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NICKEL(II) COMPLEXES CONTAINING 1,1,4,7,10, 10-HEXAPHENYL-1,4,7,10-TETRAPHOSPHADECANE: FIRST X-RAY STRUCTURES OF NICKEL-TETRAPHOS-1 COMPLEXES

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Abstract—Mono- and bimetallic Ni¹¹ complexes of rac- or meso-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) have been prepared and characterized by Xray diffraction methods, ${}^{31}P{}^{1}H$ NMR spectroscopy, elemental analyses and melting points. The first two X-ray structures of Ni-tetraphos-1 complexes show distorted square planar coordinations in rac-[NiP4](BPh₄)₂ (2) and rac-[Ni₂Cl₄P4] (5). In 2 the mean deviation of the phosphorus atoms from a least-squares plane through the phosphorus atoms and the nickel atom is 0.224 Å. The nickel atom deviates 0.034 Å from this plane. In 5 the mean deviation of the phosphorus and chlorine atoms from the corresponding plane is 0.023 Å, the nickel atom deviating 0.028 Å from this plane. The mean chelate P-Ni-P angle of 84.75° in 2 significantly deviates from the chelate angle of $86.90(11)^\circ$ in 5, which is an open-mode dimer with a Ni-Ni distance of 6.339(1) Å and a cis chelating and bridging P4 configuration. The two coordination planes of 5 include an angle of 7.2° . In contrast to rac- $[NiP4]Cl_2(1)$, the P4 coordination in 2 shows a pronounced solvent dependence. In neither meso-[NiP4]Cl₂ (3) nor meso-[NiP4](BPh₄)₂ (4) does a similar solvent effect occur. However, an easy transition between rac- or meso-[NiP4](NiCl₄) and rac-(5) or $meso-[Ni_2Cl_4P4]$ (6) is possible, depending on the solvent. This transition is discussed in view of the X-ray structures of 2 and 5. Furthermore, a comparison of the structures of 2 and 5 with the known X-ray structures of rac- or meso-[PtP4](BPh₄)₂, rac- or meso-[Pt₂Cl₄P4] and meso-[PdP4]Cl₂ is given.

In a series of recent papers the versatile coordination behaviour of 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) has been presented.^{1,2} The first two X-ray structures of Ni-tetraphos-1 complexes are described in this work. Earlier reports on Ni^{II} complexes of tetraphos-1^{3,4} lack the recognition of the two diastereomeric forms of P4 and raise some questions about the influence of non-coordinating anions on the P4 coordination mode. The X-ray structure of *rac*-[NiP4](BPh₄)₂ (2) shows a strongly distorted square planar P4 coordination, despite the presence of non-coordinating anions.⁴ The deviations from planarity are comparable to the distortions observed in rac-[PtP4](BPh₄)₂.⁵ The X-ray structure of rac-[Ni₂Cl₄P4] (5) reveals an open-mode dimer with the P4 ligand coordinating in a bridging/ chelating manner similar to [Ni₂Cl₄(eLTTP)], (Et₂PCH₂CH₂)(Ph)PCH₂ where eLTTP is $P(Ph)(CH_2CH_2PEt_2)$.⁶ The structure of 5 also resembles the X-ray structure of rac-[Pt₂Cl₄P4]^{1c} in contrast to the different coordinations of (Et₂ $PCH_2CH_2PCH_2P(CH_2CH_2PEt_2)_2$ (eHTP) in [Ni₂Cl₂(eHTP)]²⁺ and [Pt₂Cl₂(eHTP)]²⁺, respectively.7

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However, as in the case of $[NiCl_2(dppm)]^8$, where dppm is 1,2-bis(diphenylphosphino)methane, the P4-containing Ni^{II} complexes show further solvent and anion effects. Thus, depending on the solvent, the P4 coordination in **2** changes to trigonal bipyramidal. The possibility of a trigonal bipyramidal P4 stereochemistry is well established by several X-ray structures.⁹ Furthermore, an easy transition between the Magnus-type salts *rac*- or *meso*-[NiP4] (NiCl₄) and *rac*-(**5**) or *meso*-[Ni₂Cl₄P4] (**6**) occurs. A similar effect has been observed in Pd^{II} and Pt^{II} complexes of *cis*-1,2-bis(diphenylphosphino) ethene.¹⁰

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 (tetraphos-1, P4) was 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. NiCl₂ · 6H₂O was also received from Fluka.

Instrumentation

Fourier-mode ${}^{31}P{}^{1}H{}$ NMR spectra were obtained by use of a Bruker AC-200 spectrometer (internal deuterium lock) and were recorded at 80.96 MHz. Positive chemical shifts are downfield from 85% H₃PO₄ used as standard.

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.¹¹

Synthesis of Ni^{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.

Rac-[NiP4]Cl₂ (1)

To NiCl₂· $6H_2O$ (0.3 mmol, 0.071 g) in water (5 cm³) a solution of *rac*-P4 (0.3 mmol, 0.201 g) in CH₂Cl₂ (4 cm³) was added. Then EtOH was added with stirring until a clear dark red solution was

obtained. The solvent was completely removed and the reddish-brown residue dried *in vacuo*. The reddish-brown powder was recrystallized from CH₃CN: yield 0.214 g (89%); m.p. = $142-146^{\circ}$ C. Found: C, 62.8; H, 5.5. Calc. for C₄₂H₄₂Cl₂P₄Ni: C, 63.0; H, 5.3%.

$Rac-[NiP4](BPh_4)_2(2)$

To 1 (0.1 mmol, 0.080 g) dissolved in EtOH/ CH₂Cl₂ (9 cm³; v/v = 3:1) Na(BPh₄) (0.3 mmol, 0.103 g) was added with stirring. A yellow precipitate immediately formed. The reaction mixture was stirred at 50°C for 18 h. The solvent was removed, the yellow residue suspended in water, filtered off, washed with water and dried *in vacuo*. The yellow powder was recrystallized from CH₃CN, where dark red crystals formed: yield 0.128 g (85%); m.p. = 187–189°C. Found: C, 76.9; H, 6.0; N, 3.0. Calc. for C₉₀H₈₂B₂P₄Ni · 3.3CH₃CN: C, 77.2; H, 5.8; N, 3.1%. A sample for X-ray diffraction study was crystallized from CH₃CN.

Meso-[NiP4] Cl_2 (3)

Compound 3 was prepared in an analogous manner to 1, where *meso*-P4 was used instead of *rac*-P4 : yield 0.199 g (83%); m.p. = 176–180°C. Found : C, 62.7; H, 5.4. Calc. for $C_{42}H_{42}Cl_2P_4Ni$: C, 63.0; H, 5.3%.

Meso-[NiP4](BPh₄)₂ (4)

Compound 4 was prepared in an analogous manner to 2, where 3 was used instead of 1 : yield 0.109 g (80%); m.p. = 186–188°C. Found : C, 78.8; H, 6.2. Calc. for $C_{90}H_{82}B_2P_4Ni : C, 79.0$; H, 6.0%.

Rac- $[Ni_2Cl_4P4]$ (5)

To NiCl₂ \cdot 6H₂O (0.3 mmol, 0.071 g) in water (5 cm^3) a solution of rac-P4 (0.15 mmol, 0.101 g) in CH_2Cl_2 (2 cm³) was added. Then EtOH was added with stirring until a clear dark red solution was obtained. The solvent was completely removed and the dark brown residue dried in vacuo. The darkbrown powder was dissolved in EtOH and the solution was heated up to 40°C. After several days at this temperature an orange precipitate formed. The orange precipitate was filtered off, washed with water and dried in vacuo. The orange powder was recrystallized from CH₂Cl₂: yield 0.085 g (57%); $m.p. = 228-231^{\circ}C.$ Found : C, 51.0; H, 4.9; O, 3.6. Calc. for $C_{42}H_{42}Cl_4P_4Ni_2 \cdot 0.3CH_2Cl_2 \cdot 2.4H_2O$: C, 50.9; H, 4.8; O, 3.8%. A sample for X-ray diffraction study was crystallized from CH₂Cl₂.

Meso- $[Ni_2Cl_4P4]$ (6)

Compound **6** was prepared in an analogous manner to **5**, where *meso*-P4 was used instead of *rac*-P4 : yield 0.074 g (53%); m.p. = $293-295^{\circ}$ C. Found : C, 54.0; H, 4.7. Calc. for C₄₂H₄₂Cl₄P₄Ni₂ : C, 54.2; H, 4.6%.

X-ray crystallography

Crystal data. $C_{90}H_{82}B_2P_4Ni \cdot 3.3CH_3CN$ (2), M = 1503.33, dark red crystal (irregular; $0.7 \times 0.6 \times 0.5$ mm), monoclinic, a = 23.252(5), b = 13.443(3), c = 28.321(6) Å, $\beta = 113.23(3)^{\circ},$ V = 8134.80 Å³, Z = 4, space group $P2_1/c$, $D_{\rm c} = 1.228$ Mg m⁻³, F(000) = 3170, μ (Mo- K_{α}) = 0.363 mm⁻¹; C₄₂H₄₂Cl₄P₄Ni₂·0.26CH₂Cl₂· 2.4H₂O (5), M = 995.20, orange crystal (irregular; $0.3 \times 0.2 \times 0.1$ mm), tetragonal, a = 17.149(2), c = 15.770(3) Å, V = 4637.77 Å³, Z = 4, space group $P\bar{4}2_1c$, $D_c = 1.425$ Mg m⁻³, $F(000) = 2052, \, \mu(\text{Mo-}K_{\alpha}) = 1.213 \, \text{mm}^{-1}.$

Data collection. Unit-cell dimensions and intensity data were obtained at 293 K using a Siemens P4 diffractometer and graphite monochromated Mo- K_{α} radiation. 2θ range = 3.0–55.0°, scan type = ω , scan speed = variable (2.0-29.3° xmin⁻¹ in ω), index ranges = -1 < h < 27, -1 < k < 16, -33 < 1 < 33 (2) and -1 < h < 14, -1 < k < 22, 0 < 1 < 20 (5). No decay in the intensities of three standard reflections was observed during the course of each data collection. The data were corrected for Lorentz and polarization effects. In each case the empirical absorption correction was based on ψ -scans of nine reflections [range of transmission factors: 0.86–0.95 (2), 0.64– 0.97 (5)].12 A total of 16,649 (2) and 6170 (5) reflections were measured, of which 14,015 (2, $R_{\text{int}} = 0.045$) and 3387 (5, $R_{\text{int}} = 0.038$) were unique and 12,065 (2) and 2847 (5) satisfied the condition $I > 0\sigma(I)$.

Structure solution. All structure determination calculations were carried out on a 80486-PC using the PC-version of SHELXTL PLUS.¹³ The positions of the nickel atoms were found by the Patterson method. Other atom positions were located from successive difference Fourier maps.

In the case of **2** 3.3 molecules of CH₃CN per asymmetric unit were 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 0.052 (R' = 0.052) was computed for 922 parameters. The largest feature on a final difference map was 0.476 e Å⁻³ [GOF = 1.04, largest

 $\Delta/\sigma = 0.28$, weighting scheme: $w^{-1} = \sigma^2(F^2) + (0.076 P)^2$].

In the case of **5** 0.13 molecules of CH₂Cl₂ and 1.2 molecules of water per asymmetric unit were 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 0.048 (R' = 0.048) was computed for 249 parameters. The largest feature on a final difference map was 0.356 e Å⁻³ [GOF = 0.944, largest $\Delta/\sigma = 0.11$, weighting scheme: w⁻¹ = $\sigma^2(F^2)$ + (0.046 P)²].

Final atomic fractional coordinates and other relevant data have been deposited.

RESULTS

The ${}^{31}P{}^{1}H{}$ NMR parameters for compounds 1-6 are summarized in Table 1. The ${}^{31}P{}^{1}H{}$ NMR data of rac-[NiP4]Cl₂ (1) are in agreement with a square planar P4 coordination leading to an AA'MM' spin system and structure type A in Scheme 1. The large downfield shift of the PPh resonance is typical for an additive five-ring contribution, since the PPh groups are part of two fused five-rings.¹⁴ Both the ${}^{2}J(\mathbf{P},\mathbf{P})_{trans}$ and ${}^{2}J(\mathbf{P},\mathbf{P})_{cis}$ values are in the typical ranges.^{14a,15} However, replacement of the chloride anions by (BPh₄)⁻ in *rac*-[NiP4](BPh₄)₂ (2) leads to a different ${}^{31}P{}^{1}H{}$ NMR behaviour strongly dependent on the solvent. In CH₃CN (see Table 1) ${}^{2}J(\mathbf{P},\mathbf{P})_{cis}$ is not observable and in CH₃NO₂ also ${}^{2}J(\mathbf{P},\mathbf{P})_{trans}$ is lost. The ${}^{31}\mathbf{P}\{{}^{1}\mathbf{H}\}$ NMR parameters of 2 in the latter solvent are in agreement with a trigonal bipyramidal P4 coordination leading to an A2B2 spin system and structure type B in Scheme 1.^{1a} Solutions of 2 in DMF contain both structure types A and B. In order to reveal the solid state structure of 2, an X-ray structure analysis of 2 was performed.

The X-ray structures of **2** and **5** (see below) are the first X-ray structures of Ni-tetraphos-1 complexes. The structure analysis of **2** shows a discrete *rac*- $[NiP4]^{2+}$ cation, two $(BPh_4)^-$ anions and 3.3 molecules of CH₃CN per asymmetric unit (the occupancy factor of the fourth CH₃CN molecule has been refined). A view of *rac*- $[NiP4]^{2+}$ is given in Fig. 1(a); Table 2 contains selected bond distances and bond angles.

The square planar coordination in rac-[NiP4]²⁺ is strongly distorted towards a tetrahedral P4 arrangement [see Fig. 1(b)]. Two P atoms, *trans* to each other, lie below [P(1): 0.258, P(3): 0.206 Å] and above [P(2): 0.242, P(4): 0.189 Å] the least-squares plane through the Ni atom and the P atoms.

Compound	δ PPh	δPPh_2	$^{2}J(\mathbf{P},\mathbf{P})_{trans}$	$^{2}J(\mathbf{P},\mathbf{P})_{cis}$ + $^{3}J(\mathbf{P},\mathbf{P})_{cis}$
1	105.7dd	46.1dd	180	40
2	106.1d	43.7d	160	
	79.6 ^{<i>b</i>}	43.3		
	$108.4d^{\circ}$	48.6d	163	
	38.2	29.1		
3	103.4d	50.7d	194	
4	102.3d	53.3d	166	
5	35.1d	30.2d		68
6	68.3dd	60.8dd		50, 18^{d}

Table 1. ³¹P{¹H} NMR data for 1– 6^a

^{*a*} J values in Hz. d = doublet, dd = doublet of doublets. Spectra were run at 298 K. The following solvents were used : EtOH (1, 3), CH₃CN (2, 4) and CH₂Cl₂ (5, 6).

^{*b*} Spectrum of **2** in CH_3NO_2 .

^c Spectrum of **2** in DMF.

 ${}^{d 2}J(\mathbf{P},\mathbf{P})_{cis} = 50, {}^{3}J(\mathbf{P},\mathbf{P})_{cis} = 18.$

The Ni atom deviates 0.034 Å from this plane. The mean deviation of the P atoms from the best plane of 0.224 Å in **2** is comparable to the corresponding value of 0.237 Å in *rac*-[PtP4](BPh₄)₂ (7).⁵ The

Ni—PPh bonds [2.162(1) Å] are significantly shorter than the Ni—PPh₂ bonds [2.243(1) Å]. Both averaged bond lengths are shorter than the corresponding bonds in 7 [Pt—PPh: 2.258(4),



Scheme 1. Structure types observed in the compounds 1-6. The P—Ni—P angles, where the phosphorus atoms are connected by ethylene chains are constrained to ca 85°. Structure A occurs in rac-(1) or meso-[NiP4]Cl₂ (3) and rac-(2) or meso-[NiP4](BPh₂)₂ (4), structure B in CH₃NO₂ and DMF solutions of 2 (Z is a solvent molecule), structure C in the solution structure of rac-(5) or meso-[Ni₂Cl₄P4] (6) and structure D in the solid state structure of 5 or 6.



Fig. 1. View of the cation of *rac*-[NiP4](BPh₄)₂ (2). (a) The coordination plane through the Ni atom and the P atoms in the projection plane showing the atom labelling scheme; (b) projection showing the deviations from an ideal square-planar coordination.

Pt—PPh₂: 2.327(4) Å]. The PhP—Ni—PPh angle is reduced to 84.11(6)° [cf. 85.2(2)° in 7]. The Ph₂P—Ni—PPh₂ angle of 108.13(5)° is also smaller than the corresponding angle of 109.5(2)° in 7.

The above values indicate that the deviations from an ideal square planar rac-P4 arrangement are slightly smaller in 2 than in 7. By contrast, the corresponding Pd^{II} complex is strongly destabilized and its preparation failed.^{1a} Furthermore, the similarities of the tetrahedral distortions in 2 and 7 show that they are dominated by the steric requirements of rac-P4 and not by the metal. This is confirmed by the observation that in solutions of *meso*- $[NiP4]Cl_2$ (3) and *meso*- $[NiP4](BPh_4)_2$ (4) only square planar P4 coordinations occur (see Table 1). Square-planar complexes of *meso*-P4 are usually more stable than the corresponding complexes containing *rac*-P4.^{1a,5,16} The degree of destabilization of square planar compounds is the dominating factor for the occurrence of trigonal bipyramidal species.¹⁷ As a consequence in the case of Ni^{II} trigonal bipyramidal species are only formed with *rac*-P4.

The formation of *rac*-(5) or *meso*- $[Ni_2Cl_4P4]$ (6) proceeds in two steps according to eq. (1). In the first step the Magnus-type

$2NiCl_2 + rac$ - or meso-P4

$$\rightarrow$$
 rac- or meso-[NiP4](NiCl₄)

$$\Rightarrow$$
 rac- or meso-[Ni₂Cl₄P4] (1)

salts *rac*- or *meso*-[NiP4](NiCl₄) are formed showing ³¹P{¹H} NMR parameters very similar to **1** or **3**. In EtOH these Magnus-type salts can easily be converted into **5** or **6** at *ca* 40°C. However, the second step is reversible and dissolution of **5** or **6** in DMF leads to the corresponding Magnus-type salts again. Similar transitions occur between [Pd(*cis*-dppen)₂](Pd(SCN)₄) and [Pd(SCN)₂(*cis*dppen)],^{10a} where *cis*-dppen is *cis*-1,2-bis(diphenylphosphino)ethene and [Pt(*cis*-dppen)₂] (PtCl₄) and [PtCl₂(*cis*-dppen)].^{10b}

The ${}^{31}P{{}^{1}H}$ NMR data for 5 and 6 (see Table 1) are in agreement with A_2B_2 spin systems and structure types C or D in Scheme 1. One chloride ligand in 5 or 6 can easily be replaced by $(BPh_4)^-$, indicating that the solution structure corresponds to the ionic structure type C similar to the analogous Pd^{II} and Pt^{II} complexes.¹ In order to reveal the solid state structure, an X-ray structure analysis of 5 was performed.

The X-ray structure of 5 consists of half a discrete rac-[Ni₂Cl₄P4] molecule, 0.13 molecules of CH₂Cl₂ and 1.2 molecules of water per asymmetric unit (the occupancy factors of CH₂Cl₂ and water have been refined). A view of rac-[Ni₂Cl₄P4] is given in Fig. 2(a) showing the non-ionic structure type D of Scheme 1; Table 3 contains selected bond distances and bond angles.

Rac-[Ni₂Cl₄P4] is located on a two-fold symmetry axis. The square planar coordination in *rac*-[Ni₂Cl₄P4] is only slightly distorted. The mean deviation of the phosphorus and chlorine atoms from a least-squares plane through these atoms and the nickel atom is 0.023 Å [P(1): 0.030, P(2): -0.017, Cl(1): -0.014, Cl(2): 0.029 Å], the nickel atom deviating -0.028 Å from this plane towards the phenyl ring of the PPh group. By contrast, in *rac*-[Pt₂Cl₄P4] (8) the chloride and phosphorus ligands

	_		
Ni(1)—P(1) 2.16	00(14)	Ni(1)—P(2)	2.1647(14)
Ni(1) - P(3) = 2.24	22(14)	Ni(1) - P(4)	2.2436(14)
P(1) - C(5) = 1.79	9(5)	P(1) - C(11)	1.820(5)
$P(1) - C(4) = 1.82^{\circ}$	9(5)	P(2) - C(21)	1.806(5)
P(2) - C(3) = 1.82	7(5)	P(2) - C(2)	1.831(5)
P(3) - C(41) = 1.809	9(5)	P(3) - C(31)	1.817(5)
P(3)-C(1) 1.85	1(5)	P(4)—C(61)	1.814(5)
P(4) - C(51) = 1.810	6(6)	P(4) - C(6)	1.845(5)
C(1)-C(2) 1.53	1(6)	C(3)—C(4)	1.528(7)
C(5)—C(6) 1.52	1(7)		
P(1) - Ni(1) - P(2)	84.11(6)	P(1) - Ni(1) - I	P(3) 161.55(5)
P(2) - Ni(1) - P(3)	85.20(5)	P(1) - Ni(1) - I	P(4) 84.95(6)
P(2) - Ni(1) - P(4)	164.42(6)	P(3) - Ni(1) - I	P(4) 108.13(5)
C(5) - P(1) - C(11)	107.7(2)	C(5) - P(1) - C	C(4) 114.1(3)
C(11) - P(1) - C(4)	105.4(2)	C(5) - P(1) - N	li(1) 109.7(2)
C(11)-P(1)-Ni(1)	108.9(2)	C(4) - P(1) - N	Ji(1) 110.8(2)
C(21) - P(2) - C(3)	104.5(2)	C(21)—P(2)—	C(2) 105.5(2)
C(3) - P(2) - C(2)	114.5(2)	C(21)—P(2)—	Ni(1) 111.4(2)
C(3) - P(2) - Ni(1)	111.6(2)	C(2) - P(2) - N	li(1) 109.1(2)
C(41)—P(3)—C(31)	108.0(2)	C(41)—P(3)—	C(1) 103.9(2)
C(31) - P(3) - C(1)	105.8(2)	C(41) - P(3) - P(3)	Ni(1) 108.4(2)
C(31)-P(3)-Ni(1)	121.2(2)	C(1) - P(3) - N	li(1) 108.2(2)
C(61)-P(4)-C(51)	104.3(3)	C(61) - P(4) - P(4)	C(6) 104.1(2)
C(51) - P(4) - C(6)	106.9(3)	C(61)—P(4)—	Ni(1) 113.4(2)
C(51)—P(4)—Ni(1)	119.1(2)	C(6) - P(4) - N	li(1) 107.9(2)
C(2) - C(1) - P(3)	110.4(3)	C(1)C(2)-P	9(2) 104.9(3)
C(4) - C(3) - P(2)	105.6(3)	C(3) - C(4) - P	P(1) 105.3(4)
C(6) - C(5) - P(1)	105.6(4)	C(5)-C(6)-P	9(4) 110.3(4)

Table 2. Selected bond lengths (Å) and angles (°) for $rac-[NiP4](BPh_4)_2$ (2)

surrounding the platinum atom occupy a plane.^{lc} As in the case of **2**, the Ni—PPh bond length [2.141(3) Å] is significantly shorter than the Ni—PPh₂ bond length [2.152(3) Å]. However, the Ni—Cl bond distances remain identical within the standard deviations [mean value : 2.195(2) Å]. Both the Ni—P as well as the Ni—Cl bond distances are significantly shorter than the corresponding values in **8** [mean values: Pt—P = 2.217(4), Pt—Cl = 2.353(4) Å].

The deviations from ideal square planar angles are larger in 5 than in 8 (see Table 3 and ref. 1c). This leads to an opening of the Cl—Ni—Cl angle to $95.07(10)^{\circ}$, where the corresponding Cl—Pt—Cl angle is only $91.5(2)^{\circ}$. The chelate P—Ni—P angle of $86.90(11)^{\circ}$ in 5 is very similar to the corresponding value of $86.5(3)^{\circ}$ in 8, but significantly larger than the mean chelate P—Ni—P angle of 84.75° in 2. The Ni—Ni distance of 6.339(1) Å in 5 is identical with the Pt—Pt distance of 6.338(1) Å in 8. The two coordination planes in 5 include an angle of 7.2° . Within the standard deviations this is also the same value as in 8 (7.3°). Interestingly, another parameter in 5 is very similar to the analogous value in 8. To account for the different orientations of the two coordination units in 5 or 8 each containing a metal, two phosphorus and two chlorine atoms, the $M \cdots P_{int} \cdots P'_{int} \cdots M'$ torsional angles, where P_{int} and P'_{int} are the two internal phosphorus atoms of a P4-type tetraphos ligand, have been used in comparable dimers also containing oligophosphines.⁷ In Fig. 2(b) a view of 5 perpendicular to the central P(2) \cdots P(2a) vector is given. The Ni(1) \cdots P(2) \cdots P(2a) \cdots Ni(1a) torsional angle is 98.0°. In 8 the corresponding value is 99.1°.^{1b} It seems likely that it is the very nature of *rac*-P4 which dominates the stereochemistry in 5 as well as in 8.

DISCUSSION

The similarities of the deviations from an ideal square planar coordination in rac-[NiP4](BPh₄)₂ (2) and rac-[PtP4](BPh₄)₂ (7) indicate that the shorter Ni-P bond distances in 2 compared with the Pt-P



Fig. 2. View of *rac*-[Ni₂Cl₄P4] (5). (a) Projection showing the atom labelling scheme; (b) projection perpendicular to the central P(2) · · · P(2a) vector (hydrogen atoms omitted for clarity).

bond lengths in 7 are not important for the *rac*-P4 arrangement. Obviously *rac*-P4 fits well in a square planar environment in the case of Ni^{II} and Pt^{II}. However, as the X-ray structure of *meso*-[PdP4]Cl₂ shows,^{1a} the metal–phosphorus bond distances are further lengthened in the corresponding Pd^{II} complexes. This leads to a complete destabilization of a square planar Pd^{II}-*rac*-P4 complex, which could not be prepared.

In *rac*-[Ni₂Cl₄P4] (5) the deviations from an ideal square planar coordination are larger than in *rac*-[Pt₂Cl₄P4] (8). However, the almost identical values of the metal-metal distances, the angles between the coordination planes and the $M \cdots P_{int} \cdots P'_{int} \cdots M'$

torsional angles in **5** and **8** show that the sterical requirements of *rac*-P4 lead to the same rotation isomer in the Ni^{II} and Pt^{II} complexes. This is confirmed by the fact that the X-ray structure of *meso*-[Pt₂Cl₄P4] reveals a completely different rotation isomer.^{1b} Since destabilizing steric interactions will become increasingly important as the metal covalent radii decrease,¹⁸ the larger deviations from an ideal square planar environment in **5** are indicative of sterical strain. The M—P—CH₂ angles have been found to be very sensitive to sterical strain.^{1b,1c,6} In **5** the Ni(1)—P(2)—C(3) angle is 116.1(3)°, whereas the corresponding angle in **8** is only 112.3(10)°. This strain could be responsible for the easy transition

Ni(1)—P(2) 2.141	(3)	Ni(1)—P(1)	2.152(3)	
Ni(1)—Cl(1) 2.191	(3)	Ni(1)— $Cl(2)$	2.198(3)	
P(1) - C(21) = 1.808	(11)	P(1) - C(11)	1.835(11	.)
P(1) - C(1) = 1.845	(9)	P(2)-C(31)	1.818(12	2)
P(2) - C(3) = 1.819	(11)	P(2) - C(2)	1.834(9)	
C(1)—C(2) 1.519	(13)	$C(3) - C(3^{i})$	1.53(2)	
P(2) - Ni(1) - P(1)	86.90(11)	P(2)—Ni(1)—	-Cl(1)	177.89(12)
P(1) - Ni(1) - Cl(1)	91.06(11)	P(2)—Ni(1)—	-Cl(2)	86.93(11)
P(1) - Ni(1) - Cl(2)	173.15(12)	Cl(1)—Ni(1)-	Cl(2)	95.07(10)
C(21) - P(1) - C(11)	106.1(5)	C(21)—P(1)—	-C(1)	106.2(4)
C(11) - P(1) - C(1)	105.8(5)	C(21)—P(1)—	-Ni(1)	110.6(4)
C(11) - P(1) - Ni(1)	119.5(4)	C(1) - P(1) - 1	Ni(1)	107.8(3)
C(31) - P(2) - C(3)	106.7(4)	C(31)—P(2)—	-C(2)	104.0(5)
C(3) - P(2) - C(2)	104.9(5)	C(31)—P(2)—	-Ni(1)	113.7(4)
C(3) - P(2) - Ni(1)	116.1(3)	C(2) - P(2) - 1	Ni(1)	110.5(3)
C(2) - C(1) - P(1)	106.4(6)	C(1) - C(2) - 1	P(2)	108.2(6)
C(3i) - C(3) - P(2)	111.7(9)			

Table 3. Selected bond lengths (Å) and angles (°) for rac-[Ni₂Cl₄P4] (5)

Symmetry transformations used to generate equivalent atoms: (i) -x+2, -y+1, z.

between 5 and the Magnus-type salt rac-[NiP4] (NiCl₄).

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