

# Structural differences in nickel(II) and palladium(II) complexes containing *cis*-1,2-bis(diphenylphosphino)ethene or 1,2-bis(diphenylphosphino)ethane

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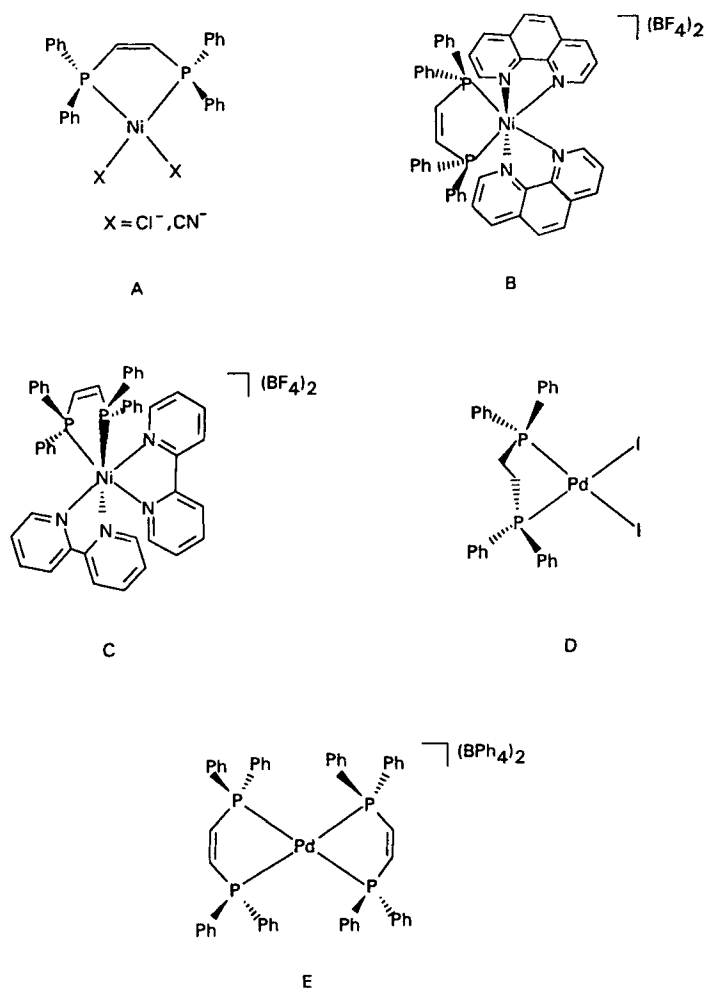
**Abstract**—Monometallic Ni<sup>II</sup> and Pd<sup>II</sup> complexes of *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppen) or 1,2-bis(diphenylphosphino)ethane (dppe) have been prepared and characterized by X-ray diffraction methods, <sup>31</sup>P <sup>1</sup>H NMR spectroscopy, FAB mass spectrometry, elemental analyses and melting points. The X-ray structure of [NiCl<sub>2</sub>(*cis*-dppen)] (**1**) is given for the first time. In **1** the mean deviation of the nickel, the phosphorus and the chlorine atoms from a least-squares plane through these atoms is only 0.025 Å. The ethene bridge is nearly coplanar with this plane, which can be explained by a π-bonding interaction. It is shown that the small deviation from coplanarity are caused by a crystal packing effect. The reaction of Ni(CN)<sub>2</sub> with *cis*-dppen leads to the novel compound [Ni(CN)<sub>2</sub>(*cis*-dppen)] (**2**). The removal of chloride in **1** by AgBF<sub>4</sub> followed by the reaction with 1,10-phenanthroline (phen) leads to the novel octahedral Ni<sup>II</sup> complex [Ni(*cis*-dppen)(phen)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**3**). In an analogous manner 2,2'-bipyridine (bipy) produces [Ni(*cis*-dppen)(bipy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**4**). The reaction of *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) with PdCl<sub>2</sub> and subsequent treatment with LiI leads to the unexpected product [PdI<sub>2</sub>(dppe)] (**5**). Compound **5** is also fully characterized by an X-ray structure analysis for the first time. The palladium, phosphorus and iodine atoms show a mean deviation of only 0.017 Å from a least-squares plane through these atoms. However, the PdP<sub>2</sub>C<sub>2</sub> chelate ring has a twist conformation, where one carbon atom of the aliphatic chain of dppe lies –0.420 Å to one side, and the second carbon atom 0.318 Å to the other side of the coordination plane. In **5** the P—Pd—P chelate angle of 85.59(5)° is significantly smaller than the corresponding P—Ni—P angle of 87.79(4)° in **1**. Furthermore, the X-ray structure of the recently reported complex [Pd(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**6**) is given. The palladium atom is located on a centre of symmetry leading to the complete planarity of the coordination plane due to crystallographic constraints. However, the two carbon atoms of the ethene bridge of *cis*-dppen lie 0.547 and 0.532 Å, respectively, to one side of the coordination plane. Compound **6** significantly shows the smallest P—M—P chelate angle of 84.78(3)° compared with the corresponding values in **1** and **5**. A comparison of the X-ray structures of **1**, **5** and **6** with several known X-ray structures of Ni<sup>II</sup> and Pd<sup>II</sup> complexes containing *cis*-dppen or dppe is given. Differences in the chelate angles and coplanar parts of these structures are discussed with respect to the observed reactivities of compounds **1–6**. © 1997 Elsevier Science Ltd

**Keywords:** crystal structures; nickel complexes; palladium complexes.

Only recently completely planar structures of Pt<sup>II</sup> complexes containing *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppen) have been described [1]. Similar to other examples [2,3], the coplanarity in these structures has been explained by a π-bonding

interaction. In this work the X-ray structure of [NiCl<sub>2</sub>(*cis*-dppen)] (**1**, structure type A in Scheme 1) is given for the first time also showing a nearly coplanar arrangement of the coordination plane and the ethene bridge. In analogous complexes containing 1,2-bis(diphenylphosphino)ethane (dppe), by contrast, the aliphatic chain of dppe has a twist conformation [4]. The same is true for [PdI<sub>2</sub>(dppe)] (**5**, structure type D in

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Scheme 1. Structure types observed in the compounds 1–6. The P—M—P (M = Ni, Pd) angles, where the phosphorus atoms are connected by aliphatic bridges, are constrained to values below 90°. Structure A occurs in  $[\text{NiCl}_2(\text{cis-dppen})]$  (1) and  $[\text{Ni}(\text{CN})_2(\text{cis-dppen})]$  (2), structure B in  $[\text{Ni}(\text{cis-dppen})(\text{phen})_2](\text{BF}_4)_2$  (3), structure C in  $[\text{Ni}(\text{cis-dppen})(\text{bipy})_2](\text{BF}_4)_2$  (4), structure D in  $[\text{PdI}_2(\text{dppe})]$  (5) and structure E in  $[\text{Pd}(\text{cis-dppen})_2](\text{BPh}_4)_2$  (6).

Scheme 1), where this compound is also fully characterized by an X-ray structure analysis for the first time in this paper.

Furthermore, several novel  $\text{Ni}^{\text{II}}$  complexes containing *cis*-dppen are presented. The reaction of  $\text{Ni}(\text{CN})_2$  with *cis*-dppen leads to  $[\text{Ni}(\text{CN})_2(\text{cis-dppen})]$  (2). Similar to  $[\text{Pd}(\text{CN})_2(\text{cis-dppen})]$  [1] the bidentate ligand *cis*-dppen produces the *cis* isomer (structure A in Scheme 1), where in the case of monodentate phosphines the *trans* form is preferred [5]. After chloride is removed in 1 by  $\text{AgBF}_4$ , treatment with 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) leads to the octahedral  $\text{Ni}^{\text{II}}$  complexes  $[\text{Ni}(\text{cis-dppen})(\text{phen})_2](\text{BF}_4)_2$  (3) and  $[\text{Ni}(\text{cis-dppen})(\text{bipy})_2](\text{BF}_4)_2$  (4, structures B and C in Scheme 1). The importance of octahedral  $\text{Ni}^{\text{II}}$  centres with N-containing heterocycles as ligands has been emphasized only recently [6]. Several metalloenzymes such as

urease, CO dehydrogenase and several hydrogenases have emerged that require  $\text{Ni}^{\text{II}}$  ions for catalysts [7].

In the case of  $\text{Pd}^{\text{II}}$  the reaction of *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) with  $\text{PdCl}_2$  followed by treatment with LiI leads to the already mentioned complex 5. Since in 5 the chelating diphosphine dppe occurs and *trans*-dppen is only able to bridge two metal centres, if both phosphorus atoms coordinate [8], the reaction producing 5 must involve a carbon-carbon bond cleavage of the double bond in *trans*-dppen and subsequent recombination. Bond cleavage reactions are typical for complexes of Pd [4b]. The addition of 2 equiv. of *cis*-dppen to 1 equiv.  $\text{PdCl}_2$  followed by metathesis with  $\text{Na}(\text{BPh}_4)$ , by contrast, leads to the recently described compound  $[\text{Pd}(\text{cis-dppen})_2](\text{BPh}_4)_2$  (6, structure E in Scheme 1). The X-ray structure of 6 is also given for the first time. Similar to  $[\text{Ni}(\text{cis-dppen})_2](\text{ClO}_4)_2$  [9] and deviating

from the structure **1**, the ethene bridges in **6** are not coplanar with the coordination plane.

## EXPERIMENTAL

### Reagents and chemicals

Reagent-grade chemicals were used as received unless stated otherwise. *cis*-1,2-Bis(diphenylphosphino)ethene (*cis*-dppen) and *trans*-1,2-bis(diphenylphosphino)ethene (*trans*-dppen) were purchased from Aldrich. All other reagents and solvents were obtained from Fluka. Solvents used for NMR measurements and crystallization purposes were of purissimum grade quality. NiCl<sub>2</sub>·6H<sub>2</sub>O and PdCl<sub>2</sub> were also received from Fluka.

### Instrumentation

Fourier-mode <sup>31</sup>P <sup>1</sup>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% H<sub>3</sub>PO<sub>4</sub> used as standard.

### Synthesis of Ni<sup>II</sup> and Pd<sup>II</sup> complexes

A Schlenk apparatus and oxygen-free, dry Ar were used in the synthesis 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.

#### [NiCl<sub>2</sub>(*cis*-dppen)] (**1**)

Compound **1** was prepared according to literature methods [10], where NiCl<sub>2</sub>·6H<sub>2</sub>O was used. A sample for X-ray diffraction study was crystallized from CH<sub>2</sub>Cl<sub>2</sub>.

#### [Ni(CN)<sub>2</sub>(*cis*-dppen)] (**2**)

Ni(CN)<sub>2</sub> (0.18 mmol, 0.020 g) and *cis*-dppen (0.18 mmol, 0.071 g) were dissolved in CHCl<sub>3</sub>/EtOH. A deep red solution was obtained. After stirring the solution at 70°C for 30 h it turned yellow and a yellow precipitate formed. The solvent was completely removed, the yellow residue was filtered off in Et<sub>2</sub>O, washed with Et<sub>2</sub>O and dried *in vacuo*. The yellow powder was recrystallized from CHCl<sub>3</sub>: yield 0.076 g (83%); m.pt = 299–302°C dec. IR (KBr, cm<sup>-1</sup>) CN: 2125 v. Found: C, 66.1; H, 4.6; N, 5.6. Calc. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>P<sub>2</sub>Ni: C, 66.3; H, 4.4; N, 5.5%.

#### [Ni(*cis*-dppen)(phen)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**3**)

[NiCl<sub>2</sub>(*cis*-dppen)] (0.15 mmol, 0.079 g) was suspended in CH<sub>2</sub>Cl<sub>2</sub>/DMF (v/v = 8:1), then AgBF<sub>4</sub> (0.30 mmol, 0.058 g) was added with stirring. After several hours a white precipitate and a greenish solution formed. AgCl was filtered off and the solvent completely removed. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and 1,10-phenanthroline·H<sub>2</sub>O (phen·H<sub>2</sub>O) (0.30 mmol, 0.060 g) was added with stirring. The solution turned greyish and a precipitate formed. The precipitate was filtered off, washed with Et<sub>2</sub>O and dried *in vacuo*. A greyish powder was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>: yield 0.065 g (44%); m.pt = 114–118°C. FAB mass spectrum: *m/z* 902.3 [Ni(*cis*-dppen)(phen)<sub>2</sub>](BF<sub>4</sub>)<sup>+</sup>, 505.9 [Ni(phen)<sub>2</sub>](BF<sub>4</sub>)<sup>+</sup>. Found: C, 60.5; H, 4.1; N, 5.8. Calc. for C<sub>50</sub>H<sub>38</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Ni: C, 60.7; H, 3.9; N, 5.7%.

#### [Ni(*cis*-dppen)(bipy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**4**)

Compound **4** was prepared in an analogous manner to **3**, where 2,2'-bipyridine (bipy 0.30 mmol, 0.046 g) was used instead of phen·H<sub>2</sub>O: yield 0.113 g (80%); m.pt = 230–234°C dec. FAB mass spectrum: *m/z* 899.4 [Ni(*cis*-dppen)(bipy)<sub>2</sub>](BF<sub>4</sub>)<sup>+</sup>·(CH<sub>3</sub>)<sub>2</sub>NH, 503.0 [Ni(bipy)<sub>2</sub>](BF<sub>4</sub>)<sup>+</sup>·(CH<sub>3</sub>)<sub>2</sub>NH. Found: C, 51.8; H, 4.3; N, 6.8; Calc. for C<sub>46</sub>H<sub>38</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Ni·2DMF·2CH<sub>2</sub>Cl<sub>2</sub>: C, 51.6; H, 4.5; N, 6.7%.

#### [PdI<sub>2</sub>(dppe)] (**5**)

PdCl<sub>2</sub> (0.20 mmol, 0.036 g) was suspended in CHCl<sub>3</sub> (5 cm<sup>3</sup>). Then *trans*-dppen (0.20 mmol, 0.079 g) was added with stirring. The reaction mixture was stirred for 24 h and a yellow solution was obtained. To this solution LiI (0.40 mmol, 0.054 g) was added with stirring. The solution turned deep brown. After 24 h the colour of the solution changed into orange. An orange product was crystallized from CHCl<sub>3</sub>: yield 0.076 g (50%); m.pt = 220–223°C. Found: C, 37.0; H, 2.8. Calc. for C<sub>26</sub>H<sub>24</sub>I<sub>2</sub>P<sub>2</sub>Pd·CHCl<sub>3</sub>: C, 36.9; H, 2.9%. A sample for X-ray diffraction study was crystallized from CHCl<sub>3</sub>.

#### [Pd(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**6**)

Compound **6** was prepared as described earlier [1]. A sample for X-ray diffraction study was crystallized from DMF.

### X-ray crystallography

*Crystal data.* C<sub>26</sub>H<sub>22</sub>Cl<sub>2</sub>P<sub>2</sub>Ni·CH<sub>2</sub>Cl<sub>2</sub> (**1**), *M* = 610.93, red crystal (prismatic; 0.5 × 0.4 × 0.3 mm), monoclinic, *a* = 12.175(2), *b* = 15.455(3), *c* = 15.560(3) Å, β = 107.13(3)°, *V* = 2797.96 Å<sup>3</sup>, *Z* = 4, space group *P*2<sub>1</sub>/*c*, *D*<sub>c</sub> = 1.813 Mg m<sup>-3</sup>,

$F(000) = 1248$ ,  $\mu(\text{Mo-K}\alpha) = 1.261 \text{ mm}^{-1}$ ,  $\text{C}_{26}\text{H}_{24}\text{I}_2\text{P}_2\text{Pd} \cdot \text{CHCl}_3$  (**5**),  $M = 877.98$ , orange crystal (irregular;  $0.5 \times 0.5 \times 0.4 \text{ mm}$ ), triclinic,  $a = 8.600(2)$ ,  $b = 11.396(2)$ ,  $c = 16.980(3) \text{ \AA}$ ,  $\alpha = 93.05(3)$ ,  $\beta = 98.56(3)$ ,  $\gamma = 109.75(3)^\circ$ ,  $V = 1539.19 \text{ \AA}^3$ ,  $Z = 2$ , space group  $P\bar{1}$ ,  $D_c = 1.894 \text{ Mg m}^{-3}$ ,  $F(000) = 840$ ,  $\mu(\text{Mo-K}\alpha) = 2.987 \text{ mm}^{-1}$ ;  $\text{C}_{100}\text{H}_{84}\text{B}_2\text{P}_4\text{Pd} \cdot 4\text{DMF}$  (**6**),  $M = 1830.07$ , yellowish crystal (irregular;  $0.6 \times 0.5 \times 0.4 \text{ mm}$ ), triclinic,  $a = 12.940(3)$ ,  $b = 13.080(3)$ ,  $c = 15.446(3) \text{ \AA}$ ,  $\alpha = 77.35(3)$ ,  $\beta = 85.63(3)$ ,  $\gamma = 76.92(3)^\circ$ ,  $V = 2483.70 \text{ \AA}^3$ ,  $Z = 1$ , space group  $P\bar{1}$ ,  $D_c = 1.224 \text{ Mg m}^{-3}$ ,  $F(000) = 960$ ,  $\mu(\text{Mo-K}\alpha) = 0.302 \text{ mm}^{-1}$ .

**Data collection.** Unit-cell dimensions and intensity data were obtained at 293 K using a Siemens P4 diffractometer and graphite monochromated Mo-K $\alpha$  radiation.  $2\theta$  range =  $2.0\text{--}60.0^\circ$ , scan type =  $\omega$ , scan speed = variable ( $2.0\text{--}29.3^\circ \text{ min}^{-1}$  in  $\omega$ ). Index ranges =  $-1 \leq h \leq 17$ ,  $-1 \leq k \leq 21$ ,  $-21 \leq l \leq 21$  (**1**);  $-1 \leq h \leq 11$ ,  $-16 \leq k \leq 15$ ,  $-23 \leq l \leq 23$  (**5**);  $-1 \leq h \leq 11$ ,  $-17 \leq k \leq 17$ ,  $-21 \leq l \leq 21$  (**6**). 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  $\psi$ -scans of nine reflections [range of transmission factors: 0.69–1.00 (**1**), 0.49–1.00 (**5**), 0.96–1.00 (**6**) [11]. A total of 9617 (**1**), 10,349 (**5**) and 13,000 (**6**) reflections were measured, of which 7972 (**1**,  $R_{\text{int}} = 0.029$ ), 8703 (**5**,  $R_{\text{int}} = 0.042$ ) and 11,257 (**6**,  $R_{\text{int}} = 0.033$ ) were unique and 3881 (**1**), 5704 (**5**) and 8522 (**6**) satisfied the condition  $I > 3\sigma(I)$ .

**Structure solution.** All structure determination calculations were carried out on 80486- and Pentium-PCs using the PC-version of SHELXTL PLUS and SHELXL93 [12]. The positions of the nickel and palladium atoms were found by the Patterson method. Other atom positions were located from successive difference-Fourier maps.

In the case of **1** all non-hydrogen atoms including one disordered molecule of  $\text{CH}_2\text{Cl}_2$  per asymmetric unit have been refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with fixed isotropic  $U$ . The final  $R$  value of 0.043 ( $R' = 0.043$ ) was computed for 325 parameters. The largest feature on a final difference map was  $0.65 \text{ e \AA}^{-3}$  [GOF = 0.98, largest  $\Delta/\sigma = 0.065$ , weighting scheme:  $w^{-1} = \sigma^2(F^2) + (0.0661 P)^2$ ].

In the case of **5** all non-hydrogen atoms including one molecule of  $\text{CHCl}_3$  per asymmetric unit have been refined with anisotropic thermal parameters. The hydrogen atoms were treated as in **1**. The final  $R$  value of 0.038 ( $R' = 0.038$ ) was computed for 316 parameters. The largest feature on a final difference map was  $1.00 \text{ e \AA}^{-3}$  [GOF = 1.02, largest  $\Delta/\sigma = 0.001$ , weighting scheme:  $w^{-1} = \sigma^2(F^2) + (0.0499 P)^2 + 0.39 P$ ].

In the case of **6** all non-hydrogen atoms, including one molecule of DMF per asymmetric unit, have been refined with anisotropic thermal parameters. In the

final refinement a second, disordered molecule of DMF was included with isotropic thermal parameters. The hydrogen atoms were added as before. The final  $R$  value of 0.040 ( $R' = 0.040$ ) was computed for 574 parameters. The largest feature on a final difference map was  $0.55 \text{ e \AA}^{-3}$  [GOF = 1.01, largest  $\Delta/\sigma = 0.051$ , weighting scheme:  $w^{-1} = \sigma^2(F^2) + (0.0645 P)^2 + 0.40 P$ ].

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

## RESULTS

Since in  $[\text{PtCl}_2(\text{cis-dppen})]$  a complete coplanarity of the coordination plane and the ethene bridge has been observed [1], for purposes of comparison an X-ray structure analysis of  $[\text{NiCl}_2(\text{cis-dppen})]$  (**1**) was performed. It shows a discrete  $[\text{NiCl}_2(\text{cis-dppen})]$  molecule and a disordered  $\text{CH}_2\text{Cl}_2$  molecule per asymmetric unit. A view of **1** is given in Fig. 1(a); Table 1 contains selected bond distances and bond angles.

Compound **1** shows two nearly coplanar parts. The deviations from a least-squares plane through the following atoms of the square planar coordination plane are: Ni(1): 0.002, P(1):  $-0.032$ , P(2): 0.032, Cl(1):

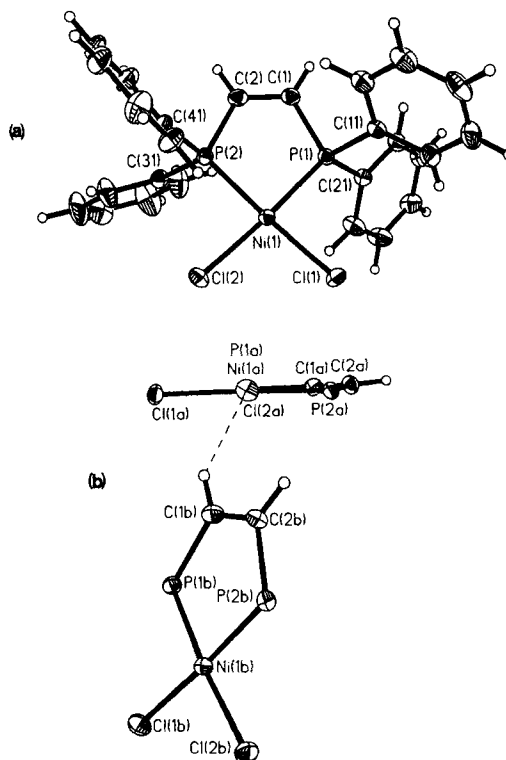


Fig. 1. View of  $[\text{NiCl}_2(\text{cis-dppen})]$  (**1**). (a) The coordination plane through the Ni atom, the P atoms and the Cl atoms in the projection plane showing the atom labelling scheme; (b) packing plot showing the small deviations from a coplanar arrangement of the coordination plane and the ethene bridge, and the shortest intermolecular contact approach (phenyl rings omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (°) for [NiCl<sub>2</sub>(*cis*-dppen)] (1)

Ni(1)—P(1)	2.1474(9)
Ni(1)—P(2)	2.1355(11)
Ni(1)—Cl(11)	2.1904(11)
Ni(1)—Cl(2)	2.2004(10)
P(1)—C(1)	1.812(3)
P(2)—C(2)	1.815(3)
P(1)—C(11)	1.812(3)
P(1)—C(21)	1.812(3)
P(2)—C(31)	1.817(4)
P(2)—C(41)	1.823(3)
C(1)—C(2)	1.316(5)
P(1)—Ni(1)—P(2)	87.79(4)
P(1)—Ni(1)—Cl(1)	88.89(4)
P(1)—Ni(1)—Cl(2)	175.11(4)
P(2)—Ni(1)—Cl(1)	176.35(4)
P(2)—Ni(1)—Cl(2)	87.67(4)
Cl(1)—Ni(1)—Cl(2)	95.69(4)
C(21)—P(1)—C(11)	106.4(2)
C(21)—P(1)—C(1)	102.8(2)
C(11)—P(1)—C(1)	105.0(2)
C(21)—P(1)—Ni(1)	116.52(11)
C(11)—P(1)—Ni(1)	115.82(10)
C(1)—P(1)—Ni(1)	108.96(12)
C(2)—P(2)—C(31)	104.1(2)
C(2)—P(2)—C(41)	102.7(2)
C(31)—P(2)—C(41)	107.6(2)
C(2)—P(2)—Ni(1)	108.87(13)
C(31)—P(2)—Ni(1)	116.35(12)
C(41)—P(2)—Ni(1)	115.70(12)
C(2)—C(1)—P(1)	116.8(3)
C(1)—C(2)—P(2)	117.4(3)

0.028, and Cl(2):  $-0.030$  Å. This corresponds to a very slight tetrahedral distortion. The second nearly coplanar part of **1** is revealed by the deviations from a least-squares plane through the following atoms: Ni(1):  $-0.021$ , P(1):  $0.010$ , P(2):  $0.032$ , C(1):  $0.014$ , and C(2):  $-0.034$  Å. The angle between these two planes is only  $1.8^\circ$ , where this slightly inclined arrangement of the coordination plane and the ethene bridge is shown in Fig. 1(b). Figure 1(b) also indicates that the deviations from a complete coplanarity in **1** could be caused by the shortest intermolecular contact of  $2.716$  Å between the hydrogen atom attached to C(1) and Cl(2). It seems likely, that the previously reported  $\pi$ -bonding interaction [1] leading to completely planar structures in [PtCl<sub>2</sub>(*cis*-dppen)] and related molecules [1,3] is disturbed in **1** by this crystal packing effect. Nevertheless, the unsaturated nature of the chelating diphosphine leads to an enhancement of Ni-to-P  $\pi$ -bonding also in **1**. As a consequence some degree of rehybridization takes place at the phosphorus and aliphatic carbon atoms [13], producing the observed partial coplanarities in **1**. Similar  $\pi$ -bonding effects are present in [(C<sub>9</sub>H<sub>5</sub>N<sub>4</sub>)PtCl(*cis*-dppen)] [2] and [Pd<sub>2</sub>Cl<sub>4</sub>(dppa)<sub>2</sub>] [14], where dppa is 1,2-bis(diphenylphosphino)acetylene. The magnitude of the

crystal packing effect in **1** is in agreement with the recently described [15] flexibility of metal complexes in crystals. Crystal packing influences on aliphatic bridges have been observed previously [8].

Due to the  $\pi$ -bonding influence throughout **1** the double-bond length of  $1.316(5)$  Å is shortened compared with the ideal value of a simple double bond of  $1.337(6)$  Å [16]. Similar to this,  $1.28(2)$  Å in [PtCl<sub>2</sub>(*cis*-dppen)] and  $1.315(5)$  Å in [Pt(*cis*-dppen)<sub>2</sub>(BPh<sub>4</sub>)<sub>2</sub>] have been found [1]. The chelate P—Ni—P angle of  $87.79(4)^\circ$  in **1** is significantly larger than the corresponding values of  $86.93(6)^\circ$  in [NiCl<sub>2</sub>(dpppe)] [17] (**7**) and  $86.90(11)^\circ$  in *rac*-[Ni<sub>2</sub>Cl<sub>4</sub>P4] [18] (**8**), where P4 is 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetra-phosphadecane. The Cl—Ni—Cl angle of  $95.69(4)^\circ$  in **1** is comparable to the same parameter of  $95.47(6)^\circ$  in **7**, but significantly larger than in **8** [ $95.07(10)^\circ$ ]. In **1** the Ni—P(1) bond length of  $2.147(9)$  Å is significantly larger than the Ni—P(2) bond length of  $2.1355(11)$  Å. Both parameters have to be compared with the mean values of the Ni—P bond lengths of  $2.151(1)$  Å in **7** and  $2.147(2)$  Å in **8**. The Ni—Cl(1) bond length of  $2.1904(11)$  Å is significantly shorter than Ni—Cl(2) of  $2.2004(10)$  Å in **1**. The mean Ni—Cl bond lengths are  $2.200(1)$  Å in **7** and  $2.195(2)$  Å in **8**.

The <sup>31</sup>P <sup>1</sup>H NMR spectrum of [Ni(CN)<sub>2</sub>(*cis*-dppen)] (**2**) shows a single resonance at  $73.0$  ppm in CHCl<sub>3</sub>/EtOH ( $\nu/\nu = 1:1$ ). This is in agreement with structure type A in Scheme 1 and the typical large downfield shift produced by a five-membered ring [19]. However, since the kinetic lability of Ni<sup>II</sup> bis(phosphine) complexes is of importance for the testing and antitumour activity of these compounds [10a], the reaction of Ni(CN)<sub>2</sub> with *cis*-dppen was investigated in detail. Treatment of Ni(CN)<sub>2</sub> with 2 equiv. of *cis*-dppen and subsequent stirring at  $70^\circ\text{C}$  for several days led to a more complicated <sup>31</sup>P <sup>1</sup>H NMR spectrum. The signal at  $73.0$  ppm is still present. A single resonance at  $47.9$  ppm also showing a downfield shift due to a five-ring contribution is attributed to the octahedral species [Ni(CN)<sub>2</sub>(*cis*-dppen)<sub>2</sub>] with four equivalent phosphorus atoms occupying the equatorial plane. Two signals of equal intensities at  $24.3$  and  $-21.0$  ppm are consistent with *cis*-dppen coordinating with only one phosphorus atom, the second remaining free. This could correspond to the trigonal bipyramidal species [Ni(CN)<sub>2</sub>(*cis*-dppen)<sub>3</sub>] with three phosphorus atoms of different *cis*-dppen ligands occupying the equatorial plane. Trigonal bipyramidal Ni<sup>II</sup> species are very common [5,20]. Furthermore, a single resonance at  $23.4$  ppm without a five-ring effect is attributed to a dimeric species containing bridging *cis*-dppen. However, it was only possible to isolate **2** from this mixture.

The <sup>31</sup>P <sup>1</sup>H NMR spectrum of [Ni(*cis*-dppen)(phen)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**3**) consists of a broad single resonance at  $57.2$  ppm in CHCl<sub>3</sub>. This is in agreement with structure B in Scheme 1 and a planar coordination of *cis*-dppen leading to equivalent phosphorus atoms and the five-ring downfield shift. [Ni(*cis*-dppen)(bipy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**4**), by contrast, shows two <sup>31</sup>P <sup>1</sup>H

NMR signals of equal intensities at 3.8 and 0.6 ppm in  $\text{CHCl}_3$ . Due to the non-equivalence of the phosphorus atoms of *cis*-dppen, no five-ring contribution is observed. In the case of **4** the  $^{31}\text{P}$   $^1\text{H}$  NMR parameters are consistent with a distorted coordination of *cis*-dppen as indicated in structure C of Scheme 1. For both compounds **3** and **4**, two optical isomers are expected [6,21]. The importance of a chiral array of different ligand groups for chiral recognition has been emphasized only recently in the case of  $\text{Ni}^{\text{II}}$  [22].

The  $^{31}\text{P}$   $^1\text{H}$  NMR spectrum of  $[\text{PdI}_2(\text{dppe})]$  (**5**) shows a single resonance at 60.7 ppm in  $\text{CHCl}_3$ . This is in agreement with structure D in Scheme 1, indicating the presence of a downfield five-ring contribution. In order to characterize the unexpected product **5** (see above) definitely, an X-ray structure analysis of **5** was performed. It shows a discrete  $[\text{PdI}_2(\text{dppe})]$  molecule and a  $\text{CHCl}_3$  molecule per asymmetric unit. A view of **5** is given in Fig. 2(a); Table 2 contains selected bond distances and bond angles.

A slight tetrahedral distortion of the square planar coordination in **5** is revealed by the deviations from a least-squares plane through the following atoms: Pd(1):  $-0.024$ , P(1):  $-0.011$ , P(2):  $0.023$ , I(1):  $0.020$ , and I(2):  $-0.008$  Å. The carbon atoms of the aliphatic chain of dppe unsymmetrically deviate from this plane: C(1)  $-0.420$  Å to one side and C(2)  $0.318$  Å to the other side. This corresponds to a distorted twist conformation of the  $\text{PdP}_2\text{C}_2$  chelate ring, which is shown in Fig. 2(b). The unsymmetrical alkyl chain

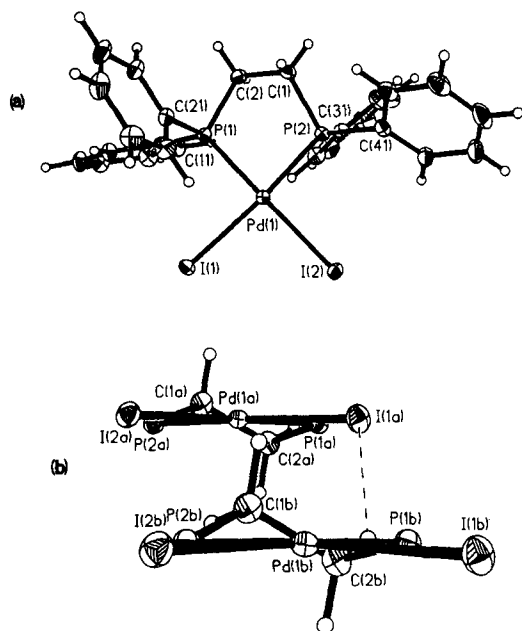


Fig. 2. View of  $[\text{PdI}_2(\text{dppe})]$  (**5**). (a) The coordination plane through the Pd atom, the P atoms and the I atoms in the projection plane showing the atom labelling scheme; (b) packing plot showing the unsymmetrical aliphatic bridge and the shortest intermolecular contact approach (phenyl rings omitted for clarity).

Table 2. Selected bond lengths (Å) and angles ( $^\circ$ ) for  $[\text{PdI}_2(\text{dppe})]$  (**5**)

Pd(1)—P(1)	2.2608(14)
Pd(1)—P(2)	2.2756(13)
Pd(1)—I(1)	2.6649(8)
Pd(1)—I(2)	2.6446(10)
P(1)—C(2)	1.832(5)
P(2)—C(1)	1.834(5)
P(1)—C(11)	1.811(5)
P(1)—C(21)	1.813(5)
P(2)—C(31)	1.812(5)
P(2)—C(41)	1.811(5)
C(1)—C(2)	1.514(7)
P(1)—Pd(1)—P(2)	85.59(5)
P(1)—Pd(1)—I(2)	177.88(3)
P(1)—Pd(1)—I(1)	89.03(4)
P(2)—Pd(1)—I(2)	92.38(4)
P(2)—Pd(1)—I(1)	174.23(3)
I(1)—Pd(1)—I(2)	92.97(3)
C(11)—P(1)—C(21)	107.3(2)
C(11)—P(1)—C(2)	105.0(2)
C(21)—P(1)—C(2)	105.2(2)
C(11)—P(1)—Pd(1)	116.5(2)
C(21)—P(1)—Pd(1)	114.0(2)
C(2)—P(1)—Pd(1)	107.9(2)
C(41)—P(2)—C(31)	104.9(2)
C(41)—P(2)—C(1)	105.3(2)
C(31)—P(2)—C(1)	103.2(2)
C(41)—P(2)—Pd(1)	124.1(2)
C(31)—P(2)—Pd(1)	110.8(2)
C(1)—P(2)—Pd(1)	106.6(2)
C(2)—C(1)—P(2)	108.4(3)
C(1)—C(2)—P(1)	108.5(3)

could be caused by the shortest intermolecular, attractive contact of 3.209 Å between the hydrogen atom attached to C(2) and I(1) also indicated in Fig. 2(b).

The P—Pd—P chelate angles in  $\text{Pd}^{\text{II}}$  complexes containing dppe differ from  $81.65(8)^\circ$  in  $[\text{Pd}(\text{dppe})_2]\text{Cl}_2$  [**9**] to  $88.3(1)^\circ$  in  $[\text{PdCl}_2(\text{dppe})]$  [**10**]. The value of  $85.59(5)^\circ$  for **5** is located within the central range of this parameter [4,25]. It is also comparable to the mean value of the P—Pt—P chelate angles of  $86.0(2)^\circ$  in  $[\text{PtI}_2(\text{dppe})]$  [26]. The smaller than ideal P—Pd—P angle in **5** leads to an opening of the I—Pd—I angle to  $92.97(3)^\circ$ . The unsymmetrical alkyl bridge produces significantly different *cis* P—Pd—I angles of  $89.03(4)$  and  $92.38(4)^\circ$ , respectively. As a consequence also the Pd—P and Pd—I bond distances significantly deviate (see Table 2). The mean value of the Pd—P bond lengths of 2.2682 Å in **5** is shorter than the corresponding value of 2.345 Å in **9**, in agreement with the weaker *trans* influence of iodine (**5**) *vs* phosphorus (**9**) [27]. However, opposite to the stronger *trans* influence of iodine *vs* chlorine [20b], the mean Pd—P bond length of 2.274 Å in **10** is larger than in **5**. It seems likely that the unusually large P—Pd—P chelate angle in **10** leads to the weaker

Pd—P bonds. This is confirmed by the fact that a second, solvated modification of **10** [25e] shows a smaller P—Pd—P chelate angle of 85.82(7)° comparable to **5** and a mean Pd—P bond length of 2.230 Å, in agreement with the *trans* influence series. The magnitude of this crystal packing effect producing the differences between the two modifications of **10** in relation to **5** is consistent with the recently described flexibility of metal complexes in crystals [15].

Since [Pt(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**11**) shows a complete coplanarity of the coordination plane and the ethene bridges due to the already mentioned  $\pi$ -bonding interaction [1], for purposes of comparison an X-ray structure analysis of the recently prepared [1] compound [Pd(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**6**, structure E in Scheme 1) was performed. It shows a discrete [Pd(*cis*-dppen)<sub>2</sub>]<sup>2+</sup> cation, two (BPh<sub>4</sub>)<sup>-</sup> anions and four molecules DMF per unit cell. A view of the cation is given in Fig. 3(a); Table 3 contains selected bond distances and bond angles.

The palladium atom is located on a centre of symmetry. Therefore, the coordination plane is completely planar due to crystallographic constraints. However, the two carbon atoms of the ethene bridge deviate 0.547 and 0.532 Å, respectively, to one side of this plane leading to an angle of 20.3° between the coordination plane and the least-squares plane through

Table 3. Selected bond lengths (Å) and angles (°) for [Pd(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**6**)

Pd(1)—P(1)	2.3621(10)
Pd(1)—P(2)	2.3215(7)
P(1)—C(2)	1.781(2)
P(2)—C(1)	1.817(2)
P(1)—C(11)	1.806(3)
P(1)—C(21)	1.844(2)
P(2)—C(31)	1.808(3)
P(2)—C(41)	1.818(3)
C(1)—C(2i)	1.338(3)
P(1)—Pd(1)—P(1i)	180.0
P(1)—Pd(1)—P(2i)	84.78(3)
P(1)—Pd(1)—P(2)	95.22(3)
P(2)—Pd(1)—P(2i)	180.0
C(2)—P(1)—C(11)	102.60(12)
C(2)—P(1)—C(21)	104.10(11)
C(11)—P(1)—C(21)	107.04(12)
C(2)—P(1)—Pd(1)	105.12(8)
C(11)—P(1)—Pd(1)	113.75(8)
C(21)—P(1)—Pd(1)	122.02(8)
C(31)—P(2)—C(1)	104.94(12)
C(31)—P(2)—C(41)	106.13(12)
C(1)—P(2)—C(41)	106.32(12)
C(31)—P(2)—Pd(1)	120.19(8)
C(1)—P(2)—Pd(1)	104.61(8)
C(41)—P(2)—Pd(1)	113.53(9)
C(2i)—C(1)—P(2)	121.1(2)
C(1i)—C(2)—P(1)	119.7(2)

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

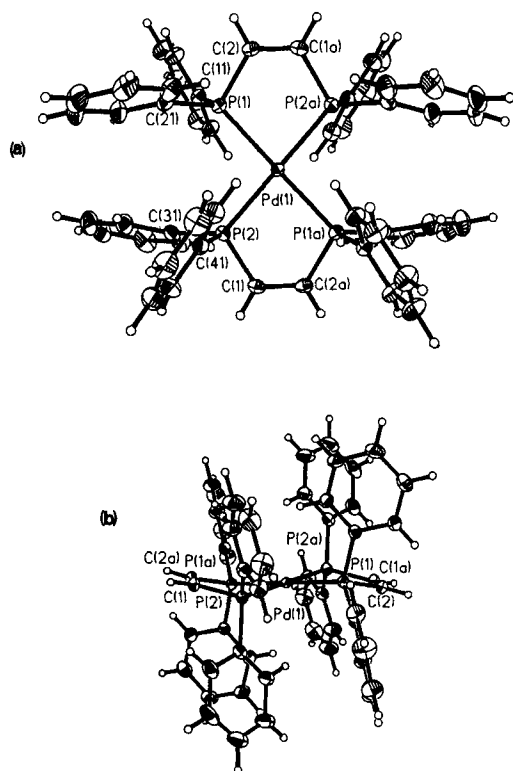


Fig. 3. View of [Pd(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> (**6**). (a) The coordination plane through the Pd atom and the P atoms in the projection plane showing the atom labelling scheme; (b) projection showing the different orientations of the ethene bridges with respect to the coordination plane.

the carbon atoms of the ethene bridge and the adjacent phosphorus atoms. The different orientations of the ethene bridges with respect to the coordination plane are shown in Fig. 3(b). [Ni(*cis*-dppen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**12**) shows an analogous coordination to **6** [9]. In **12** the angle between the coordination plane and the C<sub>2</sub>P<sub>2</sub> plane is 19.9°. Since for these [M(*cis*-dppen)<sub>2</sub>]<sup>2+</sup> complexes the only completely planar structure occurs in the case of M = Pt (**11**), it seems likely that the strongest metal–phosphorus *dπ*–*dπ* back-bonding is present in **11** in this series of compounds.

However, the chelate P—M—P angles in **6**, **11** and **12** of 84.78(3), 84.6(1), and 84.2(2)° are not significantly different. Since in all three complexes the coordination is completely planar due to crystallographic constraints, this means that the corresponding P—M—P angles not connected by ethene bridges are also identical within the standard deviations. In **6** the Pd—P bond lengths of 2.3621(10) and 2.3215(7) Å significantly differ, which is responsible for the P(1)—C(2)—C(1a)—P(2a) torsion angle of 1.5°. The double bond length of 1.338(3) Å in **6** corresponds to the ideal value of a simple double bond. This is in contrast to the shortened double bonds in the compounds **1**, [PtCl<sub>2</sub>(*cis*-dppen)], and [Pt(*cis*-dppen)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub>, where the ethene bridges are coplanar with the coordination planes.

## DISCUSSION

In both cases of complexes of the type  $[MCl_2(cis-dppen)]$  ( $M = Ni, Pt$ ) the X-ray structures show a coplanarity of the ethene bridges and the coordination planes. However, for complexes of the type  $[M(cis-dppen)_2]X_2$  ( $M = Ni, Pd, Pt$ ;  $X = anion$ ) this effect only occurs in the platinum compound. The major difference between these series of complexes is the stronger *trans* influence of phosphorus *vs* chlorine in the latter case. This leads to shorter  $M-P$  bonds for the  $[MCl_2(cis-dppen)]$  examples. It seems likely that for nickel these short bonds are necessary to facilitate the enhancement of metal-phosphorus  $d\pi-d\pi$  back-bonding required for the stabilization of a coplanar arrangement of the ethene bridges and the coordination planes, which is present only in  $[NiCl_2(cis-dppen)]$  (**1**) and not in  $[Ni(cis-dppen)_2](ClO_4)_2$  (**12**). For platinum the strong back-donation of this metal is sufficient to stabilize a coplanar arrangement for both types of complexes. An exploration of the palladium case is in progress.

In this work the X-ray structures of **1**, **5** and **6** have revealed completely different orientations of the aliphatic bridges. A planar arrangement of the ethene bridge like in **1** could also occur in  $[Ni(CN)_2(cis-dppen)]$  (**2**) and  $[Ni(cis-dppen)(phen)_2](BF_4)_2$  (**3**), stabilizing these compounds by a  $\pi$ -bonding interaction. In **5** the non-planarity of the  $PdP_2C_2$  ring is a consequence of the tetrahedral geometry at the carbon and phosphorus atoms and of the square-planar coordination of palladium [4a]. This leads to a reduced stability of dppe complexes compared with their analogous *cis*-dppen counterparts [10a]. Furthermore, the deviations from a planar arrangement of the aliphatic bridges in **5** and **6** produce a steric blocking *cis* to the bidentate phosphine ligand [9,22], which is not present in **1**. Consequently, differences in the reactivities between dppe and analogous *cis*-dppen complexes could occur. Further work on this is in progress.

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