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Selective cleavage of a P–N bond promoted by alcohols in *cis*-[$Cl_2M\{S\text{-}(Ph_2P)_2NC(H)(R')(R'')\}$] complexes (M = Pd, Pt) X-ray crystal structure of *cis*-[$Cl_2Pt(PPh_2OMe)\{S\text{-}Ph_2PN(H)C(H)(Me)(Ph)\}$] · 0.75MeOH

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Abstract

The reaction of $MCl_2(tht)_2$ (M = Pd, Pt; tht = tetrahydrothiophene) with *S*-$(Ph_2P)_2N$–C(H)(Me)(Ph) (*S*-peap) or *S*-$(Ph_2P)_2N$–C(H)$(CH_2Ph)(CO_2Me)$ (*S*-plap) results in the formation of the neutral mononuclear derivatives *cis*-'$Cl_2M(S\text{-peap})$] (M = Pd, **1**, Pt **3**) or *cis*-[$Cl_2M(S\text{-plap})$] (M = Pd **2**, Pt **4**) in which the chiral diphosphazane ligands are *P,P'*-chelate. Complexes **1–4** react with linear alcohols ROH (R = Me, Et, ^nPr; reflux temperature) resulting in the selective cleavage of only one of the P–N bonds of the diphosphazane group and formation of the neutral mononuclear derivatives *cis*-[$Cl_2M(PPh_2OR)\{S\text{-}Ph_2PN(H)C(H)(R')(R'')\}$] (R' = Me, R'' = Ph; R = Me, M = Pd **5**, Pt **7**; R = Et, M = Pt **9**; R = ^nPr, M = Pt **10**; R = CH_2CH_2OH, M = Pt **11**; and R' = CH_2Ph, R'' = CO_2Me, R = Me; M = Pd **6**, Pt **8**). The cleavage of the remaining P–N bond was not observed, even at long reaction times, suggesting that the disappearance of the steric constraint in the four-membered metallacycles **1–4** could be responsible for the observed reactivity. In spite of this, no reaction takes place between **1–4** and branched alcohols such as 2-propanol, 2-methyl-2-propanol or 2-methyl-1-butanol, nor with water or weak acids. The characterization of all of these complexes has been carried out through spectroscopic methods and through the determination of the single-crystal X-ray structure of *cis*-[$Cl_2Pt(PPh_2OMe)\{S\text{-}Ph_2PN(H)C(H)(Me)(Ph)\}$] · 0.75MeOH. © 1997 Elsevier Science S.A.

Keywords: Diphosphazane; Chiral; Palladium; Platinum; Cleavage; X-ray structure

1. Introduction

The diphosphinoamine or diphosphazane ligands $(PX_2)_2N$–R (X = halide, alkyl, aryl, alkoxy or aryloxy groups; R = H, alkyl) have attracted the interest of the chemist only some years ago, but this interest has grown very rapidly due to the proved versatility of this class of ligands [1]; the wide range of substituents on both the phosphorus and nitrogen atoms allows a subtle modulation of the electronic and steric properties of these ligands, resulting in significant changes in their coordination behaviour, in the structural parameters of the resulting complexes and in their subsequent reactivity [1].

On following our recent reports on the coordination chemistry of diphosphazanes [2,3], we have now focused our attention on the chiral derivatives (−)-*N,N*-bis(diphenylphosphino)-*S*-α-phenylethylamine (*S*-$(Ph_2P)_2NC(H)(Me)(Ph)$ or *S*-peap) and (−)-*N,N*-bis(diphenylphosphino)-*S*-α-phenylalanine methyl ester (*S*-$(Ph_2P)_2NC(H)(CH_2Ph)(CO_2Me)$ or *S*-plap), which up to the present have scarcely been studied [4–6].

In this paper we report the synthesis of the neutral Pd^{II} and Pt^{II} derivatives *cis*-[$Cl_2M(diphos)$] (diphos = *S*-peap, *S*-plap), in which the diphosphazane acts as a *P,P'*-chelate, and their reactivity towards protic solvents such as alcohols, water or weak acids. In accord with the well known hydrolytic instability of the P–N bonds of the diphosphazanes [7–9], even when they are coordinated [10–12], we have found an interesting reactivity of *cis*-[$Cl_2M(diphos)$] towards linear alcohols,

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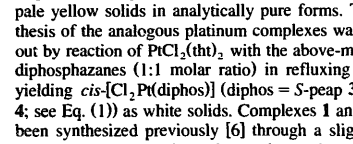
while the same starting materials are surprisingly unreactive towards branched alcohols, water and weak acids.

2. Results and discussion

2.1. Synthesis of cis-[Cl_2M(S-diphos)] 1–4

The reaction of $PdCl_2(tht)_2$ (tht = tetrahydrothiophene) with the chiral diphosphazanes *S*-peap or *S*-plap (1:1 molar ratio) in CH_2Cl_2 at room temperature results in the displacement of the weakly coordinated tht ligands and formation of the corresponding *cis*-[Cl_2Pd(diphos)] derivatives (diphos = *S*-peap **1**, *S*-plap **2**; see Eq. (1)). Complexes **1** and **2** precipitated in good yield (up to 85%) from the reaction mixtures as pale yellow solids in analytically pure forms. The synthesis of the analogous platinum complexes was carried out by reaction of $PtCl_2(tht)_2$ with the above-mentioned diphosphazanes (1:1 molar ratio) in refluxing toluene, yielding *cis*-[Cl_2Pt(diphos)] (diphos = *S*-peap **3**, *S*-plap **4**; see Eq. (1)) as white solids. Complexes **1** and **3** have been synthesized previously [6] through a slightly different procedure, and we have observed a complete coincidence of their spectroscopic parameters with those reported in the literature [6].



(1)

The cis-geometry of **1–4** can be inferred from the observation in their IR spectra (see Section 4) of two absorptions at about 300 cm^{-1} corresponding to the stretching ν(M–Cl) [13] of the *cis*-MCl_2 fragment. A strong absorption at 1747 cm^{-1} for **2** and **4** is attributed to the ν(CO) stretching of the CO_2Me group of the *S*-plap ligand. Finally, the symmetrical vibration of the P–N–P group is observed as a sharp absorption at about 900 cm^{-1} [1,14] in each case.

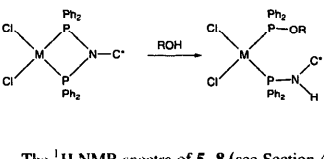
The ^{1}H NMR spectra of **1** and **3** (see Section 4) show the presence of resonances attributed to the C*H* (multiplet) and CH_3 (doublet) protons, while those of **2** and **4** show signals corresponding to the C*H* (multiplet), CO_2CH_3 (singlet) and CH_2Ph (AB spin system) protons. The $^{13}C\{^1H\}$ NMR spectra also show the presence of all of the expected resonances. The $^{31}P\{^1H\}$ NMR spectra of **1–4** show, in each case, a singlet resonance (with ^{195}Pt satellites for **3** and **4**) shifted upfield with respect to that of the free diphosphazane ($\Delta\delta = \delta_{complex} - \delta_{free\ ligand} \cong -30$ ppm for Pt complexes and -15 ppm for the Pd ones). This shift indicates that the diphosphazanes are coordinated in a *P,P'*-chelating mode, forming four-membered metallacycles [15], as has been shown by the X-ray structure determination of *cis*-[Cl_2Pd{*S*-(Ph_2P)$_2$NC(H)(Me)(Ph)}] **1** [6]. Owing to the similarity between the spectroscopic data of **2** and **4** and those of **1** and **3**, we propose the same structure for this set of complexes, as shown in Eq. (1).

2.2. Reactions of cis-[Cl_2M(diphos)] 1–4 with MeOH

When suspensions of complexes **1–4** in MeOH were refluxed, the initially suspended solid gradually dissolved, giving yellow (Pd complexes, 1.5 h reflux) or colourless (Pt complexes, 6 h reflux) solutions from which yellow (Pd complexes **5** and **6**) or colourless (Pt complexes **7** and **8**) crystalline solids deposited upon cooling. The C, H, N analytical data of these crystals (**5–8**) showed the incorporation of one equivalent of MeOH per formula unit of the starting product **1–4**. Their spectroscopic data provide relevant structural information.

Thus, the IR spectra show, in all cases, three main features: (i) the *cis*-MCl_2 unit is preserved, as can be inferred from the observation of two absorptions in the ν(M–Cl) stretching region [13]; (ii) the appearance of a weak absorption at about 3200–3300 cm^{-1}, which is attributed to a ν(N–H) stretching mode; (iii) the disappearance of the sharp absorption attributed to the symmetrical vibrations of the P–N–P group at about 900 cm^{-1} [14].

Taking into account the already reported hydrolytic instability of the P–N bonds towards protic solvents and the preceding IR observations, we suggest that the reaction of **1–4** with MeOH proceeds with cleavage of one of the P–N bonds of the *S*-peap or *S*-plap ligands and incorporation of the MeOH to the final product, resulting in the formation of two monodentate P-donor ligands, PPh_2OMe and $PPh_2N(H)C(H)(R')(R'')$, which remain coordinated to the metal centre in mutually cis positions. Two chlorine ligands, obviously also in cis positions, complete the coordination sphere of the metal centre. The reaction process is represented in Eq. (2) (complexes **5–8**).



(2)

The ^{1}H NMR spectra of **5–8** (see Section 4) show, in addition to the expected resonances of the chiral fragments C(H)(Me)(Ph) or C(H)(CH_2PH)(CO_2Me), two new resonances—a doublet of relative intensity 3 at about 2.7 ppm, attributed to the PPh_2OMe protons

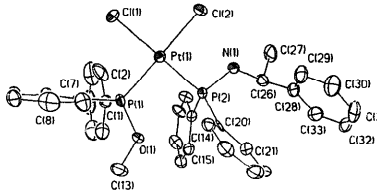


Fig. 1. Perspective view of the crystal structure of 7·0.75MeOH.

($^3J_{P-H} \cong 11$ Hz), and a doublet of doublets of relative intensity 1 at about 5.7 ppm, attributed to the $PPh_2N(H)C^*$ proton ($^2J_{P-H} \cong 14$ Hz, $^3J_{H-H} \cong 10$ Hz). The $^{31}P\{^1H\}$ NMR spectra of **5–8** show the presence of two doublets corresponding to an AX spin system with a coupling constant $^2J_{P-P} \cong 15$ Hz (Pt) and 27 Hz (Pd), indicating a cis disposition of the two P nuclei [11]. The downfield resonance appears at about 110 ppm (Pd) or 82 ppm (Pt), as is usual for phosphites, while the resonance corresponding to the amino-phosphine ligand $PPh_2N(H)C^*$ appears at about 57 ppm (Pd) or 33–40 ppm (Pt). The $^{13}C\{^1H\}$ NMR spectra show the presence of all the expected resonances for each compound. As can be seen, the structures depicted in Eq. (2) for **5–8** are in good agreement with the information provided by the NMR spectra. The single crystal X-ray structure determination of *cis*-[$Cl_2Pt(PPh_2OMe)$\{*S*-$PPh_2N(H)C(S)(Me)(Ph)$\}], **7**, provides further information.

2.3. Crystal structure of 7 · 0.75MeOH

A perspective view of the molecule is shown in Fig. 1. Crystallographic data, atomic coordinates and selected bond distances and angles are collected in Tables 1–3 respectively.

The platinum atom is located in a slightly distorted square-planar environment, surrounded by two chlorine atoms in mutually cis positions and by the two phosphorus atoms of the cis-phosphine ligands PPh_2OMe and $PPh_2N(H)C(H)(Me)(Ph)$. The disappearance of the chelate ring and the simultaneous presence of a methoxy group on a phosphorus atom and of a hydrogen on the nitrogen centre confirm the hypotheses established on the basis of the spectroscopic data and show unambiguously the cleavage of a P–N bond by methanolysis.

The bond distances Pt–Cl (2.356(2) and 2.374(2) Å) and Pt–P (2.214(2) and 2.224(2) Å) do not show remarkable deviations from the values found in the literature [16] and from those observed for other Pt-complexes containing the Cl-trans-to-P ligand arrangement [17]. The structural parameters of the PPh_2OMe ligand are also similar to those found in related complexes containing this group [11,12,17,18]. The phosphorus–nitrogen bond distance P(2)–N(1) = 1.658(7) Å) is shorter than those reported in the chelated diphosphazane [Cl_2Pd\{*S*-$(PPh_2)_2NC(H)(Me)(Ph)$\}] **1** (1.700(7) and 1.718(7) Å) [6] and is also shorter than the accepted value for a P–N single bond (1.77–1.80 Å), implying partial double bond character [18]. The environment of the N(1) centre is trigonal-planar and the value of the bond angle P(2)–N(1)–C(26) is 125.4 (6)°.

2.4. Other attempted reactions

In the same way as that described for complexes **5–8**, the reaction of *cis*-[Cl_2Pt(*S*-peap)], **3**, with EtOH, ^{n}PrOH or ethylene glycol (CH_2OH–CH_2OH) results in the formation of the neutral derivatives *cis*-[$Cl_2Pt(PPh_2OR)$\{*S*-$Ph_2PN(H)C(H)(Me)(Ph)$\}] (R = Et **9**, ^{n}Pr **10**, CH_2CH_2OH **11**). Similar reactions with the homologous palladium complexes were not attempted. The synthesis of **11** has been accomplished in a mixture

Table 1
Crystal data for 7 · 0.75MeOH

Formula	$C_{33.75}H_{36}Cl_2NO_{1.75}P_2Pt$	V (Å^3)	1636.9(3)
Crystal system	monoclinic	d_{calc} (g cm^{-3})	1.647
Space group	$P2_1$	Crystal size (mm^3)	0.60 × 0.35 × 0.25
Fw	811.57	μ (mm^{-1})	4.577
a (Å)	9.7100(10)	No. of unique reflections	5032
b (Å)	15.737(2)	No. of reflections with $I > 2\sigma(I)$	5032
c (Å)	11.2970(10)	No. of variables	383
α (ueg)	90.0	$R1^a$	0.0313
β (deg)	108.510(10)	$wR2^a$	0.0735
γ (deg)	90.0	GOF^a	1.258
Z	2	Residual electron density (e$^-$ Å^{-3})	1.463
F(000)	803	Flack parameter	0.013(9)
T (K)	150(2)	λ (Å)	0.71073

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{observns} - n_{params})]^{1/2}$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **7**·0.75MeOH

	x	y	z	U_{eq} [a]
Pt(1)	−1571(1)	−4(1)	−8445(1)	19(1)
P(1)	−809(2)	−464(1)	−9982(2)	18(1)
P(2)	−682(2)	−1161(1)	−7293(2)	17(1)
Cl(1)	−2303(3)	1280(1)	−9535(2)	29(1)
Cl(2)	−2601(2)	506(1)	−6936(2)	29(1)
C(1)	1034(9)	−185(5)	−9820(8)	24(2)
C(2)	1563(13)	592(8)	−9368(11)	46(3)
C(3)	3008(14)	803(9)	−9186(11)	60(4)
C(4)	3907(13)	224(9)	−9436(11)	56(5)
C(5)	3407(13)	−554(9)	−9931(12)	54(3)
C(6)	1970(11)	−776(7)	−10094(10)	40(2)
C(7)	−1895(8)	−106(7)	−11515(7)	23(2)
C(8)	−1311(10)	369(6)	−12274(8)	28(2)
C(9)	−2199(12)	614(6)	−13444(8)	40(3)
C(10)	−3628(12)	379(6)	−13884(9)	41(3)
C(11)	−4216(10)	−86(11)	−13134(8)	44(3)
C(12)	3366(10)	−324(6)	−11954(9)	35(2)
O(1)	−931(6)	−1473(4)	−10055(5)	24(1)
C(13)	−959(13)	−1981(6)	−11114(9)	44(3)
C(14)	1138(9)	−1463(5)	−7244(8)	21(2)
C(15)	1482(10)	−2199(5)	−7751(5)	26(2)
C(16)	2912(10)	−2370(6)	−7666(8)	29(2)
C(17)	3993(10)	−1809(6)	−7100(8)	32(2)
C(18)	3678(10)	−1069(6)	−6568(8)	29(2)
C(19)	2259(10)	−891(6)	−6661(8)	28(2)
C(20)	−1819(9)	−2098(5)	−7749(7)	22(2)
C(21)	−1427(11)	−2874(5)	−7119(9)	29(2)
C(22)	−2406(12)	−3534(6)	−7364(9)	38(2)
C(23)	−3762(12)	−3446(6)	−8238(10)	40(3)
C(24)	−4137(11)	−2701(6)	−8893(10)	33(2)
C(25)	−3165(9)	−2013(6)	−8630(8)	26(2)
N(1)	−448(8)	−927(4)	−5811(6)	23(2)
C(26)	227(10)	−1482(6)	−4750(8)	27(2)
C(27)	1066(11)	−930(7)	−3639(8)	37(2)
C(28)	−810(10)	−2074(5)	−4409(8)	25(2)
C(29)	−2277(10)	−1886(6)	−4687(9)	33(2)
C(30)	−3214(12)	−2467(7)	−4392(10)	43(3)
C(31)	−2667(12)	−3228(7)	−3839(9)	43(3)
C(32)	−1230(11)	−3417(6)	−3543(9)	34(2)
C(33)	−303(11)	−2841(6)	−3843(8)	33(2)
O(2)	−6465(15)	−2336(7)	−1914(11)	63(3)
C(34)	−5850(18)	−2408(10)	−2807(20)	64(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

of toluene–ethylene glycol (ca. 7/1) since refluxing **3** in the pure alcohol gave extensive decomposition of the product, probably due to the high boiling point of the alcohol. The analysis of the IR and NMR data of **9–11** allows us to establish for these complexes a structure analogous to that proposed for **5–8** (see Section 4 and Eq. (2)).

It is interesting to note the simultaneous presence in **11** of a hydroxyl group ($PPh_2CH_2CH_2OH$) and a P–N bond [$Ph_2PN(H)C(H)(Me)(Ph)$], and the lack of reactivity between them; in fact, the prolonged reflux of **3** (up to 12 h) in mixtures of toluene–ethylene glycol in different proportions does not afford any product other than **11**. Reflux of **11** in these mixtures did not afford the expected intramolecular cyclization; the starting product **11** was recovered unchanged. Similar results have been obtained with complexes **5–8**; thus, the prolonged reflux (up to 12 h) of **1–4** in MeOH did not afford products other than **5–8**, and from the prolonged reflux of **5–8**, the starting products were recovered unchanged; the product of double cleavage, *cis*-[$Cl_2M(PPh_2OMe)_2$], was not obtained in any case. We think, according to these results, that it is sensible to assume that the disappearance of the steric strain in the four-membered metallocycles **1–4** could be the driving force for the synthesis of **5–11**. Moreover, the cleavage of the four-membered metallocycle results in a strengthening of the remaining P–N bond, as can be seen by comparison of the P–N bond distances in **1** [6] and in **7** (see Section 2.3), and this fact could probably be related to the lack of reactivity of **5–8** towards further alcoholysis. This behaviour is similar to that reported for the Pt complexes of the related diphosphazane dppma [Ph_2P–N(Me)–PPh_2] [11]; thus, $[Pt(dppma)]^{2+}$ reacts with MeOH in the presence of halides, under very mild conditions, to give [Pt(dppma)(PPh_2OMe)(PPh_2-NHMe)]$^{2+}$ selectively.

In spite of this clear reactivity, other attempted reactions with protic solvents such as 2-propanol, 2-methyl-2-propanol, 2-methyl-1-butanol (branched alcohols), water or weak acids such as acetic acid did not give successful results. Thus, the reaction of **1** or **3** with the solvents indicated, both in pure form or as mixtures (i.e. acetone–H_2O; toluene–alcohol; acetic acid–H_2O–acetone) did not give the expected solvolyses of the P–N bond, and the starting products were recovered unchanged from the reaction mixtures. These results contrast with those observed for the above-mentioned dppma ligand [11], since $[Pt(dppma)_2](X)_2$ (X = halide) reacts with H_2O under mild conditions to give [Pt(dppma)($Ph_2PO\cdots H\cdots OPPh_2$)]$^+$.

All efforts to establish a mechanism which would account for these observations failed: neither is the reaction pathway for obtaining **5–11** known, nor has the influence of the different reaction parameters been established. The observed difference in the reaction times for Pd complexes (1.5 h reflux) with respect to the Pt analogues (6 h reflux at least) indicates that the metal is not acting only as spectator, but that it plays an important role in the reaction mechanism. On the other hand, we have proposed that the disappearance of the steric strain in the four-membered metallocycles **1–4** could be the driving force for the synthesis of **5–11**. We also think that the fact that only linear alcohols reacted with the starting complexes, but branched alcohols did not, seems suggest that steric factors, such as a hindered approach of the alcohol to the complex, could play a relevant role. However, this explanation cannot account

Table 3
Selected bond distances (Å) and angles (deg) for **7** · 0.75MeOH

Bond distances		
Pt(1)–P(1) = 2.214(2)	Pt(1)–P(2) = 2.244(2)	Pt(1)–Cl(1) = 2.356(2)
Pt(1)–Cl(2) = 2.374(2)	P(1)–O(1) = 1.592(6)	P(1)–C(1) = 1.795(8)
P(1)–C(7) = 1.808(8)	P(2)–N(1) = 1.658(7)	P(2)–C(14) = 1.814(8)
P(2)–C(20) = 1.816(8)	C(13)–O(1) = 1.432(11)	N(1)–C(26) = 1.460(11)
C(26)–C(28) = 1.509(13)	C(26)–C(27) = 1.531(13)	
Bond angles		
P(1)–Pt(1)–P(2) = 91.55(8)		P(1)–Pt(1)–Cl(1) = 89.50(8)
P(2)–Pt(1)–Cl(2) = 91.71(7)		Cl(1)–Pt(1)–Cl(2) = 87.65(8)
Pt(1)–P(1)–O(1) = 109.2(2)		Pt(1)–P(2)–N(1) = 108.1(3)
C(13)–O(1)–P(1) = 125.6(6)		C(26)–N(1)–P(2) = 125.4(6)
N(1)–C(26)–C(28) = 114.7(7)		N(1)–C(26)–C(27) = 108.5(7)
C(28)–C(26)–C(27) = 111.5(7)		

for the observed lack of reactivity of a small molecule such as water. Further work is now in progress in order to clarify the possible reaction pathway.

3. Conclusion

The susceptibility of the P–N bonds in the *P,P'*-chelated diphosphazane complexes *cis*-[Cl_2M(*S*-diphos)] **1–4** towards solvolysis has been clearly shown. The solvolysis is produced selectively by linear alcohols in only one of the two P–N bonds of the diphosphazane, resulting in the formation of *cis*-[$Cl_2M(PPh_2OR)${*S*-$Ph_2PN(H)C(H)(R')(R'')$}] **5–11**. However, the same starting complexes **1–4** do not react with branched alcohols or water. Further studies will concentrate on elucidating the mechanism involved in the formation of **5–11**.

4. Experimental section

4.1. General comments

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 infrared spectrophotometer in nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz) and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded from $CDCl_3$ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). The starting materials [*S*-$(Ph_2P)_2NC(H)(Me)(Ph)$] (*S*-peap) and [*S*-$(Ph_2P)_2NC(H)(CH_2Ph)(CO_2Me)$] (*S*-plap), were prepared according to published methods [4,6]. Complexes **1** and **3** were synthesized following a slight modification of the literature method [6]. The palladium and platinum complexes [$MCl_2(tht)_2$] were prepared according to the published method [19].

4.2. Preparation of *cis*-[Cl_2Pd[*S*-$(Ph_2P)_2NC(H)(Me)(Ph)$]] **1**

To a solution of [$PdCl_2(tht)_2$] (0.500 g, 1.41 mmol) in 20 ml of CH_2Cl_2, *S*-peap (0.692 g, 1.41 mmol) was added, resulting in the immediate precipitation of a yellow solid. After 2 h of stirring at room temperature, this solid was isolated by filtration, washed with *n*-hexane (2 × 50 ml), dried in vacuo and identified by spectroscopic methods as complex **1**. Obtained: 0.827 g (88% yield). The spectral parameters of **1** were coincident with those reported previously [6].

4.3. Preparation of *cis*-[Cl_2Pd[*S*-$(Ph_2P)_2NC(H)(CH_2Ph)(CO_2Me)$]] **2**

Complex **2** was synthesized similarly to **1**: [$PdCl_2(tht)_2$] (0.500 g, 1.41 mmol) was reacted with *S*-plap (0.774 g, 1.41 mmol) in CH_2Cl_2 at room temperature to give **2** as a pale yellow solid. Obtained: 1.032 g (90% yield).

Anal. Calc. for $C_{34}H_{31}Cl_2NO_2P_2Pd$ (724.87): C, 56.33; H, 4.31; N, 1.93. Found: C, 56.33; H, 3.89; N, 1.98. IR (ν, cm^{-1}): 1747 (s, ν_{CO}), 900 (m, ν_{PNP}), 304, 290 (m, ν_{Pd-Cl}). ^1H NMR: δ, 1.58 (dd, 1H, CH_2, $^2J_{H-H}$ = 13 Hz, $^3J_{H-CH}$ = 3 Hz), 2.30 (false t, 1H, CH_2, $^3J_{H-CH}$ = 13 Hz), 3.23 (s, 3H, CO_2Me), 3.95 (tdd, 1H, CH, $^3J_{P-H}$ = 18 Hz), 6.35–8.39 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR: δ, 35.58. $^{13}C\{^1H\}$ NMR: δ, 37.61 (CH_2), 52.40 (CO_2Me), 65.06 (t, CH, $^3J_{P-C}$ = 5 Hz), 126.12–134.46 (Ph), 168.30 (CO_2Me).

4.4. Preparation of *cis*-[Cl_2Pt[*S*-$(Ph_2P)_2NC(H)(Me)(Ph)$]] **3**

To a solution of [$PtCl_2(tht)_2$] (0.500 g, 1.13 mmol) in 30 ml of toluene, *S*-peap (0.553 g, 1.13 mmol) was added

and the resulting solution was refluxed for 4 h. After cooling, the white solid of **3** was filtered, washed with *n*-hexane (2 × 50 ml) and dried in vacuo. Obtained: 0.793 g (93% yield). The spectral parameters of **3** were coincident with those reported previously [6].

4.5. Preparation of cis-[Cl_2 Pt{S-(Ph_2P)$_2$NC(H)(CH_2Ph)(CO_2Me)}] 4

Complex **4** was synthesized similarly to **3**: [$PtCl_2$(tht)$_2$] (0.500 g, 1.13 mmol) was reacted with *S*-plap (0.619 g, 1.13 mmol) in refluxing toluene to give **4** as a white solid. Obtained: 0.864 g (94% yield).

Anal. Calc. for $C_{34}H_{31}Cl_2NO_2P_2Pt$ (813.57): C, 50.19; H, 3.84; N, 1.72. Found: C, 50.14; H, 3.75; N, 1.60. IR (ν, cm^{-1}): 1747 (s, ν_{CO}), 898 (m, ν_{PNP}), 313, 294 (m, ν_{Pt-Cl}). ^{1}H NMR: δ, 1.58 (dd, 1H, CH_2, $^2J_{H-H}$ = 12 Hz, $^3J_{H-CH}$ = 3 Hz), 2.31 (false t, 1H, CH_2, $^3J_{H-CH}$ = 12 Hz), 3.21 (s, 3H, CO_2Me), 3.85 (tdd, 1H, CH, $^3J_{P-H}$ = 18 Hz), 6.30–8.37 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 18.64 ($^1J_{Pt-P}$ = 3308 Hz). ^{13}C{^{1}H} NMR: δ, 37.51 (CH_2), 52.25 (CO_2*Me*), 65.64 (CH, $^3J_{Pt-C}$ = 105 Hz), 125.25–134.72 (Ph), 168.35 (CO_2Me).

4.6. Preparation of cis-[Cl_2 Pd(PPh_2OMe){S-Ph_2PN(H)C(H)(Me)(Ph)}] 5

Complex **1** (0.200 g, 0.30 mmol) was suspended in 15 ml of MeOH, and this suspension was refluxed until a clear yellow solution was obtained (ca. 1.5 h). This yellow solution was kept at −18 °C for 24 h, giving yellow crystals of **5**, which were collected and dried in vacuo. Obtained: 0.161 g (77% yield).

Anal. Calc. for $C_{33}H_{33}Cl_2NOP_2Pd$ (698.88): C, 56.71; H, 4.76; N, 2.00. Found: C, 56.58; H, 4.74; N, 1.89. IR (ν, cm^{-1}): 3264 (w, ν_{NH}), 317, 285 (m, ν_{Pd-Cl}). ^{1}H NMR: δ, 1.25 (d, 3H, Me, $^3J_{H-H}$ = 6 Hz), 2.65 (d, 3H, OMe, $^3J_{P-H}$ = 11 Hz), 3.76 (m, 1H, CH), 5.75 (dd, 1H, NH, $^2J_{P-H}$ = 14 Hz, $^3J_{H-CH}$ = 10 Hz), 6.95–7.55 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 56.44 (d, N–P–Pd, $^2J_{P-P}$ = 27 Hz), 109.19 (d, O–P–Pd). ^{13}C{^{1}H} NMR: δ, 26.85 (d, CH_3, $^3J_{P-C}$ = 5 Hz), 53.86 (d, OMe, $^2J_{P-C}$ = 9 Hz), 54.44 (d, CH, $^2J_{P-C}$ = 12 Hz), 125.58–145.18 (Ph).

4.7. Preparation of cis-[Cl_2 Pd(PPh_2OMe){S-Ph_2PN(H)C(H)(CH_2Ph)(CO_2Me)}] 6

Complex **6** was synthesized similarly to **5**: **2** (0.200 g, 0.27 mmol) was refluxed in MeOH (1.5 h) to give **6** as yellow crystals. Obtained: 0.146 g (70% yield).

Anal. Calc. for $C_{35}H_{35}Cl_2NO_3P_2Pd$ (756.92): C, 55.54; H, 4.66; N, 1.85. Found: C, 55.17; H, 4.27; N, 1.84. IR (ν, cm^{-1}): 3247 (w, ν_{NH}), 1746 (s, ν_{CO}), 310, 288 (m, ν_{Pd-Cl}). ^{1}H NMR: δ, 2.70 (d, 3H, P–OMe, $^3J_{P-H}$ = 11 Hz), 2.77 (m, 2H, CH_2), 3.24 (s, 3H, CO_2Me), 3.41 (m, 1H, CH), 5.77 (dd, 1H, NH, $^2J_{P-H}$ = 14 Hz, $^3J_{H-CH}$ = 11 Hz), 6.86–8.01 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 56.97 (d, N–P–Pd, $^2J_{P-P}$ = 26 Hz), 109.74 (d, O–P–Pd). ^{13}C{^{1}H} NMR: δ, 41.13 (d, CH_2, $^3J_{P-C}$ = 6 Hz), 51.77 (CO_2*Me*), 54.44 (d, CH, $^2J_{P-C}$ = 13 Hz), 58.25 (d, P–OCH_3, $^2J_{P-C}$ = 10 Hz), 126.84–133.63 (Ph), 172.73 (CO_2Me).

4.8. Preparation of cis-[Cl_2 Pt(PPh_2OMe){S-Ph_2PN(H)C(H)(Me)(Ph)}] 7

Complex **7** was synthesized similarly to **5**: **3** (0.200 g, 0.26 mmol) was refluxed in MeOH (6 h) to give **7** as colourless crystals. Obtained: 0.169 g (81% yield).

Anal. Calc. for $C_{33}H_{33}Cl_2NOP_2Pt$ (787.57): C, 50.33; H, 4.22; N, 1.78. Found: C, 50.26; H, 3.97; N, 1.78. IR (ν, cm^{-1}): 3284 (w, ν_{NH}), 317, 288 (m, ν_{Pt-Cl}). ^{1}H NMR: δ, 1.21 (d, 3H, Me, $^3J_{H-H}$ = 6 Hz), 2.70 (d, 3H, OMe, $^3J_{P-H}$ = 11 Hz), 3.78 (m, 1H, CH), 5.67 (dd, 1H, NH, $^2J_{P-H}$ = 13 Hz, $^3J_{H-CH}$ = 10 Hz), 6.66–7.94 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 32.80 (d, N–P–Pt, $^1J_{Pt-P}$ = 3937 Hz, $^2J_{P-P}$ = 15 Hz), 81.94 (d, O–P–Pt, $^1J_{Pt-P}$ = 4393 Hz). ^{13}C{^{1}H} NMR: δ, 26.77 (d, CH_3, $^3J_{P-C}$ = 5 Hz), 53.35 (d, OMe, $^2J_{P-C}$ = 7 Hz), 54.04 (d, CH, $^2J_{P-C}$ = 11 Hz), 125.52–145.14 (Ph).

4.9. Preparation of cis-[Cl_2 Pt(PPh_2OMe){S-Ph_2PN(H)C(H)(CH_2Ph)(CO_2Me)}] 8

Complex **8** was synthesized similarly to **5**: **4** (0.200 g, 0.25 mmol) was refluxed in MeOH (6 h) to give **8** as colourless crystals. Obtained: 0.187 g (90% yield).

Anal. Calc. for $C_{35}H_{35}Cl_2NO_3P_2Pt$ (845.61): C, 49.71; H, 4.17; N, 1.65. Found: C, 49.62; H, 3.84; N, 1.62. IR (ν, cm^{-1}): 3274 (w, ν_{NH}), 1746 (s, ν_{CO}), 315, 284 (m, ν_{Pt-Cl}). ^{1}H NMR: δ, 2.74 (d, 3H, P–OMe, $^3J_{P-H}$ = 11 Hz), 2.76 (m, 2H, CH_2), 3.24 (s, 3H, CO_2Me), 3.43 (m, 1H, CH), 5.75 (dd, 1H, NH, $^2J_{P-H}$ = 12 Hz, $^3J_{H-CH}$ = 11 Hz), 7.03–7.97 (m, 25H, Ph). ^{31}P{^{1}H} NMR: δ, 34.30 (d, N–P–Pt, $^1J_{Pt-P}$ = 3996 Hz, $^2J_{P-P}$ = 15 Hz), 82.89 (d, O–P–Pt, $^1J_{Pt-P}$ = 4306 Hz). ^{13}C{^{1}H} NMR: δ, 41.12 (d, CH_2, $^3J_{P-C}$ = 6 Hz), 51.73 (CO_2*Me*), 54.13 (d, CH, $^2J_{P-C}$ = 12 Hz, $^3J_{Pt-C}$ = 13 Hz), 57.94 (d, P–OCH_3, $^3J_{Pt-C}$ = 39 Hz, $^2J_{P-C}$ = 7 Hz), 126.83–136.12 (Ph), 172.81 (CO_2Me).

4.10. Preparation of cis-[Cl_2 Pt(PPh_2OEt){S-Ph_2PN(H)C(H)(Me)(Ph)}] 9

Complex **9** was synthesized similarly to **5**: **3** (0.200 g, 0.26 mmol) was refluxed in EtOH (6 h) to give, after solvent evaporation and Et_2O (25 ml) addition, **9** as a white solid. Obtained: 0.172 g (81% yield).

Anal. Calc. for $C_{34}H_{35}Cl_2NOP_2Pt$ (801.60): C, 50.94; H, 4.40; N, 1.74. Found: C, 50.77; H, 4.13; N, 1.62. IR (ν, cm^{-1}): 3289 (w, ν_{NH}), 308, 285 (m,

ν_{Pt-Cl}). ^1H NMR: δ, 0.34 (t, 3H, Me, $^3J_{H-H}$ = 6 Hz), 1.20 (d, 3H, Me, $^3J_{H-H}$ = 6 Hz), 3.10 (quart., 2H, OCH_2), 3.77 (m, 1H, CH), 5.71 (dd, 1H, NH, $^2J_{P-H}$ = 13 Hz, $^3J_{H-CH}$ = 10 Hz), 6.91–7.96 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR: δ, 32.30 (d, N–P–Pt, $^1J_{Pt-P}$ = 3927 Hz, $^2J_{P-P}$ = 16 Hz), 80.28 (d, O–P–Pt, $^1J_{Pt-P}$ = 4369 Hz). $^{13}C\{^1H\}$ NMR: δ, 14.90 (d, CH_3, $^3J_{P-C}$ = 7 Hz), 26.78 (d, CH_3, $^3J_{P-C}$ = 5 Hz), 53.20 (d, OCH_2, $^2J_{P-C}$ = 7 Hz), 64.59 (d, CH, $^2J_{P-C}$ = 12 Hz), 125.51–145.18 (Ph).

4.11. Preparation of cis-[$Cl_2Pt(PPh_2O^nPr)$(S-$Ph_2PN(H)C(H)(Me)(Ph)$)] 10

Complex **10** was synthesized similarly to **5**: **3** (0.200 g, 0.26 mmol) was refluxed in ^{n}PrOH (6 h) to give, after solvent evaporation and Et_2O (25 ml) addition, **10** as a white solid. Obtained: 0.164 g (76% yield).

Anal. Calc. for $C_{35}H_{37}Cl_2NOP_2Pt$ (815.63): C, 51.54: H, 4.57: N, 1.71. Found: C, 51.32; H, 4.46; N, 1.79. IR (ν, cm^{-1}): 3282 (w, ν_{NH}), 315, 292 (m, ν_{Pt-Cl}). ^1H NMR: δ, 0.26 (t, 3H, Me, $^3J_{H-H}$ = 7 Hz), 0.69 (qt, 2H, CH_2, $^3J_{H-H}$ = 6 Hz), 1.19 (d, 3H, Me, $^3J_{H-H}$ = 7 Hz), 3.00 (m, 2H, OCH_2, $^3J_{P-H}$ = 10 Hz), 3.77 (m, 1H, CH), 5.67 (dd, 1H, NH, $^2J_{P-H}$ = 13 Hz, $^3J_{H-CH}$ = 10 Hz), 6.68–7.92 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR: δ, 32.53 (d, N–P–Pt, $^1J_{Pt-P}$ = 3927 Hz, $^2J_{P-P}$ = 17 Hz), 80.28 (d, O–P–Pt, $^1J_{Pt-P}$ = 4360 Hz). $^{13}C\{^1H\}$ NMR: δ, 9.47 (CH_3), 22.60 (d, CH_2, $^3J_{P-C}$ = 7 Hz), 23.24 (d, CH_3, $^3J_{P-C}$ = 7 Hz), 53.25 (d, OCH_2, $^2J_{P-C}$ = 7 Hz), 70.28 (d, CH, $^2J_{P-C}$ = 11 Hz), 125.51–145.15 (Ph).

4.12. Preparation of cis-[$Cl_2Pt(PPh_2OCH_2CH_2OH)$(S-$Ph_2PN(H)C(H)(Me)(Ph)$)] 11

To a suspension of **3** (0.200 g, 0.26 mmol) in 20 ml of toluene, was added an excess of ethylene glycol (3 ml), and the mixture was refluxed for 6 h. After cooling, the white solid in suspension was filtered, dissolved in $CHCl_3$ (20 ml) and dried with $MgSO_4$. Subsequent filtration, evaporation of the solvent to dryness and treatment of the residue with Et_2O (25 ml) gave **11** as a white solid. Obtained: 0.151 g (70% yield).

Anal. Calc. for $C_{34}H_{35}Cl_2NO_2P_2Pt$ (817.60): C, 49.95; H, 4.31; N, 1.71. Found: C, 49.95; H, 3.95; N, 1.76. IR (ν, cm^{-1}): 3452 (w, ν_{OH}), 3287 (w, ν_{NH}), 307, 288 (m, ν_{Pt-Cl}). ^1H NMR: δ, 1.21 (d, 3H, Me, $^3J_{H-H}$ = 6 Hz), 1.62 (s, 1H, OH), 2.80 (m, 2H, OCH_2), 3.18 (m, 2H, OCH_2), 3.79 (m, 1H, CH), 5.76 (dd, 1H, NH, $^2J_{P-H}$ = 14 Hz, $^3J_{H-CH}$ = 10 Hz), 6.65–8.03 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR: δ, 31.94 (d, N–P–Pt, $^1J_{Pt-P}$ = 3913 Hz, $^2J_{P-P}$ = 17 Hz), 82.50 (d, O–P–Pt, $^1J_{Pt-P}$ = 4374 Hz). $^{13}C\{^1H\}$ NMR: δ, 26.75 (d, CH_3, $^3J_{P-C}$ = 6 Hz), 53.21 (d, $POCH_2$, $^2J_{P-C}$ = 7 Hz), 60.88 (d, CH_2OH, $^3J_{P-C}$ = 6 Hz), 69.75 (d, CH, $^3J_{P-C}$ = 12 Hz), 125.52–145.15 (Ph).

4.13. X-ray crystal structure determination of 7·0.75MeOH

4.13.1. Data collection

A colourless, block-shaped crystal of dimensions 0.60 × 0.35 × 0.25 mm^3 was mounted at the end of a quartz fibre and covered with epoxy. Geometric and intensity data were taken at 150 K using normal procedures on an automated four-circle diffractometer (Enraf–Nonius CAD4 Mo Kα radiation). After initial indexing of the cell, axial photos were taken for the axes **a**, **b**, **c** and [111] in order to check the lattice dimensions. The scan parameters for intensity data collection were chosen on the basis of two-dimensional (ω–θ) plots of 25 reflections. Intensity data were gathered in two shells, from 4.0–38.0° (2θ) and from 37.9–50.0° (2θ) in the quadrant ($+h, +k, \pm l$). We also gathered a shell of Friedel equivalent data from 4.0–45° (2θ) in the quadrant ($+h, -k, \pm l$). Data were collected using a variable scan-speed technique in which the weakest data were measured at the slowest scan speed. That is to say, no measurement was skipped or measured rapidly because of weak diffraction. Azimuthal scans of 11 scattering vectors were used as the basis of an absorption correction. Intensity- and orientation-monitor reflections were checked at regular intervals during data collection. For the determination of the unit cell constants, 25 reflections, well spread in reciprocal space, were centred at four different mechanical positions each.

4.13.2. Structure solution and refinement [1]

After data reduction and application of absorption corrections, [2] the heavy atoms in the asymmetric unit were located by an automated algorithm that incorporates Patterson analysis, difference direct methods, and Fourier peak-list optimization [21]. The remainder of the non-hydrogen atoms were located in difference Fourier maps. The structure was refined to F_o^2, and all positive data were used in the refinement [22]. The hydrogen atoms were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms, with a variable torsion angle about the bond between the methyl carbon atom and the adjacent non-hydrogen atom in each case. All hydrogen atoms were assigned isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. The enantiomorph was chosen on the basis of the known configuration of the *S*-C(H)(Me)(Ph)

[1] Crystallographic calculations were done on a Local Area VAX-Cluster (VAX/VMS V5.5-2), with the program XCAD4B, with the commercial package SHELXTL-PLUS, and with the program SHELXL-93.

[2] XCAD4B: program for the reduction of CAD4 data [20].

fragment. The Flack parameter [23] calculated at the end of the refinement had a value of 0.013(9). Convergence was reached with the residuals shown in Table 1.

5. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, anisotropic displacement parameters, complete list of bond lengths and angles and observed and calculated structure factors.

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References

[1] M.S. Balakrishna, V. Sreenivasa, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1, and references cited therein.
[2] R. Usón, J. Forniés, R. Navarro, J.I. Cebollada, J. Organomet. Chem. 304 (1986) 381.
[3] R. Usón, J. Forniés, R. Navarro, M. Tomás, C. Fortuño, J.I. Cebollada, Polyhedron 8 (1989) 1045.
[4] (a) P.W. Lednor, W. Beck, H.G. Fick, J. Organomet. Chem. 113 (1976) C19. (b) N.C. Payne, D.W. Stephan, J. Organomet. Chem. 221 (1981) 203.
[5] N.C. Payne, D.W. Stephan, J. Organomet. Chem. 221 (1981) 223.
[6] R.P.K. Babu, S.S. Krishnamurthy, M. Nethaji, Tetrahedron: Asymmetry 6 (1995) 427, and references cited therein.
[7] E.S. Batyeva, V.A. Al'fonsov and A.N. Pudovik, in: A.N. Pudovik (Ed.), Chemistry of Organophosphorous Compounds, Mir, Moscow, 1989.
[8] E.E. Nifantev, E.V Borisov, Zh. Obshch. Khim. 55 (1985) 1660; J. Gen. Chem. USSR 55 (1985) 1478 (Engl. Transl.).
[9] A.A. Korkin, E.N. Tsvetkov, Zh. Obshch. Khim. 57 (1987) 2155; J. Gen. Chem. USSR 57 (1987) 1929 (Engl. Transl.).
[10] R.B. King, J. Gimeno, Inorg. Chem. 17 (1978) 2396.
[11] C.S. Browning, D.H. Farrar, J. Chem. Soc. Dalton Trans. (1995) 2005.
[12] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 1283.
[13] D.M. Adams, in: Metal–Ligand and Related Vibrations, Edward Arnold, London, 1967, pp. 44–79.
[14] D.S. Payne, A.P. Walker, J. Chem. Soc. C: (1966) 498.
[15] P.E. Garrou, Chem. Rev. 81 (1981) 229.
[16] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) 51.
[17] Q.-B. Bao, S.J. Geib, A.L. Rheingold, T.B. Brill, Inorg. Chem. 26 (1987) 3453.
[18] M.S. Balakrishna, S.S. Krishnamurthy, R. Murugavel, M. Nethaji, I.I. Mathews, J. Chem. Soc. Dalton Trans. (1993) 477.
[19] R. Usón, J. Forniés, F. Martínez, M. Tomás, J. Chem. Soc. Dalton Trans. (1980) 888.
[20] K. Harms, personal communication, 1995.
[21] SHELXTL-PLUS Release 4.21/V: © 1990, Siemens Analytical X-ray Instruments, Inc., Madison, WI.
[22] G.M. Sheldrick, SHELXL-93: FORTRAN-77 Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, 1993.
[23] (a) H.D. Flack, Acta Crystallogr. Sect. A: 39 (1983) 876. (b) O. Bernardelli, H.D. Flack, Acta Crystallogr. Sect. A: 41 (1985) 500.