



Pd^{II} AND Pt^{II} COMPLEXES CONTAINING 1,1,4,7,10,10-HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE: FIRST X-RAY STRUCTURE OF A Pd-TETRAPHOS COMPLEX

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Abstract—Pd^{II} and Pt^{II} complexes of *meso*- or *rac*-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) have been prepared and characterized by X-ray diffraction methods, NMR spectroscopy (¹⁹⁵Pt{¹H}, ³¹P{¹H}), elemental analyses and melting points. The first X-ray structure of a Pd-tetraphos complex shows a strongly distorted square planar coordination in *meso*-[PdP4]Cl₂ (**1**). The Pd-atom deviates 0.231 Å from the best plane through the phosphorus atoms leading to an angle of 17.4° between the planes through Pd and the phosphorus atoms of the PPh₂, and through Pd and the phosphorus atoms of the PPh groups, respectively. *Rac*-[PdClP4]Cl (**2**) shows a trigonal bipyramidal coordination. The destabilization of a square planar P4 arrangement in **2** is discussed in view of the X-ray structure of **1**. *Meso*-(**3**) and *rac*-[Pd₂Cl₂(μ-Cl)P4]Cl (**4**) contain P4 in a chelating and bridging mode. In the case of Pt(II) three further derivatives of the earlier reported complexes *meso*- or *rac*-[Pt₂Cl₂(μ-Cl)P4]Cl have been prepared: *rac*-[Pt₂Cl₂(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**), where *t*-dppe is *trans*-1,2-bis(diphenylphosphino)ethylene, and *meso*-(**6**) and *rac*-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P4](PF₆) (**7**). The compounds **5–7** are rare examples of triply bridged Pt(II) dimers containing two five-coordinate Pt(II) centres.

Recent interest in metal complexes containing 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) stems from the versatile geometrical properties of this ligand allowing unusual coordination modes.^{1,2} In this paper the first X-ray structure of a Pd-tetraphos complex is presented. It is shown that in the case of Pd^{II} the destabilization of a square planar P4-arrangement in *meso*-[PdP4]Cl₂ (**1**) explains the occurrence of a trigonal bipyramidal coordination in *rac*-[PdClP4]Cl (**2**). The dimers *meso*-(**3**) and *rac*-[Pd₂Cl₂(μ-Cl)P4]Cl (**4**) contain P4 in a chelating and bridging mode. Furthermore, several new

derivatives of *meso*- or *rac*-[Pt₂Cl₂(μ-Cl)P4]Cl^{1b} have been prepared, where both *trans*-1,2-bis(diphenylphosphino)ethylene (*t*-dppe) as well as pyrimidine lead to triply bridged dimers with two five-coordinate Pt^{II} centres in *rac*-[Pt₂Cl₂(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**) and *meso*-(**6**) or *rac*-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P4](PF₆) (**7**). There is continuing interest in ligands like *t*-dppe, since they are heteroatom compounds that are isolobal with unsaturated hydrocarbon fragments.³ Bridging N-containing heterocycles like pyrimidine are rare^{4a} and in the case of Pt^{II} arouse interest for cytotoxicity experiments.^{4b} The reactions of *meso*- or *rac*-[Pt₂Cl₂(μ-Cl)P4]Cl with 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) or *cis*-1,2-bis(diphenylphosphino)ethylene (*c*-dppe) lead to splitting products in most cases.

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EXPERIMENTAL

Reagents and chemicals

Reagent grade chemicals were used as received unless stated otherwise. 1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane (P4), 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), *trans*-1,2-bis(diphenylphosphino)ethylene (*t*-dppe) and *cis*-1,2-bis(diphenylphosphino)ethylene (*c*-dppe) were purchased from the Strem Chemical Co. All other reagents and solvents were obtained from Fluka. Solvents used for NMR measurements and crystallization purposes were of purissimum grade quality. PdCl_2 and $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ were also received from Fluka.

Instrumentation

Fourier-mode $^{195}\text{Pt}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained by use of a Bruker AC-200 spectrometer (internal deuterium lock) and were recorded at 43.02 and 80.96 MHz, respectively. Positive chemical shifts are downfield from the standards, where 1.0 M Na_2PtCl_6 and 85% H_3PO_4 were used as standards, respectively.

Separation of the stereoisomers of P4

Commercial P4 was separated by fractional crystallization to give the pure *rac* and *meso* diastereomer, respectively, according to Brown and Canning.⁵

Syntheses of Pd^{II} and Pt^{II} complexes

A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all complexes. Solvents were degassed by several freeze–pump–thaw cycles prior to use. All reactions were carried out at room temperature unless stated otherwise. *Meso*- or *rac*- $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})\text{P4}]\text{Cl}$ was prepared according to Ref. 1b.

Meso- $[\text{PdP4}]\text{Cl}_2$ (1)

To PdCl_2 (0.3 mmol, 0.053 g) in water a solution of *meso* P4 (0.3 mmol, 0.201 g) in CH_2Cl_2 was added. Then EtOH was added under stirring until a white precipitate formed. Compound 1 was filtered off, washed with water, and dried *in vacuo*. The white powder was recrystallized from CH_2Cl_2 : yield 0.187 g (70%); m.p. = 185–188°C. Found: C, 57.0; H, 5.2. Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{P}_4\text{Pd} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 57.3; H, 4.9%. A sample for X-ray diffraction study was crystallized from CH_2Cl_2 .

X-Ray crystallography

Crystal data. $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{P}_4\text{Pd} \cdot 0.5\text{CH}_2\text{Cl}_2$, $M = 890.46$, colourless crystal (irregular; $0.5 \times 0.3 \times 0.1$ mm), monoclinic, $a = 11.324(2)$, $b = 17.562(4)$, $c = 20.871(4)$ Å, $\beta = 102.77(2)^\circ$, $V = 4047.99$ Å³, $Z = 4$, space group $\text{P2}_1/\text{c}$, $D_c = 1.461$ Mg m^{−3}, $F(000) = 1820$, $\mu(\text{Mo-K}_\alpha) = 0.845$ mm^{−1}.

Data collection. Unit cell dimensions and intensity data were obtained at 173 K using a Siemens P4 diffractometer and graphite monochromated Mo- K_α radiation. 2θ range = $7.0\text{--}45.0^\circ$, scan type = ω , scan speed = variable ($2.0\text{--}29.3^\circ \times \text{min}^{-1}$ in ω), index ranges = $-1 < h < 14$, $-1 < k < 24$, $-29 < l < 28$. No decay in the intensities of three standard reflections was observed during the course of data collection. The data were corrected for Lorentz and polarization effects. The empirical absorption correction was based on ψ -scans of nine reflections (range of transmission factors: 0.41–0.63).⁶ A total of 13 993 reflections was measured, of which 11 577 were unique ($R_{\text{int}} = 0.036$) and 9664 satisfied the condition $F_o > 3\sigma(F_o)$.

Structure solution. All structure determination calculations were done on a 80486-PC using the PC-version of SHELXTL PLUS.⁷ The position of the palladium atom was found by the Patterson method. Other atom positions were located from successive difference Fourier maps. Half a molecule of dichloromethane per asymmetric unit was included in the isotropic refinement. Final refinement was carried out with anisotropic thermal parameters for all other non-hydrogen atoms. Hydrogen atoms were included using a riding model with fixed isotropic U . The final R value of 0.041 ($R' = 0.048$) was computed for 454 parameters. The largest feature on a final difference map was $1.26 \text{ e}\text{\AA}^{-3}$ (GOF = 1.55, largest $\Delta/\sigma = 0.076$, weighting scheme: $w^{-1} = \sigma^2(F) + 0.0010 F^2$). Final atomic fractional coordinates and other relevant data have been deposited.

Rac- $[\text{PdClP4}]\text{Cl}$ (2)

Compound 2 was prepared in an analogous manner to 1, where *rac*-P4 was used instead of *meso*-P4: yield 0.140 g (55%); m.p. = 242°C. Found: C, 59.3; H, 5.3. Calc. for $\text{C}_{42}\text{H}_{42}\text{Cl}_2\text{P}_4\text{Pd}$: C, 59.5; H, 5.0%.

Meso- $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})\text{P4}]\text{Cl}$ (3) and *rac*- $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})\text{P4}]\text{Cl}$ (4)

To PdCl_2 (0.3 mmol, 0.053 g) in water a solution of *meso*- or *rac*-P4 (0.15 mmol, 0.101 g) in CH_2Cl_2 was added. Then EtOH was added under stirring

until a white precipitate formed. Compound **3** or **4** was filtered off, washed with water, and dried *in vacuo*. The white powder was recrystallized from CH₂Cl₂: yields 0.131 g (85%) (**3**), 0.121 g (79%) (**4**); m.p. = 270°C dec. (**3**), 240°C dec. (**4**). Found: C, 49.0; H, 4.3 (**3**); C, 48.9; H, 4.2% (**4**). Calc. for C₄₂H₄₂Cl₄P₄Pd₂: C, 49.2; H, 4.1%.

Rac-[Pt₂Cl₂(μ-Cl)(μ-*t*-dppe)P₄]Cl (5**)**

Rac-[Pt₂Cl₂(μ-Cl)P₄]Cl (0.2 mmol, 0.241 g) was suspended in CH₂Cl₂. A solution of *t*-dppe (0.2 mmol, 0.079 g) in CH₂Cl₂ was added under stirring. The reaction mixture was heated up to 40°C and after 5 min a clear solution was obtained. After 24 h at this temperature **5** was crystallized from the CH₂Cl₂ solution: yield 0.182 g (57%); m.p. = 184–186°C. Found: C, 51.0; H, 4.1. Calc. for C₆₈H₆₄Cl₄P₆Pt₂: C, 51.1; H, 4.0%.

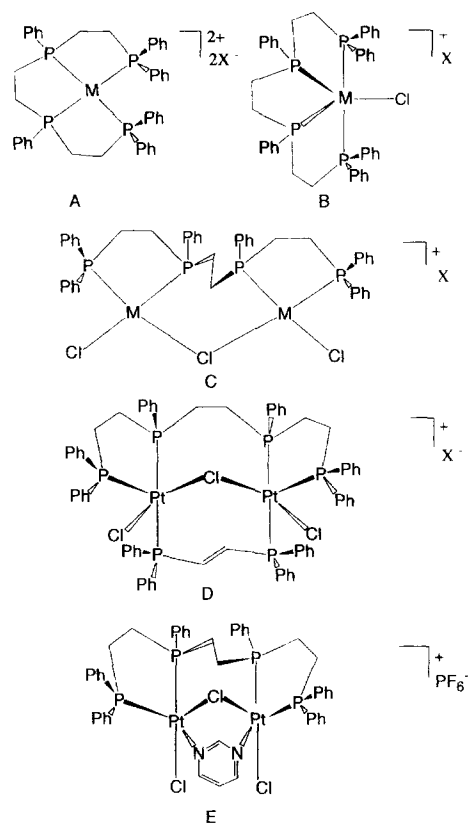
Meso-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P₄](PF₆) (6**) and *rac*-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P₄](PF₆) (**7**)**

Meso- or *rac*-[Pt₂Cl₂(μ-Cl)P₄]Cl (0.2 mmol, 0.241 g) was suspended in CH₂Cl₂/DMF (v/v = 1:1). Pyrimidine (0.2 mmol, 0.016 g) and Ag(PF₆) (0.2 mmol, 0.051 g) were added and the reaction mixture was stirred at 40°C for 3 days. The AgCl formed was filtered off. The remaining solution was evaporated, the brown residue washed with diethylether and dried *in vacuo*. The brown powder was recrystallized from DMF: yields 0.198 g (71%) (**6**), 0.181 g (65%) (**7**); m.p. = 176–177°C (**6**), >310°C (**7**). Found: C, 39.5; H, 3.5; N, 2.3 (**6**); C, 39.4; H, 3.4; N, 2.2 (**7**). Calc. for C₄₆H₄₆N₂Cl₃F₆P₅Pt₂: C, 39.7; H, 3.3; N, 2.0%.

RESULTS

In the case of Pd^{II}, reaction with P4 led to three structural types: types A and B for monomers (Scheme I) and structure C for dimers. Type A exclusively occurs in *meso*-[PdP₄]Cl₂ (**1**). *Rac*-[PdClP₄]Cl (**2**) corresponds to structure B and *meso*- (**3**) or *rac*-[Pd₂Cl₂(μ-Cl)P₄]Cl (**4**) show the solution structure C. However, addition of (BPh₄)[−] to a solution of **3** produces a mixture of compounds also containing a monomer of structure B. This is a striking result, since it means that trigonal bipyramidal monomers (type B) are possible for *meso*- and *rac*-P4, but a square planar monomer (type A) only occurs in the case of *meso*-P4. In order to reveal a possible destabilization of square planar P4 arrangements for Pd^{II}, an X-ray structure analysis of **1** was performed.

The first X-ray structure of a Pd^{II}-tetraphos com-



Scheme I. Structure types observed in the compounds **1**–**7**. The P—Pt—P angles where the phosphorus atoms are connected by ethylene chains are constrained to about 85°. Structure A occurs in *meso*-[PdP₄]Cl₂ (**1**), structure B in *rac*-[PdClP₄]Cl (**2**), structure C in *meso*- (**3**) and *rac*-[Pd₂Cl₂(μ-Cl)P₄]Cl (**4**), structure D in *rac*-[Pt₂Cl₂(μ-Cl)(μ-*t*-dppe)P₄]Cl (**5**), and structure E in *meso*- (**6**) and *rac*-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P₄](PF₆) (**7**).

plex shows a discrete *meso*-[PdP₄]²⁺ cation, two chloride anions and half a molecule of CH₂Cl₂ per asymmetric unit. A view of *meso*-[PdP₄]²⁺ is given in Fig. 1(a); Table 1 contains selected bond distances and bond angles. The square planar coordination in *meso*-[PdP₄]²⁺ is strongly distorted. Though the phosphorus atoms only slightly deviate from a best plane through these atoms (P1: −0.014, P2: 0.017, P3: −0.017, P4: 0.014 Å), the Pd-atom shows a remarkable deviation of 0.231 Å from this plane towards the phenyl-rings of the PPh₂-groups (see Fig. 1b). This leads to an angle of 17.4° between the planes through Pd and the phosphorus atoms of the PPh₂ groups, and through Pd and the phosphorus atoms of the PPh groups, respectively. The Pd—PPh bonds [2.294(1) Å] are significantly shorter than the Pd—PPh₂ bonds [2.331(1) Å]. Both averaged bond lengths are longer than the corresponding bonds in *meso*-[PtP₄]²⁺ (**8**) [Pt—PPh: 2.274(4), Pt—PPh₂: 2.327(4) Å].⁸ The PhP—Pd—PPh angle is strongly reduced to 81.8(1)°

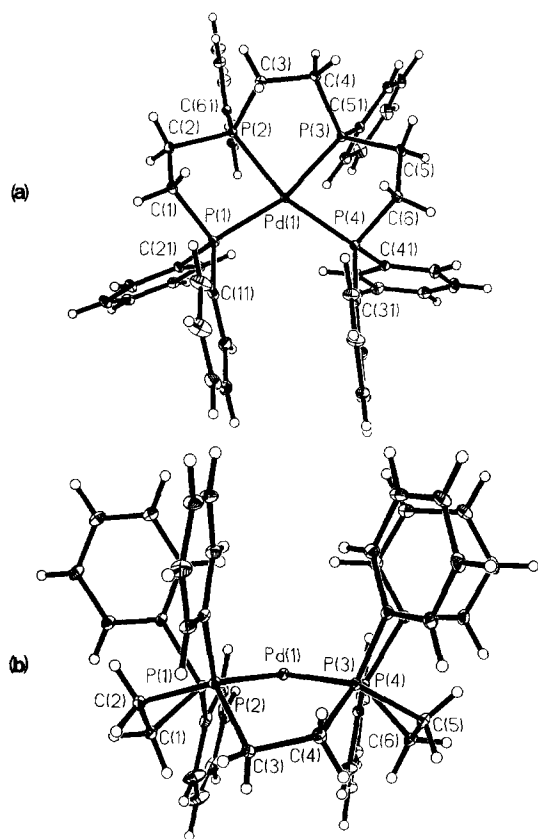


Fig. 1. View of the cation of *meso*-[PdP₄]Cl₂ (**1**). (a) The coordination plane through the Pd atom and the P atoms in the projection plane showing the atom labelling scheme; (b) projection along the coordination plane.

[compare 83.6(2)° in **8**] and the Ph₂P—Pd—PPh₂ angle is wide open [107.9(1)°; 105.8(2)° in **8**]. The shortest intermolecular contact of 2.573 Å occurs between the anion C11 and H3A (attached to C3). This possibly produces the asymmetry of the central C3—C4 bridge (see Fig. 1a).

The above values indicate a stronger destabilization of the square planar P₄ arrangement in **1** than in **8**. However, the deviations from an ideal square planar P₄ coordination are also larger in *rac*-[PtP₄]²⁺ (**9**) than in **8** [e.g. the Ph₂P—Pt—PPh₂ angle is 109.5(2)° in **9**].⁹ It seems likely that a further destabilization of the P₄ arrangement in a square planar *rac*-[PdP₄]²⁺ species is too large. As a consequence only the formation of trigonal bipyramidal *rac*-[PdClP₄]⁺ is observed.

The solution ³¹P{¹H} NMR parameters (see Table 2) of **1** are consistent with the solid state structure and with an AA'MM' spin system. As already mentioned, in the case of *rac*-P₄ no Pd^{II} species of structure type A (Scheme I) is formed. The ³¹P{¹H} NMR spectrum of *rac*-[PdClP₄]Cl (**2**) is consistent with structure B and an A₂B₂ spin system. Except for the equivalence of the PPh₂-

and PPh-groups in structure B, this coordination resembles the trigonal bipyramidal structure of [FeBrP₄](BPh₄).¹¹

The ³¹P{¹H} NMR data for *meso*- (**3**) and *rac*-[Pd₂Cl₂(μ-Cl)P₄]Cl (**4**) are in agreement with structure C and A₂B₂ spin systems. Exchange reactions with non-coordinating anions indicate monocations in **3** and **4**. Also *meso*- and *rac*-[Pt₂Cl₂(μ-Cl)P₄]Cl show the solution structure C.^{1b}

Addition of *t*-dppe to *rac*-[Pt₂Cl₂(μ-Cl)P₄]Cl led to *rac*-[Pt₂Cl₂(μ-Cl)(μ-*t*-dppe)P₄]Cl (**5**). The ³¹P{¹H} NMR spectrum of **5** is shown in Fig. 2(a) and the corresponding ³¹P{¹H} NMR parameters are summarized in Table 2. They are in agreement with structure type D (Scheme I), which contains *t*-dppe in an μ-η²-binding mode. The *trans* positions of the PPh groups of P₄ and the PPh₂ groups of *t*-dppe are clearly indicated by ²J(PPh, PPh₂(*t*-dppe)) of 378 Hz typical for the ²J(P, P) *trans* range.¹² The smaller ¹J(Pt, PPh) and ¹J(Pt, PPh₂(*t*-dppe)) values compared with ¹J(Pt, PPh₂) are also in accordance with this coordination. The ³J(Pt, PPh₂) coupling of 65 Hz shows the presence of the chloro-bridge. Like *rac*-[Pt₂Cl₂(μ-Cl)(μ-dppa)P₄](BPh₄),^{1a} where dppa is 1,2-bis(diphenylphosphino)acetylene, **5** is another rare example of two five-coordinate Pt(II) centres triply bridged by two different phosphorus ligands, P₄ and *t*-dppe, respectively, and by chloride. Also in **5** the Pt₂(μ-Cl)P₄ core (see structure D) resembles the well-known A-frame molecules.¹³

Addition of pyrimidine to *meso*- or *rac*-[Pt₂Cl₂(μ-Cl)P₄]Cl and simultaneous exchange of the chloride anion by (PF₆)[−] led to *meso*-(**6**) and *rac*-[Pt₂Cl₂(μ-Cl)(μ-pyrimidine)P₄](PF₆) (**7**). The ¹⁹⁵Pt{¹H} NMR spectrum of **6** is shown in Fig. 2(b). It consists of a superposition of three subspectra produced by the Pt—Pt, Pt—¹⁹⁵Pt and ¹⁹⁵Pt—¹⁹⁵Pt isotopomers.¹⁴ A full analysis of this spectrum using the program INSIM established, *inter alia*, the ²J(Pt, Pt) value of 1740 Hz, indicating that the two Pt(II) centres are inequivalent in solution. The ¹⁹⁵Pt{¹H} NMR spectrum of **7** is very similar [δ¹⁹⁵Pt = −4434, ²J(Pt, Pt) = 1518 Hz]. The ¹J(Pt, P) parameters of **6** and **7** are summarized in Table 2. The ³¹P{¹H} NMR spectra of **6** and **7** are consistent with A₂B₂ spin systems. In both cases the ³J(Pt, PPh₂) couplings (see Table 2) indicate the presence of the chloro-bridges.

The ¹⁹⁵Pt{¹H} and ³¹P{¹H} NMR parameters of **6** and **7** are in agreement with structure type E (Scheme I). The larger ¹J(Pt, PPh) values compared with ¹J(Pt, PPh₂) are also consistent with this structure due to the low *trans* influence of chlorine. The μ-η²-binding mode of pyrimidine is a consequence of the observation that coordination of one transition-metal fragment to a diazine does not dras-

Table 1. Selected bond lengths (Å) and angles (°) for *meso*-[PdP4]Cl₂ (1)

Pd(1)—P(4)	2.328 (1)	Pd(1)—P(3)	2.292 (1)
Pd(1)—P(2)	2.295 (1)	Pd(1)—P(1)	2.333 (1)
P(4)—C(6)	1.838 (3)	P(4)—C(31)	1.810 (3)
P(4)—C(41)	1.814 (3)	P(3)—C(5)	1.848 (3)
P(3)—C(4)	1.850 (3)	P(3)—C(51)	1.805 (2)
P(2)—C(3)	1.821 (3)	P(2)—C(2)	1.832 (3)
P(2)—C(61)	1.811 (2)	P(1)—C(1)	1.847 (3)
P(1)—C(11)	1.819 (3)	P(1)—C(21)	1.810 (3)
C(1)—C(2)	1.540 (4)	C(3)—C(4)	1.547 (4)
C(6)—C(5)	1.542 (4)		
P(4)—Pd(1)—P(3)	83.4(1)	P(4)—Pd(1)—P(2)	162.6(1)
P(3)—Pd(1)—P(2)	81.8(1)	P(4)—Pd(1)—P(1)	107.9(1)
P(3)—Pd(1)—P(1)	162.5(1)	P(2)—Pd(1)—P(1)	84.6(1)
Pd(1)—P(4)—C(6)	102.6(1)	Pd(1)—P(4)—C(31)	124.7(1)
C(6)—P(4)—C(31)	104.3(1)	Pd(1)—P(4)—C(41)	111.1(1)
C(6)—P(4)—C(41)	106.8(1)	C(31)—P(4)—C(41)	105.9(1)
Pd(1)—P(3)—C(5)	109.2(1)	Pd(1)—P(3)—C(4)	106.2(1)
C(5)—P(3)—C(4)	111.5(1)	Pd(1)—P(3)—C(51)	121.0(1)
C(5)—P(3)—C(51)	103.6(1)	C(4)—P(3)—C(51)	105.2(1)
Pd(1)—P(2)—C(3)	100.7(1)	Pd(1)—P(2)—C(2)	109.3(1)
C(3)—P(2)—C(2)	110.7(1)	Pd(1)—P(2)—C(61)	120.3(1)
C(3)—P(2)—C(61)	106.7(1)	C(2)—P(2)—C(61)	108.8(1)
Pd(1)—P(1)—C(1)	102.7(1)	Pd(1)—P(1)—C(11)	123.3(1)
C(1)—P(1)—C(11)	106.2(1)	Pd(1)—P(1)—C(21)	114.3(1)
C(1)—P(1)—C(21)	103.8(1)	C(11)—P(1)—C(21)	104.7(1)
P(1)—C(1)—C(2)	108.6(2)	P(2)—C(3)—C(4)	108.9(2)
P(2)—C(2)—C(1)	109.9(2)	P(4)—C(6)—C(5)	110.3(2)
P(3)—C(5)—C(6)	111.9(2)	P(3)—C(4)—C(3)	112.5(2)

Table 2. ³¹P{¹H} NMR data for 1–7^a

Compound	δPPh	δPPh ₂	¹ J(Pt, PPh)	¹ J(Pt, PPh ₂)
1 ^b	103.2	50.8		
2	53.3	45.5		
3	74.1	64.7		
4	70.3	63.9		
5 ^c	57.8	50.2	2535	3400
6 ^d	44.5	43.4	3512	3302
7 ^e	44.0	43.1	3500	3300

^a *J* values in Hz. Spectra were run at 298 K. The following solvents were used: CH₂Cl₂ (1, 3–5), EtOH (2), DMF (6, 7).

^b ²*J*(PPh₂, PPh)_{trans} = 331, ²*J*(PPh₂, PPh)_{cis} + ³*J*(PPh₂, PPh)_{cis} = 26.

^c δPPh₂(*t*-dppe) = 12.3, ¹*J*[Pt, PPh₂(*t*-dppe)] = 2240, ³*J*(Pt, PPh₂) = 65, ²*J*[PPh₂(*t*-dppe), PPh]_{trans} = 378.

^d ³*J*(Pt, PPh₂) = 58.

^e ³*J*(Pt, PPh₂) = 60.

7, as indicated by their ¹⁹⁵Pt{¹H} spectra, is possibly produced by an asymmetric tilting of the Pt^{II} coordination and the heterocycle planes, where this phenomenon is common for Pt^{II} complexes with aromatic N-heterocycles and phosphine ligands.¹⁵ Both 6 and 7 are rare examples of two five-coordinate Pt^{II} centres bridged by an aromatic N-heterocycle.

Reaction of *meso*- or *rac*-[Pt₂Cl₂(μ-Cl)P4]Cl with chelating diphosphines like dpmm, dppe or *c*-dppe led to splitting products and monomeric PtP4-species already known.^{12b} The splitting products were identified as [Pt(dpmm)Cl₂], [Pt(dppe)Cl₂], [Pt(dppe)₂]²⁺, [Pt(*c*-dppe)Cl₂] and [Pt(*c*-dppe)₂]²⁺. Only in the case of dpmm the triply bridged compound *rac*-[Pt₂Cl₂(μ-Cl)(μ-dpmm)P4](PF₆) corresponding to structure type D (Scheme I) was formed. However, it could not be obtained in an analytically pure form.

DISCUSSION

tically change the basicity of the second nitrogen atom.^{4a} The asymmetry of the two halves of 6 and

As can be expected from the difference in crystal field stabilization energy in the square planar

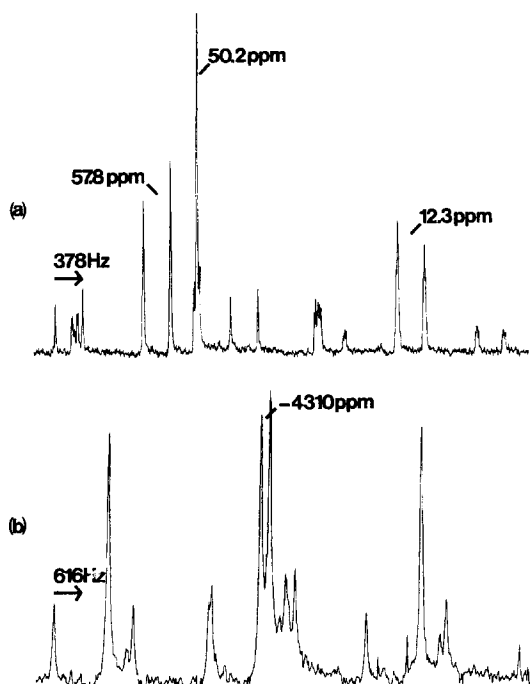


Fig. 2. (a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 80.96 MHz and 298 K of a CH_2Cl_2 solution of $\text{rac-}[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-}t\text{-dppe})\text{P}_4]\text{Cl}$ (**5**); (b) $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum at 43.02 MHz and 298 K of a DMF solution of $\text{meso-}[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-pyrimidine})\text{P}_4](\text{PF}_6)$ (**6**).

environment for Pd^{II} and Pt^{II} complexes,¹⁶ the deviations from an ideal square planar coordination are larger in **1** than in **8**. As a consequence a square planar arrangement of rac-P4 is completely destabilized for Pd^{II} . A similar diastereoselective reactivity of **P4** has also been observed in the formation of **5**, since it was not possible to obtain the corresponding *meso*-form. However, in the cases of **3** and **4**, and **6** and **7**, respectively, both diastereomers were formed with very similar structures. It seems likely that only in some cases the differences in **P4** coordination between the *meso*- and *rac*-form are large enough to produce completely different reactivity patterns. This corresponds to the results found for other **P4** containing Pt^{II} dimers,^{1a} where the diastereoselective reactivity of **P4** depends on the very nature of various bridging ligands. This effect can clearly be seen in the case of the diphosphines, since the different preferences of a chelating or bridging coordination mode lead to bridged

species only for *dppa*, *t-dppe* and *dppm*, and only for *rac-P4*.

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