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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 ($^{195}Pt\{^1H\}$, $^{31}P\{^1H\}$), 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]Cl_2 (**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 PPh_2, 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*-[Pd_2Cl_2(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*-[Pt_2Cl_2(μ-Cl)P4]Cl have been prepared: *rac*-[Pt_2Cl_2(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**), where *t*-dppe is *trans*-1,2-bis(diphenylphosphino)ethylene, and *meso*- (**6**) and *rac*-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**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]Cl_2 (**1**) explains the occurrence of a trigonal bipyramidal coordination in *rac*-[PdClP4]Cl (**2**). The dimers *meso*-(**3**) and *rac*-[Pd_2Cl_2(μ-Cl)P4]Cl (**4**) contain P4 in a chelating and bridging mode. Furthermore, several new derivatives of *meso*- or *rac*-[Pt_2Cl_2(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*-[Pt_2Cl_2(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**) and *meso*-(**6**) or *rac*-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**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*-[Pt_2Cl_2(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 $Na_2PtCl_4 \cdot 4H_2O$ were also received from Fluka.

Instrumentation

Fourier-mode $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ 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*-$[Pt_2Cl_2(\mu\text{-}Cl)P4]Cl$ was prepared according to Ref. 1b.

Meso-$[PdP4]Cl_2$ (**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 $C_{42}H_{42}Cl_2P_4Pd \cdot 0.5CH_2Cl_2$: C, 57.3; H, 4.9%. A sample for X-ray diffraction study was crystallized from CH_2Cl_2.

X-Ray crystallography

Crystal data. $C_{42}H_{42}Cl_2P_4Pd \cdot 0.5CH_2Cl_2$, M = 890.46, colourless crystal (irregular; 0.5 × 0.3 × 0.1 mm), monoclinic, a = 11.324(2), b = 17.562(4), c = 20.871(4) Å, β = 102.77(2)°, V = 4047.99 Å^3, Z = 4, space group $P2_1/c$, D_c = 1.461 Mg m^{-3}, F(000) = 1820, μ(Mo-K_α) = 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 = 7.0–45.0°, scan type = ω, scan speed = variable (2.0–29.3° × 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_{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 eÅ^{-3} (GOF = 1.55, largest Δ/σ = 0.076, weighting scheme: $w^{-1} = \sigma^2(F) + 0.0010F^2$). Final atomic fractional coordinates and other relevant data have been deposited.

Rac-[PdClP4]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 $C_{42}H_{42}Cl_2P4Pd$: C, 59.5; H, 5.0%.

Meso-$[Pd_2Cl_2(\mu\text{-}Cl)P4]Cl$ (**3**) *and* rac-$[Pd_2Cl_2(\mu\text{-}Cl)P4]Cl$ (**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 CH_2Cl_2: 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 $C_{42}H_{42}Cl_4P_4Pd_2$: C, 49.2; H, 4.1%.

Rac-[Pt_2Cl_2(μ-Cl)(μ-t-dppe)P4]Cl (**5**)

Rac-[Pt_2Cl_2(μ-Cl)P4]Cl (0.2 mmol, 0.241 g) was suspended in CH_2Cl_2. A solution of *t*-dppe (0.2 mmol, 0.079 g) in CH_2Cl_2 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 CH_2Cl_2 solution: yield 0.182 g (57%); m.p. = 184–186°C. Found: C, 51.0; H, 4.1. Calc. for $C_{68}H_{64}Cl_4P_6Pt_2$: C, 51.1; H, 4.0%.

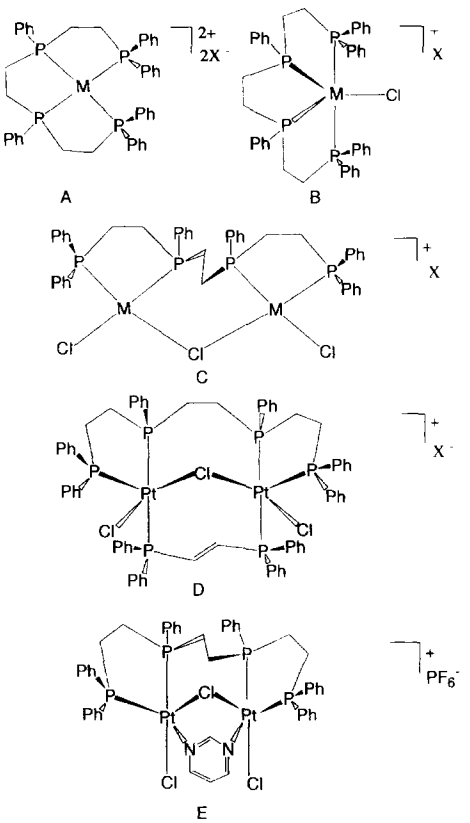
Meso-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**6**) *and* rac-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**7**)

Meso- or *rac*-[Pt_2Cl_2(μ-Cl)P4]Cl (0.2 mmol, 0.241 g) was suspended in CH_2Cl_2/DMF (v/v = 1 : 1). Pyrimidine (0.2 mmol, 0.016 g) and Ag(PF_6) (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 $C_{46}H_{46}N_2Cl_3F_6P_5Pt_2$: 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]Cl_2 (**1**). *Rac*-[PdClP4]Cl (**2**) corresponds to structure B and *meso-* (**3**) or *rac*-[Pd_2Cl_2(μ-Cl)P4]Cl (**4**) show the solution structure C. However, addition of $(BPh_4)^-$ 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]Cl_2 (**1**), structure B in *rac*-[PdClP4]Cl (**2**), structure C in *meso*-(**3**) and *rac*-[Pd_2Cl_2(μ-Cl)P4]Cl (**4**), structure D in *rac*-[Pt_2Cl_2(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**), and structure E in *meso*-(**6**) and *rac*-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**7**).

plex shows a discrete *meso*-$[PdP4]^{2+}$ cation, two chloride anions and half a molecule of CH_2Cl_2 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 PPh-groups (see Fig. 1b). This leads to an angle of 17.4° between the planes through Pd and the phosphorus atoms of the PPh_2 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—PPh_2 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-PPh_2: 2.327(4) Å].[8] The PhP—Pd—PPh angle is strongly reduced to 81.8(1)°

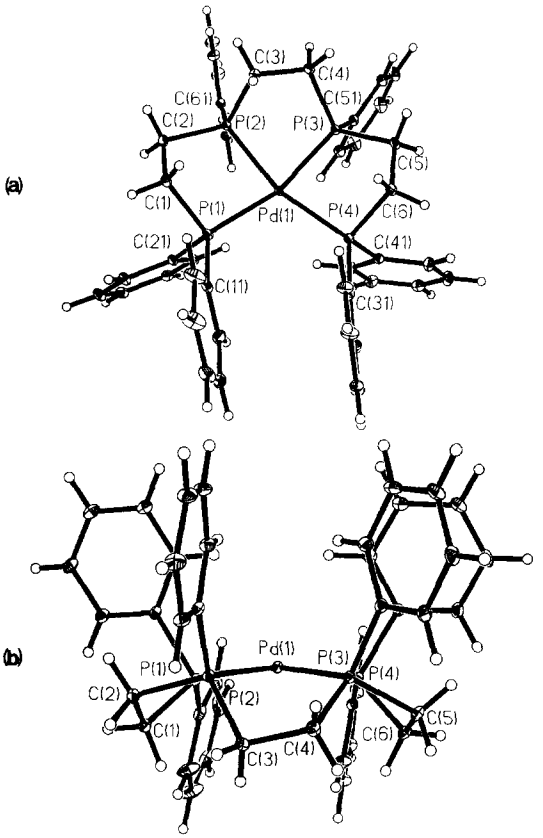


Fig. 1. View of the cation of *meso*-[PdP4]Cl_2 (**1**). (a) The coordination plane through the Pd atom and the P atoms in the projection plane showing the atom labelling scheme; (b) projection along the coordination plane.

[compare 83.6(2)° in **8**] and the Ph_2P—Pd—PPh_2 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 Ph_2P—Pt—PPh_2 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum of *rac*-[PdClP4]Cl (**2**) is consistent with structure B and an A_2B_2 spin system. Except for the equivalence of the PPh_2- and PPh-groups in structure B, this coordination resembles the trigonal bipyramidal structure of [FeBrP4](BPh_4).[11]

The $^{31}P\{^1H\}$ NMR data for *meso*- (**3**) and *rac*-$[Pd_2Cl_2(\mu\text{-Cl})P4]Cl$ (**4**) are in agreement with structure C and A_2B_2 spin systems. Exchange reactions with non-coordinating anions indicate monocations in **3** and **4**. Also *meso*- and *rac*-$[Pt_2Cl_2(\mu\text{-Cl})P4]Cl$ show the solution structure C.[1b]

Addition of *t*-dppe to *rac*-$[Pt_2Cl_2(\mu\text{-Cl})P4]Cl$ led to *rac*-$[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-}t\text{-dppe})P4]Cl$ (**5**). The $^{31}P\{^1H\}$ NMR spectrum of **5** is shown in Fig. 2(a) and the corresponding $^{31}P\{^1H\}$ NMR parameters are summarized in Table 2. They are in agreement with structure type D (Scheme I), which contains *t*-dppe in an μ-η^2-binding mode. The *trans* positions of the PPh groups of P4 and the PPh_2 groups of *t*-dppe are clearly indicated by ^2J(PPh, PPh_2(*t*-dppe)) of 378 Hz typical for the ^2J(P, P) *trans* range.[12] The smaller ^1J(Pt, PPh) and ^1J(Pt, PPh_2(*t*-dppe)) values compared with ^1J(Pt, PPh_2) are also in accordance with this coordination. The ^3J(Pt, PPh_2) coupling of 65 Hz shows the presence of the chloro-bridge. Like *rac*-$[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-dppa})P4](BPh_4)$,[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 $Pt_2(\mu\text{-Cl})P_4$ core (see structure D) resembles the well-known A-frame molecules.[13]

Addition of pyrimidine to *meso*- or *rac*-$[Pt_2Cl_2(\mu\text{-Cl})P4]Cl$ and simultaneous exchange of the chloride anion by $(PF_6)^-$ led to *meso*-(**6**) and *rac*-$[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-pyrimidine})P4](PF_6)$ (**7**). The $^{195}Pt\{^1H\}$ NMR spectrum of **6** is shown in Fig. 2(b). It consists of a superposition of three subspectra produced by the Pt—Pt, Pt—^{195}Pt and ^{195}Pt—^{195}Pt 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 $^{195}Pt\{^1H\}$ NMR spectrum of **7** is very similar [δ^{195}Pt = −4434, ^2J(Pt, Pt) = 1518 Hz]. The ^1J(Pt, P) parameters of **6** and **7** are summarized in Table 2. The $^{31}P\{^1H\}$ NMR spectra of **6** and **7** are consistent with A_2B_2 spin systems. In both cases the ^3J(Pt, PPh_2) couplings (see Table 2) indicate the presence of the chloro-bridges.

The $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ 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, PPh_2) are also consistent with this structure due to the low *trans* influence of chlorine. The μ-η^2-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]Cl_2 (**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. $^{31}P\{^1H\}$ NMR data for **1**–**7**[a]

Compound	δPPh	δPPh_2	^1J(Pt, PPh)	^1J(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: CH_2Cl_2 (**1**, **3**–**5**), EtOH (**2**), DMF (**6**, **7**).

[b] $^2J(PPh_2, PPh)_{trans} = 331$, $^2J(PPh_2, PPh)_{cis} + {}^3J(PPh_2, PPh)_{cis} = 26$.

[c] δPPh_2(*t*-dppe) = 12.3, ^1J[Pt, PPh_2(*t*-dppe)] = 2240, ^3J(Pt, PPh_2) = 65, ^2J[PPh_2(*t*-dppe), PPh]$_{trans}$ = 378.

[d] ^3J(Pt, PPh_2) = 58.

[e] ^3J(Pt, PPh_2) = 60.

tically change the basicity of the second nitrogen atom.[4a] The asymmetry of the two halves of **6** and **7**, as indicated by their $^{195}Pt\{^1H\}$ 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*-[Pt_2Cl_2(μ-Cl)P4]Cl with chelating diphosphines like dppm, dppe or *c*-dppe led to splitting products and monomeric PtP4-species already known.[12b] The splitting products were identified as [Pt(dppm)Cl_2], [Pt(dppe)Cl_2], [Pt(dppe)$_2$]$^{2+}$, [Pt(*c*-dppe)Cl_2] and [Pt(c-dppe)$_2$]$^{2+}$. Only in the case of dppm the triply bridged compound rac-[Pt_2Cl_2(μ-Cl)(μ-dppm)P4](PF_6) corresponding to structure type D (Scheme I) was formed. However, it could not be obtained in an analytically pure form.

DISCUSSION

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

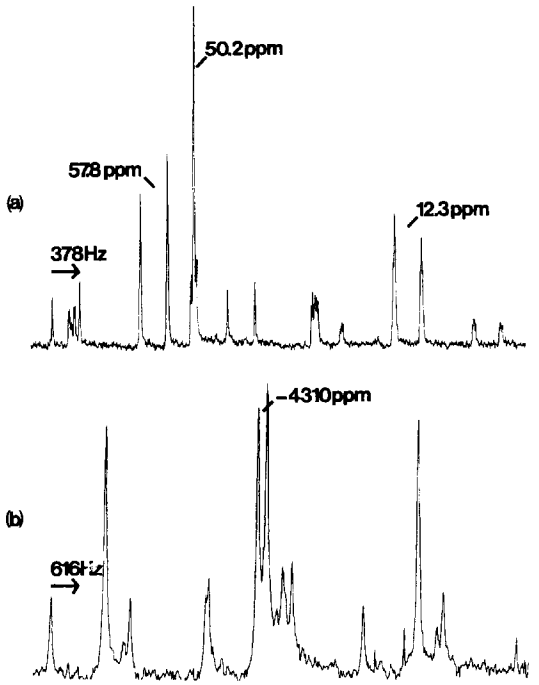


Fig. 2. (a) $^{31}P\{^1H\}$ NMR spectrum at 80.96 MHz and 298 K of a CH_2Cl_2 solution of *rac*-[Pt_2Cl_2(μ-Cl)(μ-*t*-dppe)P4]Cl (**5**); (b) $^{195}Pt\{^1H\}$ NMR spectrum at 43.02 MHz and 298 K of a DMF solution of *meso*-[Pt_2Cl_2(μ-Cl)(μ-pyrimidine)P4](PF_6) (**6**).

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 brigding 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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