions [4] and their utility in the determination of absolute configurations of α-amino acids [5]. In these complexes, the chirality comes from the presence of a *C*,*N*-cyclometallated ligand [2-(1-(*R*)-(dimethylamino)ethyl)phenyl-C^1,*N*, or (*R*)-dmphea] [1–4] or from the *N*,*O*-coordinated α-amino acid [5].

Aiming to expand the scope of applicability of these useful chiral ligands, we have now focused our attention on the chiral diphosphazanes *S*-$(Ph_2P)_2NC(H)(Me)(Ph)$ (*S*-peap) and *S*-$(Ph_2P)_2NC(H)(CH_2Ph)(CO_2Me)$ (*S*-plap). In spite of the wide interest shown by the chemist for diphosphazanes [6], these chiral derivatives have scarcely been studied [7–10]. Our choice of these ligands is based, besides the presence of the stereogenic centre, on their easy accessibility and their high stability.

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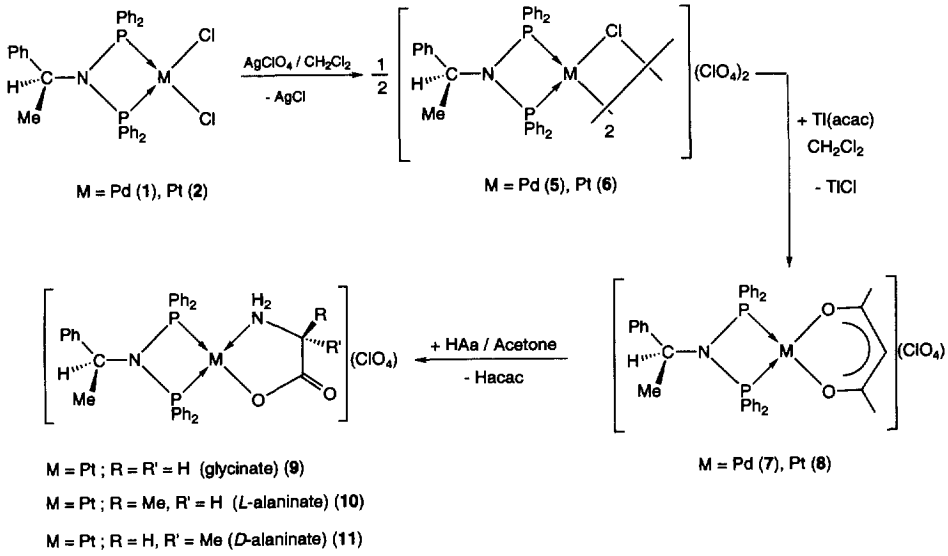

Fig. 1. The reaction of neutral *cis*-dichloro complexes (**1**, **2**) with $AgClO_4$ in CH_2Cl_2 at room temperature to give the corresponding cationic dinuclear complexes (**5**, **6**). The treatment of these dinuclear complexes with Tl(acac) in CH_2Cl_2 at room temperature obtains the corresponding acetylacetonato-*O,O'* derivatives (**7**, **8**) which can then react in refluxing acetone with an excess of amino acids, such as glycine or L-alanine, to give the corresponding amino acidato derivatives (**9**, **10**, **11**).

Two main processes have been studied; (i) the synthesis of cationic complexes of stoichiometry $[M(Aa)(S\text{-diphos})]^+$ (Aa = α-amino acidato group); (ii) the insertions of diazoderivatives N_2CHR (R = H, CO_2Et) in the Pt–Cl bonds of *cis*-$[Cl_2Pt(S\text{-diphos})]$. We report in this paper the obtained results in this study.

2. Results and discussion

2.1. Synthesis of complexes of stoichiometry [M(Aa)(S-diphos)](ClO4).

We have previously shown that an efficient preparative method for α-amino acidato complexes was the reaction of acetylacetonato-*O,O'* derivatives with the corresponding α-amino acids in refluxing MeOH [5,11]. Due to the simplicity of the involved processes, we have developed here a similar synthetic method.

The starting neutral *cis*-dichloro complexes $[Cl_2M(S\text{-peap})]$ (M = Pd **1**, Pt **2**) react with the stoichiometric amount of $AgClO_4$ (1:1 molar ratio, see Fig. 1) in CH_2Cl_2 at room temperature to give the corresponding cationic dinuclear complexes $[M(\mu\text{-Cl})(S\text{-peap})]_2(ClO_4)_2$ (M = Pd **5**, Pt **6**) in good yields. Both the analytical and the spectroscopic data for **5** and **6** (see Section 3) are in good agreement with the proposed stoichiometries. The IR spectra of **5** and **6** show the expected shift to lower wavenumbers of the M–Cl stretching absorption, as corresponds to the change of terminal Cl to bridging Cl [12], the presence of absorptions due to ionic ClO_4^- [13] and the presence of the absorption attributed to internal vibrations of the four-membered metallacycle [MPNP] [14]. The ^1H NMR spectra of **5**, **6** (see Section 3) show the expected resonances for the presence of the *S*-peap ligand, and the $^{31}P\{^1H\}$ NMR spectra show a singlet resonance, in spite of the presence of a chiral centre, as it has already been observed for **1**, **2** [14]. This resonance appears shifted upfield with respect to the corresponding precursors **1**, **2** and shows ^{195}Pt satellites for **6**.

The treatment of the dinuclear complexes **5**, **6** with Tl(acac) (1:2 molar ratio, see Fig. 1) in CH_2Cl_2 at room temperature results in the formation of the corresponding acetylacetonato-*O,O'* derivatives $[M(acac\text{-}O,O')(S\text{-peap})](ClO_4)$ (M = Pd **7**, Pt **8**), according with their elemental analyses of C, H, N (see Section 3). The IR spectra of **7**, **8** show the disappearance of the M–Cl stretching absorptions and the presence of absorptions attributed to the $acac^-$ ligand *O,O'*-coordinated (1580–1520 and 800 cm^{-1}) [15–17] and to the [MPNP] metallacycle [14]. The ^1H NMR spectra of **7**, **8** show the expected pattern of resonances for the presence of the $acac^-$ and *S*-peap ligands and the $^{31}P\{^1H\}$ NMR spectra show, once again, a singlet resonance for the P atoms of the *S*-peap ligand.

The next step in the synthesis of the α-amino acidato complexes was the reaction of the acac-*O,O'* derivatives **7**, **8** with α-amino acids. However, this synthesis has shown some problems. In a first attempt, we performed the reactions between **7**, **8** and the amino acids in refluxing MeOH, since all species were adequately soluble in this solvent, and because this procedure had already shown to be very efficient [5,11]. However, the reaction product of **8** with glycine in MeOH showed $^{31}P\{^1H\}$ resonances at very low field (about 80 ppm)

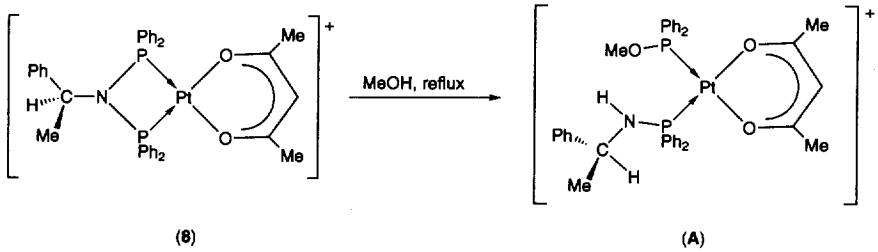

Fig. 2. The refluxing of complex **8** in MeOH resulting in the formation of complex (**A**).

and, on the other hand, the IR spectrum of this product showed the disappearance of the absorption attributed to the [PtPNP], these facts indicating that the *S*-peap ligand had undergone an important transformation, probably a side-reaction between the diphosphazane and the solvent. This fact was confirmed by refluxing of complex **8** in MeOH, which results in the formation of complex (**A**) (see Fig. 2) by selective cleavage of only one P–N bond of the *S*-peap ligand and generation of the phosphine ligands PPh_2OMe and *S*-$Ph_2PN(H)C(H)(Me)(Ph)$. This kind of P–N cleavage was already reported in the literature [18] and we have also studied in some detail this reaction using the *cis*-dichloro derivatives **1**–**4** [14].

We discarded using alcoholic solvents and tried using biphasic media, such as CH_2Cl_2/H_2O or toluene/H_2O (since the diphosphazane is inert towards hydrolysis [14]), but in this case very complex mixtures of unidentified products were obtained. Finally, the use of acetone as solvent, at the reflux temperature, allowed us to obtain the desired products avoiding side-reactions. Thus, **8** reacts in refluxing acetone with an excess of amino acids such as glycine or L-alanine (molar ratio 1:2) to give, after work-up, the corresponding amino acidato derivatives [Pt(Aa)(*S*-peap)](ClO_4) (Aa = gly **9**, L-ala **10**) according with their elemental analyses of C, H, N and mass spectra (see Section 3). The spectroscopic data are also in good agreement with the proposed stoichiometry. The IR spectra (see Section 3) show the disappearance of the absorptions attributed to the $acac^-$ ligand, and the presence of new bands attributed to the amino acidate group: a weak absorption about 3300 cm^{-1} (ν_{NH}) and a strong absorption about 1600 cm^{-1} (ν_{COO}) [11]. Moreover, the IR spectra show the presence of the absorption assigned to the [PtPNP] metallacycle. The ^1H NMR spectra (see Section 3) show the expected resonances for the presence of *S*-peap and glycinate **9** or L-alaninate **10**, and the $^{31}P\{^1H\}$ NMR spectra show an AB spin system, which corresponds to the two chemically unequivalent P atoms of the chelated diphosphazane.

Once we optimised the synthetic procedure, our interest in these complexes was directed in order to check the discriminatory ability of the *S*-peap ligand towards coordination of α-amino acids of opposite configuration, i.e. the stereoselective coordination of one enantiomer induced by the *S*-peap ligand. Thus, we have performed the reaction between **8** and the racemic mixture D,L-alanine, using an excess of amino acid. The spectroscopic characterisation of the resulting product showed an equimolecular mixture of **10** and its diastereoisomer [Pt(D-ala)(*S*-peap)](ClO_4) **11** (molar ratio **10**:**11** = 1:1), showing that the process is not stereoselective in these conditions. The same result was obtained if enantiomerically pure D- and L-alanine were mixed in different molar ratios; the reaction product was always a mixture of complexes **10** and **11** in the same molar ratio as the starting mixture of amino acids. In addition, attempts of resolution of the diastereomeric mixture by fractional crystallisation failed, probably due to the similar solubility of these products in the usual organic solvents. Other α-amino acids with different side-chains, such as 2-aminobutiric acid, valine or proline, were used instead of alanine in similar reactions. We observed in all cases a similar lack of stereoselectivity, together with the presence of small amounts of unidentified products. For these reasons they were not included here.

In conclusion, the disphosphazane *S*-peap does not behave as a good precursor of stereoselective inductions under the conditions aforementioned. Some sensible explanations could account for this behaviour: (i) the *exo*-cyclic location of the chiral centre; (ii) the remote location of the chiral centre from the reaction site (in this case, the remote location of the respective chiral centres, which precludes any interaction between them); (iii) the free rotation of the C(H)(Me)(Ph) fragment around the C–N bond. All these facts point out in the same direction, making equivalents in all directions around the chiral centre and 'dissipating' its own chirality. Moreover, these facts could be also the responsible for the lack of dissymmetry observed in the $^{31}P\{^1H\}$ NMR spectra of complexes **1**–**8**.

2.2. Insertion of diazoderivatives in the Pt–Cl bonds of *cis*-[Cl_2Pt(*S*-diphos)]

Following our research of the reactivity of complexes with chiral diphosphazane ligands, we have explored another interesting reaction, such as the insertion of

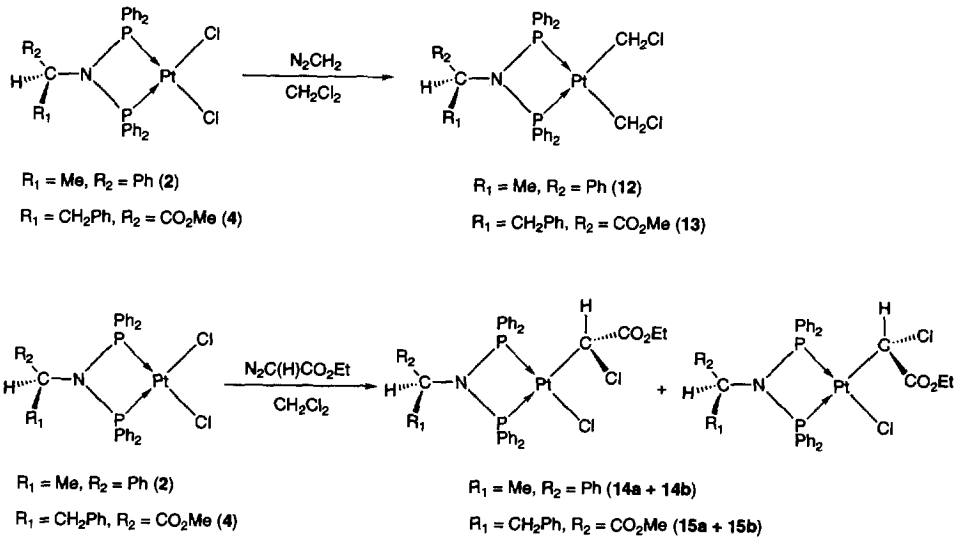

Fig. 3. The reaction of the platinum derivatives **2** and **4** with N_2CH_2 results in the corresponding bis-insertion products (**12**, **13**). The reaction of *cis*-[Cl_2Pt(*S*-diphos)] (*S*-diphos = *S*-peap **2**, *S*-plap **4**) with N_2CHCO_2Et in CH_2Cl_2 at room temperature results in the corresponding chloro(chloroalkyl) derivatives, both of which occur as two diastereoisomers (**14a/14b**; **15a/15b**).

diazocompounds N_2CHR in a metal–halogen bond. We are interested in this reaction because of the possibility of forming complexes containing an asymmetric M-C(H)(R)(X) unit. Moreover, the use of a chiral diphosphazane ligand could provide an easy access to optically stable metal–alkyl bonds containing an asymmetric α-carbon atom. Similar reactions using chiral diphosphine ligands are reported in the literature [19–21].

In the first step, we performed the reaction of *cis*-[Cl_2M(*S*-diphos)] (*S*-diphos = *S*-peap, M = Pd **1**, Pt **2**; *S*-diphos = *S*-plap, M = Pd **3**, Pt **4**) with an excess of N_2CH_2, the most reactive precursor. The platinum derivatives **2** and **4** react in a very clean way with N_2CH_2 giving the corresponding neutral bis(-chloromethyl) derivatives [Pt(CH_2Cl)$_2$(*S*-diphos)] (*S*-diphos = *S*-peap **12**, *S*-plap **13**) in good yields (see Fig. 3). However, the palladium precursors **1** and **3** gave products which spectroscopic data revealed a more complex reactivity than that derived from a simple insertion of the CH_2 group in the Pd–Cl bond. This complex behaviour is currently under study and it will not be described here.

Complexes **12** and **13** show satisfactory elemental analyses for the proposed stoichiometry (see Section 3). The IR spectra show the disappearance of the absorptions attributed to the Pt–Cl stretching, confirming the insertion of the CH_2 unit in the two Pt–Cl bonds, and the presence of the absorption attributed to the four-membered ring [PtPNP], showing that the metallacycle remains unchanged. The ^{1}H NMR spectra show the expected resonances for the presence of the *S*-peap (**12**) and *S*-plap (**13**) ligands, in addition to an AB spin system with ^{195}Pt satellites, which integrates as four protons, centred around 3.8 ppm and attributed to the PtCH_2Cl protons. The values of the coupling constants $^2J_{H-H}$ (about 10 Hz) and $^2J_{Pt-H}$ (about 50 Hz) are similar to those found in the related complex [Pt(CH_2Cl)$_2$(dppe)] [22]. The ^{13}C{^{1}H} NMR spectra show also the presence of the chloromethyl ligand σ-bonded to the platinum atom. This carbon appears as a doublet of doublets (coupling with the *trans*- and *cis*-P atoms of *S*-diphos) centred about 37–39 ppm and with ^{195}Pt satellites ($^1J_{Pt-C}$ about 820 Hz). The ^{31}P{^{1}H} NMR spectra show a singlet resonance, strongly shifted to low field when compared with the starting compounds. The value of the coupling constant $^1J_{Pt-P}$ shows a clear decrease (compared with the starting compounds) as corresponds to the change in the *trans* position of the chlorine ligand by an alkyl group, which shows a higher *trans* influence [19–21]. All data show a good agreement with the proposed stoichiometry.

In these reactions, an excess of N_2CH_2 is needed to insure the complete conversion of the starting compounds. Otherwise, the reactions performed with equimolecular amounts of N_2CH_2 or using a slight excess of N_2CH_2 resulted in mixtures of the starting dichloro derivatives (**2**, **4**), the products of bis-insertion (**12**, **13**), and very small amounts of mono-insertion products (not enough for a complete characterisation).

Finally, we have also attempted insertion reactions but using a prochiral diazo derivative, N_2CHCO_2Et, in order to check the possible stereoselective induction of the chiral diphosphazane in the insertion process. Thus, *cis*-[Cl_2Pt(*S*-diphos)] (*S*-diphos = *S*-peap **2**, *S*-plap **4**) reacted with N_2CHCO_2Et (molar ratio 1:1.5) in CH_2Cl_2 at room temperature to give very good yields of the corresponding chloro(chloroalkyl) derivatives [Pt-

Cl(CHClCO$_2$Et)(*S*-diphos)] (*S*-diphos = *S*-peap **14**, *S*-plap **15**), according to their elemental analytical data. In this case, only one insertion of the fragment CHCO$_2$Et has taken place. Even upon prolonged treatment with excess reagent, no clear evidence could be found indicating the presence of bis-insertion products, this behaviour contrasting with the easy bis-insertion of diazomethane (**12**, **13**). The role of electronic and steric factors in the competition mono- *versus* bis-insertion has already been discussed [20] and, from this, it seems that the steric factors are the main responsible of the hindered second insertion.

The IR spectra of **14**, **15** show the presence of a strong absorption at 1715 cm^{-1} due to the carbonyl group of the inserted CHCO$_2$Et fragment and only one absorption (about 303 cm^{-1}) corresponding to the Pt–Cl stretching mode. In addition, the presence of the absorption attributed to the [PtPNP] metallocycle indicates that this ring remains unchanged. The ^{1}H NMR spectra of **14**, **15** show, in each spectrum, the presence of two sets of signals, this fact indicating the expected presence of the two diastereoisomers (*SR*/*SS*; **14a**/**14b**; **15a**/**15b**) (see Fig. 3). The integration of the corresponding resonances of the two diastereoisomers show clearly that the molar ratios of the components of each mixture is **14a**/**14b** = **15a**/**15b** = 1/1, i.e. the reaction is not diastereoselective. Similar conclusions can be inferred from the ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra. In each spectrum. the presence of two sets of resonances of equal intensity shows the absence of diastereoselectivity in the insertion process.

In conclusion, *cis*-[Cl$_2$Pt(*S*-diphos)] complexes react in the expected way towards diazo derivatives. However, in spite of the presence of a chiral centre in the disphosphazane ligand, the reactions with the prochiral reagent N$_2$CHCO$_2$Et are not diastereoslective. These results, together with those obtained in Section 2.1, show that the chiral diphosphazanes *S*-peap and *S*-plap are not efficient discriminating agents for stereoselective reactions.

3. Experimental section

3.1. General comments

Solvents were dried and distilled prior to use by standard methods. Elemental analyses of C, H, N were carried out on a Perkin-Elmer 2400 microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 IR spectrophotometer in nujol mulls between polyethylene sheets. ^{1}H (300.13 MHz), ^{13}C{^{1}H} (75.47 MHz) and ^{31}P{^{1}H} (121.49 MHz) NMR spectra were recorded using CDCl$_3$ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^{1}H and ^{13}C{^{1}H} were referenced using the solvent signal as an internal standard and ^{31}P{^{1}H} was externally referenced to H$_3$PO$_4$ (85%). Mass spectra (positive ion FAB) were recorded on a VG Autospec. spectrometer using CH$_2$Cl$_2$ solutions. The starting materials *cis*-[Cl$_2$M(*S*-peap)] (M = Pd **1**, Pt **2**), *cis*-[Cl$_2$M(*S*-plap)] (M = Pd **3**, Pt **4**) [10,14] and Tl(acac) [23] were prepared according to published methods. Diazomethane (N$_2$CH$_2$) was prepared through a slight modification of the published method [24]. The α-amino acids glycine, L-alanine and D,L-alanine and the diazoderivative N$_2$C(H)CO$_2$Et are commercially available (Aldrich) and were used as purchased.

3.2. Preparation of [Pd(μ-Cl)(*S*-peap)]$_2$(ClO$_4$)$_2$ **5**

To a suspension of *cis*-[Cl$_2$Pd(*S*-peap)] (1.606 g, 2.41 mmol) in 20 ml of CH$_2$Cl$_2$, AgClO$_4$ (1.000 g, 4.82 mmol) was added, resulting in the immediate precipitation of AgCl. After 1 h of stirring at room temperature the AgCl was eliminated by filtration, the resulting solution was evaporated to dryness and the pale yellow solid was washed with *n*-hexane (2 × 50 ml), dried *in vacuo* and identified as complex **5**. Obtained: 3.063 g (87% yield).

Anal. Calc. for C$_{64}$H$_{58}$Cl$_4$N$_2$O$_8$P$_4$Pd$_2$ (1461.7 g mol^{-1}): C, 52.59; H, 4.00; N, 1.91. Found: C, 52.29; H, 4.09; N, 1.89. IR (ν, cm^{-1}): 1094, 623 (s, ν_{ClO_4}), 888 (m, ν_{PNP}), 283, 279 (m, ν_{Pd-Cl}). ^{1}H NMR: δ, 1.15 (d, 3H, CH$_3$, $^3J_{H-H}$ = 6 Hz), 5.16 (m, 1H, CH), 6.62–7.88 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 28.25.

3.3. Preparation of [Pt(μ-Cl)(*S*-peap)]$_2$(ClO$_4$)$_2$ **6**

Complex **6** was synthesised similarly to **5**: *cis*-[Cl$_2$Pt(*S*-peap)] (1.821 g, 2.41 mmol) and AgClO$_4$ (1.000 g, 4.82 mmol) reacted in 20 ml of CH$_2$Cl$_2$ to give **6** as a white solid. Obtained: 3.120 g (79% yield).

Anal. Calc. for C$_{64}$H$_{58}$Cl$_4$N$_2$O$_8$P$_4$Pt$_2$ (1639.0 g mol^{-1}): C, 46.90; H, 3.57; N, 1.71. Found: C, 46.47; H, 3.75; N, 1.70. IR (ν, cm^{-1}): 1078, 623 (s, ν_{ClO_4}), 878 (m, ν_{PNP}), 290, 279 (m, ν_{Pd-Cl}). ^{1}H NMR: δ, 1.04 (d, 3H, CH$_3$, $^3J_{H-H}$ = 7 Hz), 4.89 (m, 1H, CH), 6.63–7.81 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 11.37 ($^1J_{Pt-P}$ = 3444 Hz).

3.4. Preparation of [Pd(acac)(*S*-peap)](ClO$_4$) **7**

To a solution of [Pd(μ-Cl)(*S*-peap)]$_2$(ClO$_4$)$_2$ (0.482 g, 0.329 mmol) in 30 ml of CH$_2$Cl$_2$, Tl(acac) (0.200 g, 0.659 mmol) was added, resulting in the immediate precipitation of TlCl. After 1 h of stirring at room temperature the TlCl was eliminated by filtration, the resulting solution was evaporated to dryness and the yellow solid was washed with *n*-hexane (2 × 25 ml), dried *in vacuo* and identified as complex **7**. Obtained: 0.288 g (55% yield).

Anal. Calc. for $C_{37}H_{36}ClNO_6P_2Pd$ (794.5 g mol^{-1}): C, 55.93; H, 4.56; N, 1.76. Found: C, 55.94; H, 4.52; N, 1.85. IR (ν, cm^{-1}): 1578, 1517 (s, ν_{CO}, acac), 1098, 623 (s, ν_{ClO4}), 883 (m, ν_{PNP}). ^{1}H NMR: δ, 1.19 [d, 3H, CH_3 (*S*-peap), $^3J_{H-H}$ = 6 Hz], 1.83 [s, 6H, CH_3 (acac)], 5.18 [m, 1H, CH (*S*-peap)], 5.31 [s, 1H, CH (acac)], 6.61–7.90 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 33.42.

3.5. Preparation of [Pt(acac)(S-peap)](ClO$_4$) 8

Complex **8** was synthesised similarly to **7**: [Pt(μ-Cl)(*S*-peap)]$_2$(ClO$_4$)$_2$ (0.540 g, 0.329 mmol) and Tl(acac) (0.200 g, 0.659 mmol) reacted in 30 ml of CH_2Cl_2 to give **8** as a white solid. Obtained: 0.407 g (70% yield).

Anal. Calc. for $C_{37}H_{36}ClNO_6P_2Pt$ (883.2 g mol^{-1}): C, 50.32; H, 4.11; N, 1.59. Found: C, 50.54; H, 3.67; N, 1.63. IR (ν, cm^{-1}): 1582, 1563, 1528 (s, ν_{CO}, acac), 1101, 623 (s, ν_{ClO_4}), 882 (m, ν_{PNP}). Mass spectrum (FAB+, *m*/*z*, %): 783 (100%) [M$^+$]. ^{1}H NMR: δ, 1.13 [d, 3H, CH_3 (*S*-peap), $^3J_{H-H}$ = 7 Hz], 1.86 [s, 6H, CH_3 (acac)], 4.90 [tq, 1H, CH (*S*-peap), $^3J_{P-H}$ = 12 Hz], 5.50 [s, 1H, CH (acac)], 6.71–7.88 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 12.20 ($^1J_{Pt-P}$ = 3444 Hz). ^{13}C{^{1}H} NMR: δ, 186.14 (CO, acac), 138.20–125.61 (Ph), 102.32 (CH, acac), 63.22 (CH, *S*-peap), 27.36, 26.92 (CH_3, acac), 22.04 (CH_3, *S*-peap).

3.6. Preparation of [Pt(gly)(S-peap)](ClO$_4$) 9

To a solution of [Pt(acac)(*S*-peap)](ClO$_4$) (0.200 g, 0.226 mmol) in 30 ml of acetone was added glycine (0.034 g, 0.453 mmol) and the mixture was refluxed for 3 h. After cooling, the excess of glycine was filtered off and the resulting colourless solution was evaporated to dryness. The white residue of **9** was washed with Et_2O, filtered and air dried. Obtained: 0.161 g (83% yield).

Anal. Calc. for $C_{34}H_{33}ClN_2O_6P_2Pt$ (858.1 g mol^{-1}): C, 47.58; H, 3.87; N, 3.26. Found: C, 47.49; H, 4.14; N, 3.03. IR (ν, cm^{-1}): 3236 (w, ν_{NH}), 1588 (s, ν_{CO}, gly), 1101, 623 (s, ν_{ClO_4}), 874 (m, ν_{PNP}). Mass spectrum (FAB+, *m*/*z*, %): 758 (100%) [M$^+$]. ^{1}H NMR: δ, 1.00 [d, 3H, CH_3 (*S*-peap), $^3J_{H-H}$ = 7 Hz], 3.26 [s, broad, 2H, CH_2 (gly)], 4.45 [m, 3H, CH (*S*-peap) + NH_2 (gly)], 6.50–7.81 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 15.02 (d, P–*trans*-N, $^2J_{P-P}$ = 55 Hz, $^1J_{Pt-P}$ = 3163 Hz), 21.35 (d, P–*trans*-O, $^1J_{Pt-P}$ = 3070 Hz). ^{13}C{^{1}H} NMR: δ, 184.34 (CO, gly), 138.21–124.70 (Ph), 62.99 (CH, *S*-peap), 43.45 (CH_2, gly), 21.42 (CH_3, *S*-peap).

3.7. Preparation of [Pt(L-ala)(S-peap)](ClO$_4$) 10

Complex **10** was synthesised similarly to **9**: [Pt(acac)(*S*-peap)](ClO$_4$) (0.200 g, 0.226 mmol) and L-alanine (0.040 g, 0.453 mmol) reacted in 30 ml of acetone to give **10** as a white solid. Obtained: 0.172 g (87% yield).

Anal. Calc. for $C_{35}H_{35}ClNO_6P_2Pt$ (872.2 g mol^{-1}): C, 48.20; H, 4.04; N, 3.21. Found: C, 48.20; H, 4.29; N, 2.99. IR (ν, cm^{-1}): 3229 (w, ν_{NH}), 1639 (s, ν_{CO}, L-ala), 1109, 623 (s, ν_{ClO_4}), 875 (m, ν_{PNP}). Mass spectrum (FAB+, *m*/*z*, %): 772 (100%) [M$^+$]. ^{1}H NMR: δ, 1.01 [d, 3H, CH_3 (*S*-peap), $^3J_{H-H}$ = 7 Hz], 1.22 [d, 3H, CH_3 (L-ala), $^3J_{H-H}$ = 5 Hz], 3.50 [m, 1H, CH (L-ala)], 3.75 [m, 1H, NH (L-ala)], 4.53 [tq, 1H, CH (*S*-peap), $^3J_{P-H}$ = 12 Hz], 5.16 [m, 1H, NH (L-ala)], 6.65–7.91 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 15.57 (d, P–*trans*-N, $^2J_{P-P}$ = 55 Hz, $^1J_{Pt-P}$ = 3110 Hz), 21.46 (d, P–*trans*-O, $^1J_{Pt-P}$ = 3076 Hz).

3.8. Preparation of [Pt(D,L-ala)(S-peap)](ClO$_4$) 10, 11

The mixture of complexes **10** and **11** was synthesised similarly to **10**: [Pt(acac)(*S*-peap)](ClO$_4$) (0.200 g, 0.226 mmol) and D,L-alanine (0.040 g, 0.453 mmol) reacted in 30 ml of acetone to give acetone to give a white solid identified spectroscopically as a mixture (1:1 molar ratio) of complexes **10** and **11**. Obtained: 0.182 g (92% yield).

Anal. Calc. for $C_{35}H_{35}ClNO_6P_2Pt$ (872.2 g mol^{-1}): C, 48.20; H, 4.04; N, 3.21%. Found: C, 47.61; H, 4.21; N, 3.03%. IR (ν, cm^{-1}): 3229 (w, ν_{NH}), 1639 (s, ν_{CO}, L-ala), 1109, 623 (s, ν_{ClO_4}), 875 (m, ν_{PNP}). Mass spectrum (FAB+, *m*/*z*, %): 772 (100%) [M$^+$]. ^{1}H NMR: δ, 1.00, 1.01 [2d, 6H, CH_3 (*S*-peap), $^3J_{H-H}$ = 7 Hz], 1.23, 1.27 [d, 6H, CH_3 (D,L-ala), $^3J_{H-H}$ = 5 Hz], 3.64, 3.76 [2m, 2H, CH (D,L-ala)], 3.90 [m, 2H, NH (D,L-ala)], 4.32, 4.53 [2tq, 2H, CH (*S*-peap), $^3J_{P-H}$ = 12 Hz], 5.03, 5.13 [2m, 2H, NH (D,L-ala)], 6.51–7.70 (m, 50H, Ph). ^{31}P{^{1}H} NMR: δ, 15.32, 15.57 (2d, P–*trans*-N, $^2J_{P-P}$ = 55 Hz, $^1J_{Pt-P}$ = 3126 Hz, $^1J_{Pt-P}$ = 3110 Hz), 21.28, 21.46 (2d, P–*trans*-O, $^1J_{Pt-P}$ = 3082 Hz, $^1J_{Pt-P}$ = 3076 Hz).

3.9. Preparation of [Pt(CH$_2$Cl)$_2$(S-peap)] 12

To a cold solution (0°C) of *cis*-[PtCl$_2$(*S*-peap)] (0.200 g, 0.265 mmol) in 20 ml of CH_2Cl_2 was slowly added an excess (1:10 molar ratio) of N_2CH_2 (CH_2Cl_2 solution, prepared from 1-methyl-3-nitro-1-nitrosoguanidine and KOH) and the mixture was stirred for 12 h at room temperature. The pale yellow solution was dried by addition of anhydrous $MgSO_4$, filtered, and the solvent was evaporated to dryness. The yellow residue of **12** was washed with *n*-hexane, filtered and air dried. Obtained: 0.166 g (80% yield).

Anal. Calc. for $C_{34}H_{33}Cl_2NP_2Pt$ (783.6 g mol^{-1}): C, 52.11; H, 4.24; N, 1.78. Found: C, 52.68; H, 4.22; N, 1.83. IR (ν, cm^{-1}): 862 (m, ν_{PNP}). ^{1}H NMR: δ, 0.90 [d, 3H, CH_3 (*S*-peap), $^3J_{H-H}$ = 7 Hz], 3.74, 3.85 (AB spin system, 4H, CH_2Cl, $^2J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 50 Hz), 4.36 [tq, 1H, CH (*S*-peap) $^3J_{P-H}$ = 12 Hz], 6.54–7.87 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 50.70 ($^1J_{Pt-P}$ = 1812 Hz). ^{13}C{^{1}H} NMR: δ, 140.35–126.69 (Ph), 63.41 (t, CH,

S-peap, $^2J_{P-C} = 57$ Hz), 38.13 (dd, CH_2Cl, $^2J_{P-trans-C} = 129$ Hz, $^2J_{P-cis-C} = 4$ Hz, $^1J_{Pt-C} = 820$ Hz), 21.22 (CH_3, *S*-peap).

3.10. Preparation of [Pt(CH$_2$Cl)$_2$(S-plap)] 13

Complex **13** was synthesised similarly to **12**: *cis*-[$PtCl_2$(*S*-plap)] (0.200 g, 0.246 mmol) and N_2CH_2 (excess) reacted in 30 ml of CH_2Cl_2 at 0°C to give **13** as a yellow solid. Obtained: 0.153 g (74% yield).

Anal. Calc. for $C_{36}H_{35}Cl_2NO_2P_2Pt$ (841.6 g mol^{-1}): C, 51.37; H, 4.19; N, 1.66. Found: C, 51.42; H, 4.33; N, 1.73. IR (ν, cm^{-1}): 1743 (s, ν_{CO}), 896 (m, ν_{PNP}). ^{1}H NMR: δ, 1.55 [dd, 1H, CH_2 (*S*-plap), $^2J_{H-H} = 13$ Hz, $^3J_{H-H} = 3$ Hz], 2.33 [pseudo triplet, 1H, CH_2 (*S*-plap), $^2J_{H-H} \cong {}^3J_{H-H} = 13$ Hz], 3.03 (s, 3H, OMe), 3.77, 3.99 (AB spin system, 4H, CH_2Cl, $^2J_{H-H} = 10$ Hz, $^2J_{Pt-H} = 52$ Hz), 3.85 [m, 1H, CH (*S*-plap)], 6.32–8.32 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 51.66 ($^1J_{Pt-P} = 1808$ Hz). ^{13}C{^{1}H} NMR: δ, 176.20 (COO, *S*-plap), 135.98–125.26 (Ph), 66.84 (t, CH, *S*-plap, $^2J_{P-C} = 41$ Hz), 51.53 (OCH_3), 37.78 (dd, CH_2Cl, $^2J_{P-trans-C} = 127$ Hz, $^2J_{P-cis-C} = 3$ Hz, $^1J_{Pt-C} = 816$ Hz), 37.21 (CH_2, *S*-plap).

3.11. Preparation of [Pt(CHClCO$_2$Et)Cl(S-peap)] 14 [14a (RS), 14b (SS)]

To a solution of *cis*-[$PtCl_2$(*S*-peap)] (0.200 g, 0.265 mmol) in 20 ml of CH_2Cl_2 was slowly added N_2CHCO_2Et (0.041 ml, 0.397 mmol) and the mixture was stirred for 12 h at room temperature. The pale yellow solution was dried by addition of anhydrous $MgSO_4$, filtered, and the solvent was evaporated to dryness. By addition of *n*-hexane (20 ml) to the yellow residue **14** was obtained as a mixture of diastereoisomers (**14a**, **14b**) in a 1:1 molar ratio (**14a**:**14b**). Obtained: 0.212 g (95% yield).

Anal. Calc. for $C_{36}H_{35}Cl_2NO_2P_2Pt$ (841.6 g mol^{-1}): C, 51.37; H, 4.19; N, 1.66. Found: C, 51.76; H, 4.21; N, 1.71. IR (ν, cm^{-1}): 1714 (s, ν_{CO}), 870 (m, ν_{PNP}), 303 (m, ν_{Pt-Cl}). ^{1}H NMR: δ, 0.90, 0.92 [2d, 6H, CH_3 (*S*-peap), **14a** and **14b**, $^3J_{H-H} = 6.5$ Hz], 0.97, 0.99 [2t, 6H, CH_2CH_3, **14a** and **14b**, $^3J_{H-H} = 7$ Hz], 3.17, 3.40, 3.52, 3.67 (4m, 4H, OCH_2CH_3, **14a** and **14b**), 4.37 [m, 2H, CH (*S*-peap), **14a** and **14b**], 4.55, 4.56 [2d, 2H, PtCHCl, **14a** and **14b**, $^3J_{P-H} = 11$ Hz, $^2J_{Pt-H} = 50$ Hz], 6.52–7.85 (m, 50H, Ph). ^{31}P{^{1}H} NMR: δ, 31.78 (d, P–*trans*-to-Cl, $^2J_{P-P} = 46$ Hz, $^1J_{Pt-P} = 3900$ Hz), 32.60 (d, P–*trans*-to-Cl, $^2J_{P-P} = 46$ Hz, $^1J_{Pt-P} = 3900$ Hz), 38.26 (d, P–*trans*-to-C, $^2J_{P-P} = 46$ Hz, $^1J_{Pt-P} = 1785$ Hz), 38.49 (d, P–*trans*-to-C, $^2J_{P-P} = 46$ Hz, $^1J_{Pt-P} = 1788$ Hz) (**14a** and **14b**). ^{13}C{^{1}H} NMR: δ, 176.20, 176.05 (COO, **14a** and **14b**), 139.40–125.23 (Ph), 62.56 (s, CH, *S*-peap, **14a** and **14b**), 59.54, 59.39 (2s, OCH_2, **14a** and **14b**), 48.78, 48.62 (2d, PtCHCl, $^2J_{P-trans-C} = 114$ Hz, $^2J_{P-trans-C} = 112$ Hz, **14a** and **14b**), 21.09 (s, CH_3, *S*-peap, **14a** and **14b**), 14.30, 14.04 (2s, CH_3CH_2, **14a** and **14b**).

3.12. Preparation of [Pt(CHClCO$_2$Et)Cl(S-plap)] 15 [15a (RS), 15b (SS)]

Complex **15** was synthesised similarly to **14**: *cis*-[$PtCl_2$(*S*-plap)] (0.200 g, 0.246 mmol) and N_2CHCO_2Et (0.038 ml, 0.369 mmol) reacted in 30 ml of CH_2Cl_2 at room temperature to give **15** as a yellow solid. Obtained: 0.199 g (90% yield).

Anal. Calc. for $C_{38}H_{37}Cl_2NO_4P_2Pt$ (899.6 g mol^{-1}): C, 50.73; H, 4.14; N, 1.56. Found: C, 51.06; H, 4.17; N, 1.59. IR (ν, cm^{-1}): 1738 (s, ν_{CO}, *S*-plap), 1714 (s, ν_{CO}, CO_2Et), 902 (m, ν_{PNP}), 304 (m, ν_{Pt-Cl}). ^{1}H NMR: δ, 0.94, 1.01 [2t, 6H, CH_2CH_3, $^3J_{H-H} = 6$ Hz, **15a** and **15b**], 1.53, 1.57 [2dd, 2H, CH_2 (*S*-plap), $^2J_{H-H} = 12$ Hz, $^3J_{H-H} = 3$ Hz, **15a** and **15b**], 2.18 [pseudo triplet, 1H, CH_2 (*S*-plap), $^2J_{H-H} \cong {}^3J_{H-H} = 13$ Hz], 2.33 [pseudo triplet, 1H, CH_2 (*S*-plap), $^2J_{H-H} \cong {}^3J_{H-H} = 13$ Hz] (**15a** and **15b**), 3.04, 3.05 (2s, 6H, OMe, **15a** and **15b**), 3.50–3.87 [broad m, 6H, CH (*S*-plap) + OCH_2, **15a** and **15b**], 4.60 (d, 1H, PtCHCl, $^3J_{P-H} = 10$ Hz, $^2J_{Pt-H} = 50$ Hz), 4.64 (d, 1H, PtCHCl, $^3J_{P-H} = 9$ Hz, $^2J_{Pt-H} = 50$ Hz) (**15a** and **15b**), 6.31–8.32 (m, 50H, Ph). ^{31}P{^{1}H} NMR: δ, 33.47 (d, P–*trans*-to-Cl, $^2J_{P-P} = 43$ Hz, $^1J_{Pt-P} = 3929$ Hz), 34.46 (d, P–*trans*-to-Cl, $^2J_{P-P} = 43$ Hz, $^1J_{Pt-P} = 3926$ Hz), 37.70 (d, P–*trans*-to-C, $^2J_{P-P} = 43$ Hz, $^1J_{Pt-P} = 1786$ Hz), 38.68 (d, P–*trans*-to-C, $^2J_{P-P} = 43$ Hz, $^1J_{Pt-P} = 1782$ Hz) (**15a** and **15b**). ^{13}C{^{1}H} NMR: δ, 176.05 (s, CO_2Et), 168.25, 168.21 (COO, *S*-plap), 135.21–126.16 (Ph), 65.87, 65.81 (2s, CH, *S*-plap), 59.73, 59.57 (2s, OCH_2), 51.86, 51.83 (2s, OCH_3), 48.64, 48.47 (2d, PtCHCl, $^2J_{P-trans-C} = 114$ Hz), 37.17, 37.08 (2s, CH_2, *S*-plap), 14.35, 14.10 (2s, CH_2CH_3) (**15a** and **15b**).

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