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Nickel(II), palladium(II), platinum(II) and platinum(IV) complexes of *cis*-1,2-bis(diphenylphosphino)ethene and nitrogen-containing heterocycles or sulfur ligands

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Abstract

Several novel Ni(II), Pd(II), Pt(II) and Pt(IV) complexes containing the diphos ligand *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppen) have been prepared and characterized by X-ray diffraction methods, NMR spectroscopy (^{195}Pt{^{1}H}, ^{31}P{^{1}H}, ^{13}C{^{1}H}, ^{1}H), fast atom bombardment mass spectrometry, IR spectroscopy, elemental analyses, and melting points. In the case of [$PtCl_2$(*cis*-dppen)] (**1**) a second crystal modification was found and definitely characterized by an X-ray structure analysis: monoclinic, $P2_1/n$, $Z=4$, $a=8.312(1)$, $b=14.578(2)$, $c=19.868(4)$ Å, $\beta=91.27(1)°$, $R=0.028$ for 3862 observed reflections $(I>3\sigma(I))$. In contrast to the former reported X-ray structure of the other modification of **1**, which shows a complete coplanarity of the coordination plane and the ethene bridge, this coplanarity is slightly disturbed by a crystal packing effect in the second modification of **1**. Nevertheless, both conformations are dominated by a π bonding interaction. Furthermore, the X-ray structures of the recently prepared complexes [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**) and [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**), where bipy and phen are 2,2′-bipyridine and 1,10-phenanthroline, respectively, are given for the first time: **2**: monoclinic, $P2_1/c$, $Z=4$, $a=12.649(3)$, $b=26.114(5)$, $c=14.665(3)$ Å, $\beta=111.62(3)°$, $R=0.057$ for 4260 observed reflections $(I>3\sigma(I))$; **3**: monoclinic, $P2_1$, $Z=2$, $a=8.779(2)$, $b=17.297(3)$, $c=13.059(3)$ Å, $\beta=93.79(3)°$, $R=0.045$ for 3589 observed reflections $(I>3\sigma(I))$. These two X-ray structures are the first examples of square-planar structures of Pt(II) complexes containing bipy or phen together with phosphines. The different conformations of **2** and **3** are of interest with respect to the known differences between bipy and phen in photoactivation processes. The reaction of **1** with an equimolar amount of anhydrous Na_2S leads to the dimer [$Pt_2(\mu_2\text{-}S)_2$(*cis*-dppen)$_2$] (**4**). A similar treatment of **1** with the phosphoniodithioformate S_2CPCy_3, where Cy is cyclohexyl, produces the dimer [$Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)$(*cis*-dppen)$_2$]$(BF_4)_2$ (**5**). However, the reactions of [MCl_2(*cis*-dppen)] (M = Ni, Pd) with anhydrous Na_2S give the trinuclear complexes [$M_3(\mu_3\text{-}S)_2$(*cis*-dppen)$_3$]X_2 (M = Ni, $X^- = PF_6^-$ (**6**); M = Pd, $X^- = BF_4^-$ (**7**)). In the case of **1** $Na_2S\cdot 9H_2O$ is needed to produce the corresponding Pt(II) complex [$Pt_3(\mu_3\text{-}S)_2$(*cis*-dppen)$_3$]Cl_2 (**8**). Interestingly, treatment of [$NiCl_2$(*cis*-dppen)] with S_2CPCy_3 leads to the unexpected mononuclear compound [$Ni(CS_2)_4$(*cis*-dppen)]$(BF_4)_2$ (**9**). Oxidation of [Pt(*cis*-dppen)$_2$]Cl_2 by chlorine gives the mononuclear complex [$PtCl_2$(*cis*-dppen)$_2$]Cl_2 (**10**). The common feature of the compounds **1–10** is the presence of *cis*-dppen as a chelating ligand. The goal of this article is to reveal possible π bonding interactions due to the unsaturated nature of this diphos ligand.

Keywords: Crystal structures; Nickel complexes; Palladium complexes; Platinum complexes; Diphosphine complexes; Diamine complexes

1. Introduction

Recent studies [1–3] have shown that in complexes of diphosphines with unsaturated backbones such as *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppen) or 1,2-bis(diphenylphosphino)acetylene (dppa) π bonding interactions between the aliphatic double or triple bonds and the metal–ligand bonds are present. In the case of *cis*-dppen this leads to completely planar structures in [$PtCl_2$(*cis*-dppen)] and [Pt(*cis*-dppen)$_2$]$(BPh_4)_2$ [1]. However, in [$NiCl_2$(*cis*-dppen)] the coplanarity of the coordination plane and the ethene bridge is slightly disturbed by a crystal packing effect [3]. These induced deviations are in agreement with the recently described flexibility of metal complexes in crystals [4]. In this paper the X-ray structure of a second crystal

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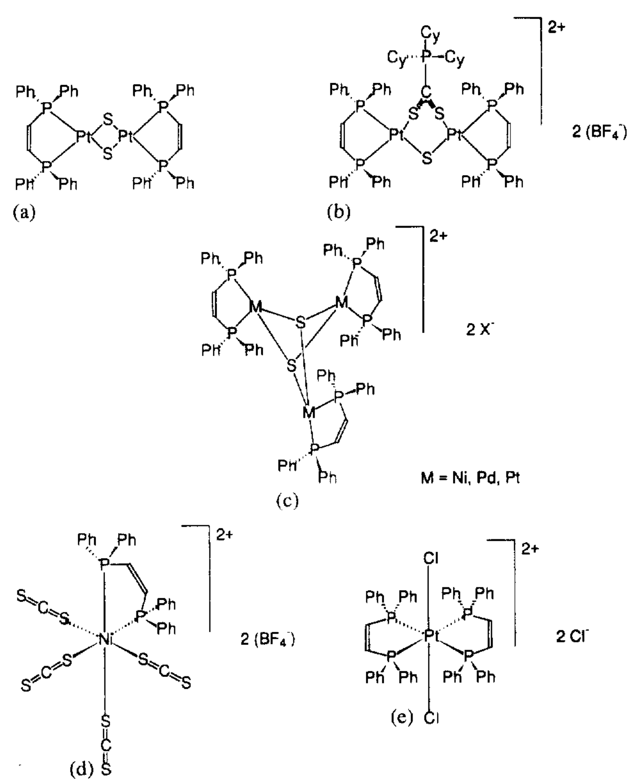
modification of [PtCl$_2$(*cis*-dppen)] (**1**) is presented also showing a small deviation from coplanarity due to crystal packing and clearly demonstrating the flexibility of complexes in the same molecule.

Furthermore, the novel X-ray structures of the recently prepared compounds [Pt(*cis*-dppen)(bipy)](PF$_6$)$_2$ (**2**) and [Pt(*cis*-dppen)(phen)](BF$_4$)$_2$ (**3**), where bipy and phen are 2,2′-bipyridine and 1,10-phenanthroline, respectively, are presented. Bipy containing Pt(II) complexes have been used in supramolecular arrays for photoactivation processes [5]. In this context the structural characteristics of the acceptor ligands such as bipy or phen determine the lifetimes of excited states [6]. The possibility of twist distortions in pyridyl complexes also plays a large role for the effect of intersystem crossing, where a complex converts from one state to another which has a different spin multiplicity [7].

It has been shown that in compounds of the type [Pt$_2$(μ_2-S)$_2$L$_4$], where L is a monophosphine, the hinge angle between the two coordination planes and hence the stability of these complexes depend on the Pt$_2$S$_2$ through-ring antibonding interaction between the in-plane sulfur p orbitals [8]. Since in its complexes *cis*-dppen is capable of the abovementioned π bonding interactions between the ethene bridge and the coordination plane, this should also influence the M$_2$S$_2$ (M = Ni, Pd, Pt) antibonding interactions producing different S^{2-} bridged compounds containing *cis*-dppen, where as far as we know, no example is given in the literature. In this class of complexes, the molecules tend to aggregate and trinuclear and higher clusters are possible [9]. The interaction of S^{2-} with transition metals is widespread in nature and responsible for the formation of ores as well as [M$_x$S$_y$] clusters in active centers of redox enzymes such as ferredoxines or nitrogenases [10]. The nephrotoxicity of platinum containing antitumor drugs is believed to result from the binding of platinum to sulfur-functionalized protein residues [11].

[Pt$_2$(μ_2-S)$_2$(*cis*-dppen)$_2$] (**4**) corresponds to structure (a) in Scheme 1. The same structure type is found in [Pt$_2$(μ_2-S)$_2$(PPh$_3$)$_4$] and related dimers containing monophosphines similar to PPh$_3$ [12]. In the case of the analogous dimers bridged by thiolato groups instead of sulfido ligands monophosphines as well as the diphosphine 1,2-bis(diphenylphosphino)ethane (dppe) occur [13]. The unsymmetrically bridged dimer [Pt$_2$(μ_2-S)(μ_2-S$_2$CPCy$_3$)(*cis*-dppen)$_2$](BF$_4$)$_2$ (**5**) shows structure (b) in Scheme 1. Though different binding modes of phosphoniodithioformates are well known, this is the first case where S$_2$CPCy$_3$ produces sulfido ligands in situ [14]. The trinuclear complexes [M$_3$(μ_3-S)$_2$(*cis*-dppen)$_3$]X$_2$ (M = Ni, $X^- = PF_6^-$ (**6**), M = Pd, $X^- = BF_4^-$ (**7**), M = Pt, $X^- = Cl^-$ (**8**)) correspond to structure (c) in Scheme 1. This structure type has been found in analogous complexes of Ni(II) [15], Pd(II) [16], and Pt(II) [17] containing monophosphines as well as dppe. [Ni(CS$_2$)$_4$(*cis*-dppen)](BF$_4$)$_2$ (**9**) shows structure (d) in Scheme 1. Linear S-bonded instead of π-bonded CS$_2$ ligands are rare, where reactions of CS$_2$ are of interest, also with respect to reactions of the structurally closely related CO$_2$ [18]. The novel Pt(IV) complex [PtCl$_2$(*cis*-dppen)$_2$]Cl$_2$ (**10**) corresponds to structure (e) in Scheme 1. Pt(IV) complexes of diphosphines have been prepared in a wide variety of structure types, where also thiolato-bridged dimers occur [2,19]. In this article emphasis is given to the fact that the unsaturated nature of *cis*-dppen leads to several novel compounds not observed with other phosphines and to a drastic alteration of structural characteristics in complexes also known with other phosphines.



Scheme 1. Structure types observed in the compounds **4**–**10**. The P–M–P (M = Ni, Pd, Pt) angles, where the phosphorus atoms are connected by ethene bridges, are constrained to values below 90°. Structure (a) occurs in [Pt$_2$(μ_2-S)$_2$(*cis*-dppen)$_2$] (**4**); structure (b) in [Pt$_2$(μ_2-S)(μ_2-S$_2$CP-Cy$_3$)(*cis*-dppen)$_2$](BF$_4$)$_2$ (**5**); structure (c) in [M$_3$(μ_3-S)$_2$(*cis*-dppen)$_3$]X$_2$ (M = Ni, $X^- = PF_6^-$ (**6**); M = Pd, $X^- = BF_4^-$ (**7**); M = Pt, $X^- = Cl^-$ (**8**)); structure (d) in [Ni(CS$_2$)$_4$(*cis*-dppen)](BF$_4$)$_2$ (**9**); structure (e) in [PtCl$_2$(*cis*-dppen)$_2$]Cl$_2$ (**10**).

2. Experimental

2.1. Reagents and chemicals

Reagent grade chemicals were used as received unless stated otherwise. *cis*-1,2-Bis(diphenylphosphino)ethene (*cis*-dppen) was purchased from Aldrich and S$_2$CPCy$_3$ from Strem. All other chemicals and solvents were obtained from Fluka. Solvents used for NMR measurements and crystallization purposes were of purissimum grade quality. NiCl$_2$·6H$_2$O, PdCl$_2$, and Na$_2$PtCl$_4$·4H$_2$O were also received from Fluka.

2.2. *Instrumentation*

Fourier-mode $^{195}Pt\{^1H\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were obtained by use of a Bruker AC-200 spectrometer (internal deuterium lock) and were recorded at 43.02, 80.96, 50.29, and 200 MHz, respectively. Positive chemical shifts are downfield from the standards; 1.0 M Na_2PtCl_6 for the $^{195}Pt\{^1H\}$ resonances, 85% H_3PO_4 for the $^{31}P\{^1H\}$ resonances, and TMS for the $^{13}C\{^1H\}$ and ^1H resonances.

2.3. *X-ray data collection*

The X-ray data collections were performed on a Siemens P4 diffractometer. Colorless crystals of [$PtCl_2$(*cis*-dppen)] (**1**), [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**), and [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**) were fixed on quartz pins. The lattices were found to be monoclinic in all three cases by standard procedures using the software of the Siemens P4 diffractometer. No decay in the intensities of three standard reflections was observed during the course of data collection in each case. The data were corrected for Lorentz and polarization effects. The empirical absorption corrections were based on ψ-scans of nine reflections, respectively ($\chi = 75$–$105°$, 360° scans in 10° steps in ψ) [20].

2.4. *Structure solution and refinement*

All structure determination calculations were carried out on 80486 and Pentium PCs using the PC version of SHELXTL PLUS and SHELXL93 [21]. The positions of the platinum atoms were found by the Patterson method. Other atom positions were located from successive difference Fourier maps.

In the case of **1** final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included using a riding model with isotropic U values depending on U_{eq} of the adjacent carbon atoms. The final R value of 0.028 was computed for 280 parameters and 3862 reflections.

In the case of **2** all non-hydrogen atoms including 1.8 molecules of CH_2Cl_2 per asymmetric unit were anisotropically refined. The occupancy factor of one CH_2Cl_2 molecule has been refined. The hydrogen atoms were treated as in **1**. The final R value of 0.057 was computed for 550 parameters and 4260 reflections.

In the case of **3** final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms including one molecule of CH_2Cl_2 per asymmetric unit. The hydrogen atoms were treated as in **1**. The final R value of 0.045 was computed for 506 parameters and 3589 reflections.

In all cases upon convergence the last difference Fourier maps showed no significant features. The structure determinations are summarized in Table 1. Tables 2–4 show positional parameters for [$PtCl_2$(*cis*-dppen)] (**1**), [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**), and [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**), respectively.

2.5. *Syntheses of Ni(II), Pd(II), Pt(II) and Pt(IV) 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.

2.5.1. *[$PtCl_2$(cis-dppen)] (1), [Pt(cis-dppen)(bipy)]$(PF_6)_2$ (2), and [Pt(cis-dppen)(phen)]$(BF_4)_2$ (3)*

1, **2** and **3** were prepared as described earlier [1]. The second crystal modification of **1** suitable for an X-ray structure analysis was obtained from a DMF solution of **1**. Suitable single crystals with the compositions [Pt(*cis*-dppen)(bipy)]$(PF_6)_2 \cdot 1.8CH_2Cl_2$ or [Pt(*cis*-dppen)(phen)]$(BF_4)_2 \cdot CH_2Cl_2$ were obtained from CH_2Cl_2 solutions of **2** or **3**, respectively.

2.5.2. *[$Pt_2(\mu_2\text{-}S)_2$(cis-dppen)$_2$] (4)*

To a solution of [$PtCl_2$(*cis*-dppen)] (**1**) (0.2 mmol, 0.132 g) in 6 ml EtOH/DMF (vol./vol. = 1:1) was added anhydrous Na_2S (0.2 mmol, 0.016 g). The reaction mixture was stirred for 3 h at 50°C and an orange solution was obtained. The solvent was completely evaporated and the residue washed with H_2O and EtOH, filtered off and dried in vacuo. An orange powder was recrystallized from CH_2Cl_2: yield 0.032 g (26%); m.p. > 300°C dec; FAB mass spectrum: *m/z* 1247.1 [$Pt_2(\mu_2\text{-}S)_2$(*cis*-dppen)$_2$]$^+$, 1215.0 [$Pt_2(\mu_2\text{-}S)$(*cis*-dppen)$_2$]$^+$. *Anal.* Calc. for $C_{52}H_{44}P_4Pt_2S_2$: C, 50.1; H, 3.6; S, 5.1. Found: C, 49.9; H, 3.4; S, 5.2%.

2.5.3. *[$Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)$(cis-dppen)$_2$]$(BF_4)_2$ (5)*

To a solution of [$PtCl_2$(*cis*-dppen)] (**1**) (0.2 mmol, 0.132 g) in 6 ml CH_2Cl_2/DMF (vol./vol. = 6:1) was added $AgBF_4$ (0.4 mmol, 0.078 g). Then the reaction mixture was stirred for 48 h at 45°C. The solvent was completely evaporated, CH_2Cl_2 was added and AgCl was filtered off. S_2CPCy_3 (0.2 mmol, 0.071 g) was added to the colorless solution at −18°C. The solution immediately turned red. It was slowly warmed to room temperature and stirred for 12 h. The solvent was completely evaporated and EtOH was added. The red solution was stirred for 2 h and a yellow precipitate formed. The yellow residue was filtered off, washed with EtOH and dried in vacuo. A yellow powder was recrystallized from EtOH: yield 0.047 g (27%); m.p. = 227°C; FAB mass spectrum: *m/z* 1658.4 [$Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)$(*cis*-dppen)$_2$]$(BF_4)^+$, 1571.6 [$Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)$(*cis*-dppen)$_2$]$^+$. IR (KBr, cm^{-1}) C=S: 1102, 1060, 998 ν. *Anal.* Calc. for $C_{71}H_{77}B_2F_8P_5Pt_2S_3$: C, 48.9; H, 4.4; S, 5.5. Found: C, 49.0; H, 4.2; S, 5.3%.

2.5.4. *[$Ni_3(\mu_3\text{-}S)_2$(cis-dppen)$_3$]$(PF_6)_2$ (6)*

[$NiCl_2$(*cis*-dppen)] was prepared as described earlier [3,22]. To a red solution of [$NiCl_2$(*cis*-dppen)] (0.2 mmol, 0.105 g) in 6 ml EtOH/DMF (vol./vol. = 1:1) was added anhydrous Na_2S (0.13 mmol, 0.010 g). The solution immediately turned red–brown. It was stirred for 24 h at 45°C. Then the solvent was completely evaporated, EtOH was added, and the red–brown solution was filtered. To this solution, $NaPF_6$ (0.6 mmol, 0.101 g) dissolved in EtOH was added with stirring. A light brown precipitate immediately

Table 1
Structure determination data for [PtCl$_2$(*cis*-dppen)] (**1**), [Pt(*cis*-dppen)(bipy)](PF$_6$)$_2$ (**2**), and [Pt(*cis*-dppen)(phen)](BF$_4$)$_2$ (**3**)

	1	**2**	**3**
Formula	$C_{26}H_{22}Cl_2P_2Pt$	$C_{36}H_{30}F_{12}N_2P_4Pt \cdot 1.8CH_2Cl_2$	$C_{38}H_{30}B_2F_8N_2P_2Pt \cdot CH_2Cl_2$
Formula weight	662.39	1190.46	1030.23
Color; habit	colorless; prismatic	colorless; prismatic	colorless; prismatic
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1$
a (Å)	8.312(1)	12.649(3)	8.779(2)
b (Å)	14.578(2)	26.114(5)	17.297(3)
c (Å)	19.868(4)	14.665(3)	13.059(3)
β (°)	91.27(1)	111.62(3)	93.79(3)
V (Å)	2406.9	4503.3	1978.7
T (K)	173	193	193
Z	4	4	2
Crystal dimensions (mm)	0.6 × 0.5 × 0.2	0.5 × 0.4 × 0.25	0.5 × 0.4 × 0.2
D_{calc} (Mg m^{-3})	1.828	1.756	1.730
Radiation, λ (Å)	Mo Kα, 0.71073		
μ (mm^{-1})	6.208	3.455	3.830
$F(000)$	640	2326	1008
Diffractometer	Siemens P4		
Monochromator	highly oriented graphite crystal		
Scan type	ω	ω	ω
2θ range (°)	4.1–55.0	5.6–51.3	4.0–55.0
Index ranges	$-1 \leq h \leq 10$	$-1 \leq h \leq 15$	$-1 \leq h \leq 8$
	$-1 \leq k \leq 17$	$-1 \leq k \leq 30$	$-1 \leq k \leq 22$
	$-25 \leq l \leq 25$	$-17 \leq l \leq 17$	$-16 \leq l \leq 16$
No. reflections collected	7119	9245	5015
No. independent reflections	5501	7760	4169
No. observed ($I > 3\sigma(I)$) reflections	3862	4260	3589
No. parameters refined	280	550	506
Final R indices (observed data)			
R	0.028	0.057	0.045
R_w	0.028	0.057	0.045
	$w^{-1} = \sigma^2(F^2) + (0.022P)^2$	$w^{-1} = \sigma^2(F^2) + (0.0894P)^2 + 1.67P$	$w^{-1} = \sigma^2(F^2) + (0.056P)^2 + 9.96P$
GOF	1.04	1.08	1.05
Largest and mean Δ/σ	−0.001, 0.0005	0.017, 0.001	0.050, 0.004
Largest difference peak (e Å^{-3})	0.54	1.58	1.76
R_{int}	0.019	0.038	0.047
Transmission	0.614–0.919	0.750–0.901	0.780–0.930

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for [PtCl$_2$(*cis*-dppen)] (**1**)

	x	y	z	U_{eq} [a]
Pt(1)	2936(1)	1876(1)	1694(1)	18(1)
P(1)	736(1)	1860(1)	2304(1)	18(1)
P(2)	1376(2)	2320(1)	834(1)	20(1)
Cl(1)	5194(1)	1835(1)	992(1)	31(1)
Cl(2)	4569(2)	1509(1)	2647(1)	32(1)
C(1)	−977(6)	2156(3)	1749(2)	23(1)
C(2)	−673(6)	2354(3)	1118(2)	25(1)
C(11)	167(6)	757(3)	2639(2)	21(1)
C(12)	1188(7)	10(4)	2596(2)	28(1)
C(13)	693(7)	−841(4)	2833(3)	39(1)
C(14)	−812(8)	−947(4)	3108(3)	43(2)
C(15)	−1831(8)	−203(4)	3142(3)	43(2)
C(16)	−1350(7)	647(4)	2912(3)	32(1)
C(21)	653(6)	2642(3)	3010(2)	22(1)
C(22)	1051(7)	2344(4)	3661(2)	31(1)
C(23)	985(7)	2952(4)	4196(3)	38(1)
C(24)	535(7)	3853(4)	4089(3)	42(2)
C(25)	164(7)	4162(4)	3436(3)	40(1)
C(26)	218(7)	3566(4)	2908(3)	34(1)
C(31)	1777(6)	3481(4)	549(2)	24(1)
C(32)	1126(7)	4229(4)	899(3)	34(1)
C(33)	1482(8)	5114(4)	706(3)	43(2)
C(34)	2500(8)	5270(4)	181(3)	45(2)
C(35)	3171(8)	4540(4)	−159(3)	44(2)
C(36)	2796(8)	3648(4)	26(3)	36(1)
C(41)	1323(6)	1614(4)	88(2)	26(1)
C(42)	540(7)	1924(4)	−503(2)	37(1)
C(43)	433(8)	1357(5)	−1061(3)	48(2)
C(44)	1102(7)	501(5)	−1034(3)	40(1)
C(45)	1844(7)	178(4)	−461(3)	38(1)
C(46)	1940(6)	734(4)	106(2)	29(1)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i a_j A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for [Pt(*cis*-dppen)(bipy)](PF$_6$)$_2$ (**2**)

	x	y	z	U_{eq} [a]
Pt(1)	1464(1)	1293(1)	2930(1)	34(1)
P(1)	2294(2)	1965(1)	3899(2)	35(1)
P(2)	−44(2)	1815(1)	2334(2)	38(1)
N(1)	2876(7)	796(3)	3316(7)	38(2)
N(2)	705(7)	639(3)	2105(7)	33(2)
C(1)	3939(9)	883(4)	3926(9)	42(3)
C(2)	4829(10)	555(4)	4085(10)	45(3)
C(3)	4562(11)	100(5)	3553(10)	48(3)
C(4)	3481(9)	−8(4)	2926(9)	41(3)
C(5)	2634(9)	343(4)	2817(8)	32(3)
C(6)	1435(10)	249(4)	2166(9)	39(3)
C(7)	1075(12)	−209(5)	1689(11)	64(4)
C(8)	−51(12)	−268(5)	1142(14)	86(6)
C(9)	−822(11)	115(5)	1058(12)	68(5)
C(10)	−405(10)	563(5)	1584(11)	52(4)
C(01)	308(9)	2436(4)	2910(10)	43(3)
C(02)	1339(10)	2503(4)	3581(8)	37(3)
C(11)	3579(9)	2194(4)	3770(10)	39(3)
C(12)	3740(10)	2072(5)	2925(11)	51(4)
C(13)	4650(11)	2286(5)	2740(12)	59(4)
C(14)	5376(12)	2623(5)	3413(12)	60(4)
C(15)	5205(12)	2745(5)	4258(12)	66(4)
C(16)	4304(10)	2530(5)	4437(11)	53(4)
C(21)	2535(11)	1850(4)	5161(10)	47(3)
C(22)	1621(12)	1908(6)	5498(12)	63(4)
C(23)	1764(17)	1780(7)	6460(14)	81(5)
C(24)	2782(19)	1595(7)	7085(12)	83(5)
C(25)	3684(16)	1525(6)	6787(12)	75(5)
C(26)	3580(12)	1657(5)	5836(10)	54(4)
C(31)	−1277(10)	1586(4)	2570(11)	45(3)
C(32)	−2359(11)	1614(5)	1918(11)	58(4)
C(33)	−3262(12)	1427(7)	2126(17)	87(6)
C(34)	−3090(17)	1236(8)	3025(18)	97(7)
C(35)	−2030(17)	1210(6)	3667(15)	84(6)
C(36)	−1086(13)	1370(5)	3478(12)	59(4)
C(41)	−532(9)	1943(4)	1034(9)	41(3)
C(42)	−1288(11)	2344(5)	646(11)	52(3)
C(43)	−1709(10)	2444(5)	−338(10)	51(3)
C(44)	−1406(10)	2135(5)	−961(11)	52(3)
C(45)	−649(10)	1747(5)	−584(10)	46(3)
C(46)	−174(10)	1649(4)	395(10)	42(3)
P(3)	−2832(3)	1401(1)	6350(3)	56(1)
F(1)	−3123(15)	1569(4)	5271(8)	158(7)
F(2)	−3160(10)	1951(3)	6620(7)	103(4)
F(3)	−1587(9)	1593(4)	6669(12)	151(6)
F(4)	−4078(8)	1190(4)	6104(10)	117(4)
F(5)	−2496(8)	852(3)	6081(7)	81(3)
F(6)	−2594(11)	1228(3)	7434(7)	107(4)
P(4)	2966(3)	1124(1)	371(3)	42(1)
F(7)	2046(9)	1199(3)	−684(7)	89(3)
F(8)	3867(8)	1062(4)	1446(7)	88(3)
F(9)	2018(7)	915(3)	728(7)	76(3)
F(10)	3198(8)	561(3)	103(8)	87(3)
F(11)	2706(7)	1699(3)	617(6)	71(2)
F(12)	3900(8)	1331(4)	11(9)	100(4)
C(03)	5667(15)	566(8)	9558(13)	96(6)
Cl(1)	4634(6)	340(3)	8471(5)	129(2)
Cl(2)	6698(5)	940(2)	9356(4)	107(2)
C(04)	1659(26)	184(16)	6765(36)	214(24)
Cl(3)	338(12)	522(8)	6338(15)	330(11)
Cl(4)	1984(13)	342(5)	5301(12)	240(6)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i a_j A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for [Pt(*cis*-dppen)(phen)](BF$_4$)$_2$ (**3**)

	x	y	z	U_{eq} [a]
Pt(1)	1450(1)	0(1)	8070(1)	26(1)
P(1)	1636(5)	594(2)	9601(3)	28(1)
P(2)	−8(5)	1020(2)	7560(3)	28(1)
N(1)	2869(14)	−945(7)	8481(9)	31(3)
N(2)	1377(15)	−622(7)	6672(8)	31(3)
C(1)	3584(23)	−1102(10)	9350(14)	46(5)
C(2)	4674(20)	−1717(9)	9521(13)	34(4)
C(3)	4979(21)	−2171(9)	8704(12)	42(4)
C(4)	4168(17)	−2025(9)	7741(11)	30(3)
C(5)	3144(17)	−1402(8)	7655(10)	29(3)
C(6)	2332(18)	−1233(8)	6710(11)	29(3)
C(7)	2568(20)	−1679(9)	5822(12)	38(4)
C(8)	1676(19)	−1497(9)	4919(12)	35(4)
C(9)	665(19)	−892(10)	4936(11)	41(4)
C(10)	508(18)	−472(9)	5824(11)	35(3)
C(51)	4418(21)	−2466(9)	6848(12)	40(4)
C(52)	3618(25)	−2323(11)	5906(15)	54(5)
C(01)	−22(21)	1703(9)	8587(13)	42(4)
C(02)	696(18)	1528(8)	9496(11)	33(3)
C(11)	629(16)	109(10)	10553(10)	26(4)
C(12)	565(18)	418(9)	11546(11)	35(3)
C(13)	−287(21)	60(17)	12274(11)	46(5)
C(14)	−1024(21)	−635(12)	11998(14)	54(5)
C(15)	−947(21)	−945(11)	11048(13)	51(5)
C(16)	−119(18)	−605(8)	10342(11)	36(4)
C(21)	3597(17)	809(8)	10061(11)	29(3)
C(22)	4219(20)	565(9)	10998(12)	43(4)
C(23)	5760(21)	725(12)	11272(13)	53(5)
C(24)	6603(22)	1114(11)	10572(13)	49(4)
C(25)	5991(19)	1374(10)	9658(12)	39(4)
C(26)	4453(23)	1230(11)	9413(11)	40(4)
C(31)	622(17)	1593(8)	6481(10)	26(3)
C(32)	1824(19)	2102(9)	6710(13)	38(4)
C(33)	2371(22)	2518(11)	5904(15)	51(5)
C(34)	1732(20)	2437(11)	4917(13)	43(4)
C(35)	561(25)	1928(10)	4702(13)	53(5)
C(36)	−4(20)	1498(9)	5511(11)	38(4)
C(41)	−1960(18)	756(8)	7226(11)	32(3)
C(42)	−2950(17)	1321(10)	6880(10)	32(3)
C(43)	−4491(22)	1130(11)	6632(12)	47(4)
C(44)	−5003(21)	424(13)	6695(15)	51(5)
C(45)	−4030(25)	−163(12)	7040(21)	79(7)
C(46)	−2449(17)	3(19)	7333(12)	51(4)
B(1)	972(31)	2718(10)	2010(14)	49(6)
F(1)	1026(18)	3301(7)	2680(10)	81(4)
F(2)	−513(19)	2378(11)	2046(19)	128(7)
F(3)	1919(15)	2131(7)	2200(12)	71(4)
F(4)	1038(37)	2989(11)	1051(11)	181(12)
B(2)	4059(33)	8266(11)	2292(16)	56(6)
F(5)	2788(18)	7986(9)	1848(16)	102(6)
F(6)	4297(19)	8990(8)	1995(11)	93(4)
F(7)	5250(17)	7804(8)	1980(9)	80(4)
F(8)	4113(13)	8177(7)	3364(7)	58(3)
C(03)	4880(22)	−36(26)	4178(20)	96(8)
Cl(1)	3563(8)	658(4)	4087(5)	83(2)
Cl(2)	6815(7)	267(4)	4210(5)	91(2)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i a_j A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

formed. It was filtered off, washed with H_2O, and dried in vacuo. A light brown powder was recrystallized from EtOH: yield 0.030 g (26%); m.p. = 260–264°C; FAB mass spectrum: *m/z* 1592.4 $[Ni_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3](PF_6)^+ \cdot H_2O$, 1574.4 $[Ni_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3](PF_6)^+$, 1429.4 $[Ni_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3]^+$. *Anal.* Calc. for $C_{78}H_{66}F_{12}Ni_3P_8S_2 \cdot H_2O$: C, 53.9; H, 3.8; S, 3.7. Found: C, 53.8; H, 3.6; S, 3.9%.

2.5.5. $[Pd_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3](BF_4)_2$ (**7**)

$[PdCl_2(\textit{cis}\text{-dppen})]$ was prepared as described earlier [1,23]. $[PdCl_2(\textit{cis}\text{-dppen})]$ (0.15 mmol, 0.086 g) was suspended in 5 ml CH_2Cl_2/DMF (vol./vol. = 10:1) and $AgBF_4$ (0.3 mmol, 0.058 g) was added with stirring. The reaction mixture was stirred for 2 h at 45°C and then the formed AgCl was filtered off. The solvent was completely evaporated and the residue dissolved in 5 ml CH_2Cl_2/EtOH. To this solution was added anhydrous Na_2S (0.45 mmol, 0.035 g) with stirring. After 5 min the solution turned dark red and a precipitate formed. The slurry was stirred for 12 h at 45°C. Then the solvent was completely evaporated, the residue dissolved in CH_2Cl_2, and the yellow solution filtered. After addition of n-hexane a yellow powder was recrystallized from CH_2Cl_2/n-hexane: yield 0.038 g (42%); m.p. = 160–162°C; FAB mass spectrum: *m/z* 1792.2 $\mathbf{7}^+ \cdot C_2H_5OH$, 1659.3 $[Pd_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3](BF_4)^+$, 1572.5 $[Pd_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3]^+$. *Anal.* Calc. for $C_{78}H_{66}B_2F_8P_6Pd_3S_2 \cdot C_2H_5OH$: C, 53.6; H, 4.0; S, 3.6. Found: C, 53.5; H, 4.1; S, 3.4%.

2.5.6. $[Pt_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3]Cl_2$ (**8**)

$[PtCl_2(\textit{cis}\text{-dppen})]$ (**1**) (0.1 mmol, 0.066 g) was suspended in 7 ml EtOH/DMF (vol./vol. = 2:5) and $Na_2S \cdot 9H_2O$ (0.2 mmol, 0.048 g) was added. The reaction mixture was stirred for 2 min at room temperature and a light brown solution was obtained. The volume of the solvent was reduced, the solution filtered, and then the solvent completely evaporated. To the light brown residue was added H_2O and the slurry was stirred for 2 h. Then the precipitate was filtered off, washed with H_2O, and dried in vacuo. A light brown powder was recrystallized from EtOH/DMF: yield 0.050 g (78%); m.p. = 215–218°C; FAB mass spectrum: *m/z* 1836.6 $[Pt_3(\mu_3\text{-}S)_2(\textit{cis}\text{-dppen})_3]^+$. *Anal.* Calc. for $C_{78}H_{66}Cl_2P_6Pt_3S_2$: C, 49.1; H, 3.5; S, 3.4. Found: C, 49.0; H, 3.5; S, 3.3%.

2.5.7. $[Ni(CS_2)_4(\textit{cis}\text{-dppen})](BF_4)_2$ (**9**)

To a solution of $[NiCl_2(\textit{cis}\text{-dppen})]$ (0.2 mmol, 0.105 g) in CH_2Cl_2/DMF (vol./vol. = 6:1) was added $AgBF_4$ (0.4 mmol, 0.078 g) with stirring. After several hours a white precipitate and a greenish solution formed and AgCl was filtered off. To this solution S_2CPCy_3 (0.8 mmol, 0.285 g) was added. The solution was stirred for 12 h at room temperature and its color turned light brown. The solution was filtered and the solvent completely evaporated. Then EtOH was added and a yellowish residue was filtered off and dried in vacuo. A yellowish powder was recrystallized from CH_2Cl_2: yield 0.168 g (90%); m.p. = 216–218°C; FAB mass spectrum: *m/z* 933.2 $\mathbf{9}^+$, 901.1 $[Ni(CS_2)_3(CS)(\textit{cis}\text{-dppen})](BF_4)_2^+$. IR (KBr, cm^{-1}) C=S: 1656, 1165, 1057, 998 ν. *Anal.* Calc. for $C_{30}H_{22}B_2F_8NiP_2S_8$: C, 38.6; H, 2.4; S, 27.5. Found: C, 38.8; H, 2.3; S, 27.4%.

2.5.8. $[PtCl_2(\textit{cis}\text{-dppen})_2]Cl_2$ (**10**)

$[Pt(\textit{cis}\text{-dppen})_2]Cl_2$ was prepared as described earlier [1]. Chlorine was bubbled through a solution of $[Pt(\textit{cis}\text{-dppen})_2]Cl_2$ (0.1 mmol, 0.106 g) in 20 ml CH_2Cl_2 for 30 min at room temperature. The solution turned yellow and a precipitate formed. The precipitate was filtered off and dried in vacuo. A yellow powder was recrystallized from DMSO: yield 0.092 g (81%); m.p. = 160°C dec. *Anal.* Calc. for $C_{52}H_{44}Cl_4P_4Pt$: C, 55.3; H, 3.9. Found: C, 55.1; H, 3.8%.

3. Results

Recently, a flexibility of complexes due to crystal packing effects has been revealed [4]. Since in many cases these effects also reflect the flexibility of complexes in solution, they are important for the reactivity of these molecules. The best possibilities to study the conformational variability of complexes by crystallographic methods are the rare examples where more than one crystal modifications have been obtained for the same molecule. In this work the X-ray structure of a second crystal modification of $[PtCl_2(\textit{cis}\text{-dppen})]$ (**1**) is presented. The structure of the corresponding first modification has been given earlier [1]. The latter modification shows a completely planar arrangement of the coordination plane and the ethene bridge due to a π bonding interaction. Though both crystal forms were obtained by quite different methods and solvent molecules are present in the first modification, but not in the second, there are no intermolecular contact approaches below 3.0 Å disturbing the complete coplanarity in the first modification. Furthermore, the occurrence of a mirror plane through **1** in the first modification, which is absent in the second, is interesting but not essential, since also a non-planar arrangement could fulfil this symmetry requirement. A view of the second modification of **1** is given in Fig. 1(a). Table 5 contains selected bond distances and bond angles. The crystal structure of this modification consists of four discrete $[PtCl_2(\textit{cis}\text{-dppen})]$ molecules per unit cell. The disturbance of the coplanarity of the coordination plane and the ethene bridge is revealed in Fig. 1(b). The shortest intermolecular contact between Pt(1b) and the hydrogen atom attached to C(13a) of 2.833 Å produces a slight inclination of a coordination plane away from a second molecule. This contact is the only intermolecular approach below 3.0 Å and therefore the only reason for the observed deviation from coplanarity. P(2) shows the largest deviation of 0.072 Å from a least-squares plane through Pt(1), P(1), P(2), Cl(1), and Cl(2), whereas the P_2C_2 arrangement is completely planar within experimental error. These two planes include an angle of 3.5°. Nevertheless, the remaining π bonding interaction throughout the coordination plane and the ethene bridge produces a shorter

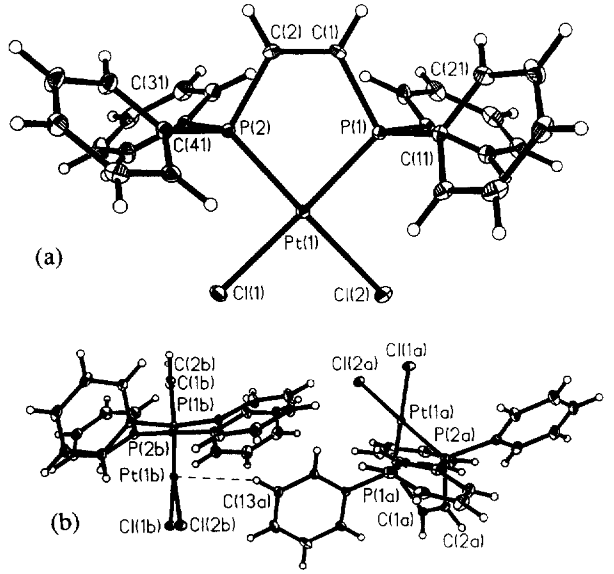


Fig. 1. (a) View of [$PtCl_2$(*cis*-dppen)] (**1**), showing the atomic numbering; (b) packing plot showing the deviations from a coplanar arrangement of the coordination plane and the ethene bridge, and the shortest intermolecular contact approach.

Table 5
Selected bond distances (Å) and bond angles (°) for [$PtCl_2$(*cis*-dppen)] (**1**)

Pt(1)–P(1)	2.2167(12)
Pt(1)–P(2)	2.2189(12)
Pt(1)–Cl(1)	2.3633(12)
Pt(1)–Cl(2)	2.3667(12)
P(1)–C(11)	1.808(5)
P(1)–C(21)	1.810(5)
P(1)–C(1)	1.832(5)
P(2)–C(31)	1.818(5)
P(2)–C(41)	1.804(5)
P(2)–C(2)	1.807(5)
C(1)–C(2)	1.317(7)
P(1)–Pt(1)–P(2)	87.08(5)
P(1)–Pt(1)–Cl(1)	176.37(4)
P(2)–Pt(1)–Cl(1)	90.63(5)
P(1)–Pt(1)–Cl(2)	91.44(5)
P(2)–Pt(1)–Cl(2)	175.78(5)
Cl(1)–Pt(1)–Cl(2)	91.03(5)
C(11)–P(1)–C(21)	105.1(2)
C(11)–P(1)–C(1)	102.9(2)
C(21)–P(1)–C(1)	106.0(2)
C(11)–P(1)–Pt(1)	115.9(2)
C(21)–P(1)–Pt(1)	117.6(2)
C(1)–P(1)–Pt(1)	107.9(2)
C(41)–P(2)–C(2)	105.4(2)
C(41)–P(2)–C(31)	106.1(2)
C(2)–P(2)–C(31)	104.6(2)
C(41)–P(2)–Pt(1)	118.0(2)
C(2)–P(2)–Pt(1)	107.8(2)
C(31)–P(2)–Pt(1)	113.8(2)
C(2)–C(1)–P(1)	117.5(4)
C(1)–C(2)–P(2)	119.6(4)

than ideal aliphatic double bond length of 1.317(7) Å versus 1.337(6) Å [24]. The same effect has already been observed in the first modification of **1** [1]. Owing to the packing distortion shown in Fig. 1(b), all corresponding P–Pt–Cl angles significantly differ (see Table 5), where these angles are equal as a consequence of crystallographic constraints in the first modification. However, all other analogous bond lengths and bond angles of the coordination planes are not significantly different in the two modifications. The small deviations between both modifications are in agreement with the recently given quantification of crystal packing effects [4]. The change from complete to partial coplanarities in these modifications retains the presence of π bonding interactions [1,3,25].

Although several X-ray structures of Pt(II) complexes containing 2,2′-bipyridine or 1,10-phenanthroline are known [26], the two X-ray structures of [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**) and [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**) are the first examples of square-planar structures together with phosphines. A view of the cation of **2** is given in Fig. 2(a). Table 6 contains selected bond distances and bond angles. The crystal structure of **2** consists of a discrete [Pt(*cis*-dppen)(bipy)]$^{2+}$ cation, two $(PF_6)^-$ anions, and 1.8 molecules of CH_2Cl_2 per asymmetric unit. The square-planar coordination of the Pt atom is distorted. Fig. 2(b) reveals that the deformation in **2** resembles the twist configuration of *trans*-dipyridine complexes [26e]. The platinum, the phosphorus atoms and the ethene bridge are nearly coplanar; the deviations from a least-squares plane through the following atoms are as follows: Pt(1), −0.026; P(1), 0.031;

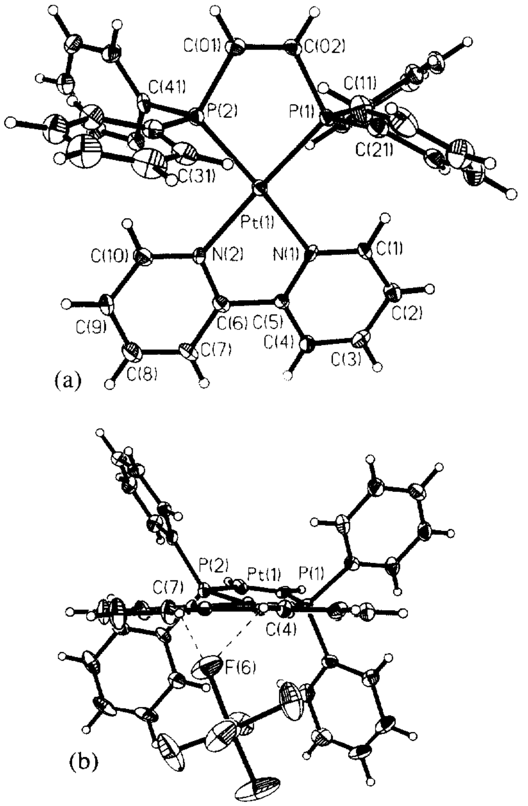


Fig. 2. (a) View of [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**), showing the atomic numbering; (b) packing plot showing the distorted square-planar coordination of the Pt atom, and the shortest intermolecular contact approaches.

Table 6
Selected bond distances (Å) and bond angles (°) for [Pt(*cis*-dppen)(bipy)]$(PF_6)_2$ (**2**)

Pt(1)–N(1)	2.111(8)
Pt(1)–N(2)	2.109(8)
Pt(1)–P(1)	2.258(3)
Pt(1)–P(2)	2.243(3)
P(1)–C(11)	1.807(12)
P(1)–C(21)	1.786(13)
P(1)–C(02)	1.800(11)
P(2)–C(31)	1.819(11)
P(2)–C(41)	1.806(13)
P(2)–C(01)	1.805(12)
N(1)–C(1)	1.331(14)
N(1)–C(5)	1.367(14)
N(2)–C(10)	1.342(14)
N(2)–C(6)	1.354(14)
C(1)–C(2)	1.37(2)
C(2)–C(3)	1.39(2)
C(3)–C(4)	1.37(2)
C(4)–C(5)	1.37(2)
C(5)–C(6)	1.48(2)
C(6)–C(7)	1.38(2)
C(7)–C(8)	1.36(2)
C(8)–C(9)	1.37(2)
C(9)–C(10)	1.39(2)
C(01)–C(02)	1.32(2)
N(2)–Pt(1)–N(1)	79.4(3)
N(2)–Pt(1)–P(2)	97.3(2)
N(1)–Pt(1)–P(2)	173.2(3)
N(2)–Pt(1)–P(1)	176.4(3)
N(1)–Pt(1)–P(1)	99.0(3)
P(2)–Pt(1)–P(1)	84.54(11)
C(21)–P(1)–C(02)	104.0(6)
C(21)–P(1)–C(11)	110.3(6)
C(02)–P(1)–C(11)	105.0(5)
C(21)–P(1)–Pt(1)	112.6(4)
C(02)–P(1)–Pt(1)	109.3(4)
C(11)–P(1)–Pt(1)	114.8(4)
C(01)–P(2)–C(41)	104.9(6)
C(01)–P(2)–C(31)	106.7(5)
C(41)–P(2)–C(31)	106.2(6)
C(01)–P(2)–Pt(1)	109.6(4)
C(41)–P(2)–Pt(1)	115.7(4)
C(31)–P(2)–Pt(1)	113.1(4)
C(1)–N(1)–C(5)	118.7(9)
C(1)–N(1)–Pt(1)	128.4(8)
C(5)–N(1)–Pt(1)	112.9(7)
C(10)–N(2)–C(6)	118.1(9)
C(10)–N(2)–Pt(1)	127.2(7)
C(6)–N(2)–Pt(1)	114.5(7)
N(1)–C(1)–C(2)	124.9(10)
C(1)–C(2)–C(3)	115.2(11)
C(4)–C(3)–C(2)	121.9(11)
C(3)–C(4)–C(5)	119.0(11)
N(1)–C(5)–C(4)	120.3(10)
N(1)–C(5)–C(6)	117.4(9)
C(4)–C(5)–C(6)	122.3(10)
N(2)–C(6)–C(7)	122.0(11)
N(2)–C(6)–C(5)	115.5(9)
C(7)–C(6)–C(5)	122.5(11)
C(8)–C(7)–C(6)	118.4(13)
C(7)–C(8)–C(9)	121.8(13)
C(8)–C(9)–C(10)	116.8(12)
N(2)–C(10)–C(9)	122.8(11)
C(02)–C(01)–P(2)	118.2(8)
C(01)–C(02)–P(1)	118.2(8)

P(2), 0.023; C(01), −0.004; C(02), −0.024 Å. This plane includes an angle of 11.2° with the least-squares plane through bipy. However, the two six-membered rings of bipy are not completely coplanar including an angle of 5.2° as a consequence of the different attractive contact approaches between F(6) and the hydrogen atom attached to C(7) of 2.419 Å and F(6) and the hydrogen atom attached to C(4) of 2.553 Å. This can also be seen in Fig. 2(b). In solution the two phosphorus atoms of *cis*-dppen in **2** are equivalent [1]. This strongly suggests that, as in the second crystal modification of **1**, the deviations from an ideal square-planar coordination in **2** are produced by a packing effect of $(PF_6)^-$. Nevertheless, also in this case the remaining π bonding interaction throughout the nearly coplanar five-membered ring containing *cis*-dppen produces a slightly reduced aliphatic double bond length of 1.32(2) Å. Distances and angles in the bipy ligand are normal [26a]. Owing to the strong *trans* influence of phosphorus the mean value of the Pt–N distances of 2.110(6) Å in **6** is slightly longer than the corresponding values in $[PtI_2(bipy)]$ (2.029(7) Å), $[Pt(CN)_2(bipy)]$ (2.00(1) Å), $[Pt(bipy)_2]^{2+}$ (2.025(4), 2.028(5) Å), and $[PtCl_2(bipy)]$ (2.001(6) Å) [26a,d,e,g]. The N–Pt–N angle of 79.4(3)° in **2** is in the usual range. Also the mean Pt–P bond length of 2.251(2) Å is typical for a Pt–P bond *trans* to N-containing heterocycles [27]. The P–Pt–P chelate angle is strongly influenced by the coordination of bipy, since its value of 87.08(5)° in **1** is reduced to 84.54(11)° in **2**.

A view of the cation of **3** is given in Fig. 3(a). Table 7 contains selected bond distances and bond angles. The crystal structure of **3** consists of a discrete $[Pt(\textit{cis}\text{-dppen})(phen)]^{2+}$ cation, two $(BF_4)^-$ anions, and one molecule of CH_2Cl_2 per asymmetric unit. Fig. 3(b) reveals that the deformation of **3** corresponds to the bow conformation of *trans*-dipyridine complexes, where **3** is the first example of complexes with phen showing this deformation [26e]. It is well known that square-planar d^8 complexes of bipy or phen exhibit intermolecular attractive interactions between molecules stacked within a chain comparable with the packing in high-temperature superconductors [26a,d,f,g]. Although the Pt···Pt distance of 8.779(1) Å in **3** is too long for any significant metal–metal interaction (< 3.5 Å), the nearly coplanar alignment of the phen groups in **3** (Fig. 3(b)) is indicative of a retained attractive interaction between the phen ligands. Owing to the steric bulk of *cis*-dppen this leads to the shortest intermolecular contact of 3.160 Å between Pt(1b) and the proton attached to C(44a) and a bowing of the molecule. This bowing produces a successive inclination of the least-squares planes through Pt(1), P(1), P(2), C(01), C(02), through Pt(1), P(1), P(2), N(1), N(2), and through phen of 3.5 and 8.4°, respectively. In contrast to that in **1** and **2**, the double bond length of 1.34(2) Å in **3** is normal, which could be the consequence of an enhanced back donation of π electron density to phen in agreement with its attractive alignment. However, no significant change in the usual distances and angles of the phen ligand could be observed [26b]. The mean value of the Pt–N distances of 2.109(8) Å

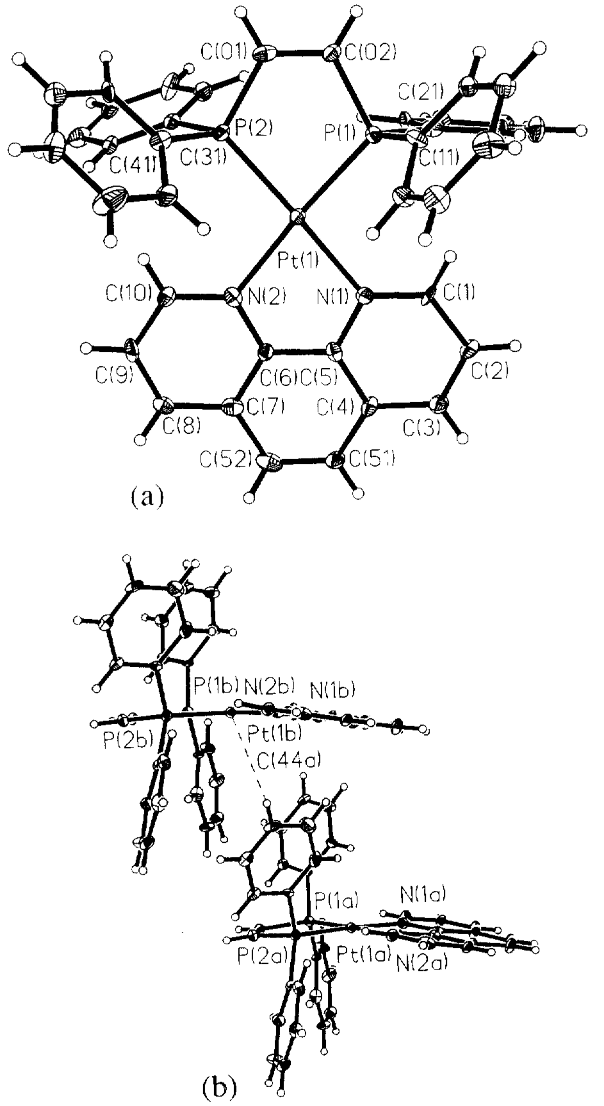


Fig. 3. (a) View of [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**), showing the atomic numbering; (b) packing plot showing the bow deformation, and the shortest intermolecular contact approach.

in **3** is similar in [$(C_6F_5)_2$Pt(μ-PPh_2)$_2$Pt(phen)] (2.131(4) Å), but longer than in [Pt$(phen)_2$]$^{2+}$ (2.033(6) Å) [26b,f], again reflecting the strong *trans* influence of phosphorus. The N–Pt–N angle of 79.0(5)° is comparable with the same parameter in **2** and also in the usual range. The mean Pt–P bond length of 2.250(3) Å is nearly identical with the same value in **2** and again typical for a Pt–P bond *trans* to N-containing heterocycles [27]. As in **2** the P–Pt–P chelate angle of 84.88(14)° in **3** is reduced owing to the coordination of the aromatic heterocycle.

In the syntheses of the complexes **4–9** (see Scheme 1) the reactions of [MCl_2(*cis*-dppen)] (M = Ni, Pd, Pt) with anhydrous Na_2S, $Na_2S \cdot 9H_2O$ or S_2CPCy_3 has been investigated. The use of anhydrous Na_2S leads to **4**, **6**, and **7**, whereas $Na_2S \cdot 9H_2O$ produces **8**. It is well known that different sulfide donating reactants are responsible for variations in reaction pathways [9,12c,15a,b,28]. The main reason is the occurrence of different species such as S^{2-}, SH^{-}, H_2S, and S_2^{2-}

Table 7
Selected bond distances (Å) and bond angles (°) for [Pt(*cis*-dppen)(phen)]$(BF_4)_2$ (**3**)

Pt(1)–N(1)	2.103(12)
Pt(1)–N(2)	2.115(11)
Pt(1)–P(1)	2.245(3)
Pt(1)–P(2)	2.254(4)
P(1)–C(11)	1.783(14)
P(1)–C(21)	1.82(2)
P(1)–C(02)	1.81(2)
P(2)–C(31)	1.838(13)
P(2)–C(41)	1.80(2)
P(2)–C(01)	1.79(2)
N(1)–C(1)	1.29(2)
N(1)–C(5)	1.37(2)
N(2)–C(10)	1.33(2)
N(2)–C(6)	1.35(2)
C(1)–C(2)	1.44(2)
C(2)–C(3)	1.37(2)
C(3)–C(4)	1.43(2)
C(4)–C(5)	1.40(2)
C(4)–C(51)	1.42(2)
C(5)–C(6)	1.41(2)
C(6)–C(7)	1.42(2)
C(7)–C(8)	1.41(2)
C(7)–C(52)	1.45(3)
C(8)–C(9)	1.37(2)
C(9)–C(10)	1.38(2)
C(51)–C(52)	1.40(3)
C(01)–C(02)	1.34(2)
N(1)–Pt(1)–N(2)	79.0(5)
N(1)–Pt(1)–P(1)	97.0(3)
N(2)–Pt(1)–P(1)	175.9(4)
N(1)–Pt(1)–P(2)	177.2(3)
N(2)–Pt(1)–P(2)	99.2(4)
P(1)–Pt(1)–P(2)	84.88(14)
C(11)–P(1)–C(02)	103.2(7)
C(11)–P(1)–C(21)	111.5(7)
C(02)–P(1)–C(21)	105.0(7)
C(11)–P(1)–Pt(1)	113.3(5)
C(02)–P(1)–Pt(1)	109.5(5)
C(21)–P(1)–Pt(1)	113.4(5)
C(01)–P(2)–C(41)	107.2(8)
C(01)–P(2)–C(31)	103.6(7)
C(41)–P(2)–C(31)	106.3(7)
C(01)–P(2)–Pt(1)	109.1(6)
C(41)–P(2)–Pt(1)	112.7(5)
C(31)–P(2)–Pt(1)	117.0(5)
C(1)–N(1)–C(5)	118.1(14)
C(1)–N(1)–Pt(1)	129.4(11)
C(5)–N(1)–Pt(1)	112.3(9)
C(10)–N(2)–C(6)	120.3(12)
C(10)–N(2)–Pt(1)	127.1(11)
C(6)–N(2)–Pt(1)	112.6(9)
N(1)–C(1)–C(2)	125(2)
C(3)–C(2)–C(1)	118(2)
C(2)–C(3)–C(4)	118(2)
C(5)–C(4)–C(51)	118.6(13)
C(5)–C(4)–C(3)	119.2(13)
C(51)–C(4)–C(3)	122.1(13)
N(1)–C(5)–C(4)	121.6(13)
N(1)–C(5)–C(6)	117.6(14)
C(4)–C(5)–C(6)	120.8(13)
N(2)–C(6)–C(5)	118.0(13)

(*continued*)

Table 7 (*continued*)

N(2)–C(6)–C(7)	121.3(13)
C(5)–C(6)–C(7)	120.6(14)
C(8)–C(7)–C(6)	117.4(14)
C(8)–C(7)–C(52)	124(2)
C(6)–C(7)–C(52)	119(2)
C(9)–C(8)–C(7)	118.8(13)
C(8)–C(9)–C(10)	120.9(14)
N(2)–C(10)–C(9)	120.9(14)
C(52)–C(51)–C(4)	122(2)
C(51)–C(52)–C(7)	119(2)
C(02)–C(01)–P(2)	119.2(12)
C(01)–C(02)–P(1)	117.0(12)

[29]. In the case of S_2CPCy_3 and **5** one phosphoniodithioformate ligand acts as a bridging four-electron donor, where this coordination behavior has already been observed [14a]. However, as far as we know **5** is the first example containing a sulfide bridge produced from S_2CPCy_3 in situ. The first step of a splitting reaction in phosphoniodithioformate complexes leading to CS_2 and the corresponding phosphines is known [14c,e,16c], where subsequent coordination of CS_2 forms complexes such as **9**. For an explanation of the sulfide bridge in **5** a further splitting of CS_2 is necessary. It seems likely that as a consequence of a nucleophilic attack on π-bonded CS_2 [18g], CS_2 acts as a source of CS. Similar to the production of S_2 units fom CS_2 [18a], CS could form the required sulfide ions.

The ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR parameters of compounds **4**–**10** are summarized in Table 8. [$Pt_2(\mu_2\text{-}S)_2$(*cis*-dppen)$_2$] (**4**) is the first example of a Pt(II) dimer with a Pt_2S_2 ring and a chelating diphosphine [8,12a,b]. The ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR data of **4** are in agreement with structure A in Scheme 1. The presence of three isotopomers in this kind of dimer and hence the occurrence of three subspectra have been explained [30]. The spectra of **4**, **5**, and **8** have been successfully simulated using the program INSIM. δ(Pt) of −4336 in **4** is similar to the same parameter in thiolato-bridged dimers [13a]. ^2J(Pt,Pt) of 86 Hz is small compared with the value of 476 Hz in $[Pt_3S_2(PMe_2Ph)_6]^{2+}$, but it is known that in general J(Pt,Pt) coupling constants show no correlation with Pt–Pt distance or even with the presence or absence of a metal–metal bond [17c]. Furthermore, in dimeric platinum complexes where the Pt–Pt distance exceeds 3.0 Å, i.e. where no direct Pt–Pt bonding is invoked, J(Pt,Pt) values below 100 Hz are not unusual [31]. δ(P) of 49.1 is shifted downfield owing to the typical five-membered ring contribution of chelating *cis*-dppen [32]. The ^1J(Pt,P) and ^3J(Pt,P) parameters of **4** are in the usual range for sulfur-bridged di- and trinuclear Pt(II) complexes [12a,13a,17c].

[$Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)$(*cis*-dppen)$_2$]$(BF_4)_2$ (**5**) is the first example of a compound where the bridging sulfide has been generated from a phophoniodithioformate in situ. The multinuclear NMR data of **5** are consistent with structure B in Scheme 1. The δ(Pt) and ^2J(Pt,Pt) values of −4367 and 97 Hz in **5** are comparable with **4**. Structure B in Scheme 1 clearly reveals the three different phosphorus nuclei in **5**. By comparison with **4** the signal at 48.7 with ^1J(Pt,P) = 2909 Hz is attributed to the phosphorus atoms *trans* to the sulfide bridge. The signal at 50.1 with ^1J(Pt,P) = 3257 Hz corresponds to the phosphine groups *trans* to S_2CPCy_3, indicating that S_2CPCy_3 exerts a slightly lower *trans* influence than sulfide. The phosphoniodithioformate shows a ^{31}P{^{1}H} resonance at 38.9 with ^3J(Pt,P) = 45 Hz, where the latter value is smaller than the corresponding parameters of 79 and 75 Hz in [$Pt(C_6X_5)_2(S_2CPCy_3)(CO)$] (X = F, Cl) [14c]. The ^{13}C{^{1}H} NMR spectrum of **5** in CH_2Cl_2 shows the cyclohexyl carbon atoms at 26.0–34.0 and all other carbon atoms at 130.7–134.6, where no further assignment is possible. The ^{1}H NMR spectrum in CH_2Cl_2-d^2 reveals the cyclohexyl protons at 0.8–2.1 and the aromatic protons including the protons of the ethene bridges at 6.7–7.9 in the expected intensity ratio. The IR bands at 1102, 1060, and 998 cm^{-1} are characteristic for bidentate S_2CPCy_3 [14c].

Table 8
^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR data for **4**–**10** [a]

Compound	δ(Pt)	^2J(Pt,Pt)	δ(P)	^1J(Pt,P)	^3J(Pt,P)
4	−4336	86	49.1	2965	50
5	−4367ddd	97	50.1	3257	
			48.7	2909	
			38.9		45
6			62.1		
7			60.7		
8	−4556 [b]	67	48.5	2706	57
9			3.6d [c]		
			0.45d [c]		
10			58.5	2264	

[a] J values in Hz. d = doublet, ddd = doublet of doublets of doublets. Spectra were run at 298 K. The following solvents were used: CH_2Cl_2 (**4**–**7**, **9**), EtOH/DMF (vol./vol. = 1:4) (**8**), DMSO (**10**).
[b] ^{195}Pt{^{1}H} spectrum in DMF.
[c] ^2J(P,P) + ^3J(P,P) = 18.

[$M_3(\mu_3\text{-}S)_2$(*cis*-dppen)$_3$]X_2 (M = Ni, $X^- = PF_6^-$ (**6**); M = Pd, $X^- = BF_4^-$ (**7**); M = Pt, $X^- = Cl^-$ (**8**)) are novel trinclear complexes of structure C in Scheme 1. The analogous compounds containing dppe are known [17a,b]. The single ^{31}P{^{1}H} NMR resonance of **6** at 62.1 is in agreement with structure C and shows the typical downfield five-membered ring contribution [32]. The same is true for **7** with its single ^{31}P{^{1}H} NMR signal at 60.7. In the case of **8** the ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR parameters are also consistent with structure C. The δ(Pt) and ^2J(Pt,Pt) values of −4556 and 67 Hz are comparable with **4** and **5**. δ(P) of 48.5 shows the five-membered ring effect. ^1J(Pt,P) of 2706 Hz is smaller than the corresponding values in **4** and **5**, suggesting that a triply bridging sulfide exerts a stronger *trans* influence than a double bridging sulfide. However, data in the literature for related compounds containing triply bridging sulfides show that $^{1}J(Pt,P)$ values strongly depend on the actual geometries of these complexes leading to a $^{1}J(Pt,P)$ range of 2700–3200 Hz [12b]. Since the replacement of a double bridging sulfide by a triply bridging sulfide is always accompanied by a drastic structural change, it is difficult to predict the relative positions of double or triply bridging sulfides in the *trans* influence series. The $^{3}J(Pt,P)$ value of 57 Hz in **8** is in line with previous results [17c].

Although numerous attempts including metathesis reactions with BPh_4^- have been made to crystallize compounds **4–8** and some crystalline products have been obtained, no crystals suitable for X-ray diffraction studies formed. However, a preliminary X-ray structure ($R = 0.057$) of the closely related compound $[Ag_2Pd_4(\mu_3\text{-}S)_4(\textit{cis}\text{-dppen})_4](BF_4)_2$ (**11**) containing two silver-bridged $[Pd_2S_2(\textit{cis}\text{-dppen})_2]$ subunits corresponding to structure A in Scheme 1 clearly confirms the structure types present in the complexes **4–8** [33]. Furthermore, the most remarkable structural feature in **11** is an opening of nearly 10° of the S–M–S angles compared with similar complexes. Since this effect is neither present in $[Ag_2Pt_4(\mu_3\text{-}S)_4(PPh_3)_8](BF_4)_2$ [34] containing the same structure type as **11**, nor in $[Pt_3(\mu_3\text{-}S)_2(dppe)_3]^{2+}$ [17a] with a chelating diphosphine and is independent of the kind of d^8 metal, Pd(II) or Pt(II), it is a consequence of the presence of *cis*-dppen in **11**. Thus, it seems likely that some of the features in the compounds **4**, **5** and **8** such as low $J(Pt,Pt)$ values or relative *trans* influences of double versus triply bridging sulfides, stem from a special impact of *cis*-dppen on the actual geometries of these complexes.

$[Ni(CS_2)_4(\textit{cis}\text{-dppen})](BF_4)_2$ (**9**) of structure D in Scheme 1 is a rare example of a S-bonded CS_2 complex [18a,b,c,g]. The two $^{31}P\{^1H\}$ NMR resonances at 0.45 and 3.6 are consistent with structure D, where a distortion of the octahedral coordination leads to the nonequivalence of the phosphorus atoms of *cis*-dppen and to the loss of the downfield five-membered ring contribution. This effect has also been observed in $[Ni(\textit{cis}\text{-dppen})(bipy)_2](BF_4)_2$ [3]. The $^{2}J(P,P)_{cis} + {}^{3}J(P,P)_{cis}$ value of 18 Hz in **9** is in the typical range of comparable Ni(II) complexes [35]. The $^{13}C\{^1H\}$ NMR spectrum in CH_2Cl_2 shows the carbon atoms of the CS_2 groups at 145.7 and all other carbon atoms in the region 129.9–132.8, where the resonance of S-bonded CS_2 is shifted towards higher field compared with π-bonded CS_2 [18c]. The IR band at 1656 cm^{-1} is characteristic for S-bonded CS_2 [18g].

Similar to the recently described production of $[Pt_2Cl_8(dppa)_2]$ [2], the novel Pt(IV) compound $[PtCl_2(\textit{cis}\text{-dppen})_2]Cl_2$ (**10**) can be obtained by chlorine oxidation from the corresponding Pt(II) complex. The $^{31}P\{^1H\}$ NMR parameters of **10** are in agreement with structure (e) in Scheme 1. $\delta(P)$ of 58.5 shows the usual downfield five-membered ring contribution. Also in this case the easy production of **10** is certainly a consequence of the fact that **10** is a neutral complex, since there is a general decrease in stability as Pt(IV) becomes more electron poor [19c].

4. Discussion

In the X-ray structures of **1** and **3** the molecular geometries are influenced by intermolecular C–H···Pt contact approaches of 2.833 and 3.160 Å, respectively. Only recently, a range of 2.65–3.5 Å has been found for this kind of interaction [36]. In this publication it is stated that the nature of the C–H···M(d^8) interaction remains unclear until the structural anomalies can be explained. Therefore no attempt seems possible, to energetically evaluate this kind of interaction. However, in the C–H···M(d^8) systems and also in **1** and **3** the structural evidence does not point to the presence of a hydrogen-bonded system. Since also the square-planar ML_4 arrays are retained, the metals have not rehybridized in a way that would allow them to accept a pair of electrons from the CH bond in a typical agostic bond. Instead of these two possibilities, in **1** and **3** the molecular geometries are altered in such a way as to avoid too close intermolecular C–H···Pt contacts. In **3** this leads to a tilting of the phen ring with respect to the coordination plane by 8.4° (Fig. 3(b)). Similar to this, the pyridine ring in *trans*-$[PtCl_2(benzoquinoline)(PEt_3)]$ is tilted by 10.5° in just this way [37]. It seems likely that the nature of these C–H···M(d^8) interactions is mainly repulsive.

Although the reduction of the aliphatic double bond lengths to 1.317(7) and 1.32(2) Å in **1** and **2** below the ideal value of 1.337(6) Å is not significant, this effect has now been observed in numerous comparable cases [1–3,25]. Together with the obvious complete or partial coplanarities in these molecules, it is indicative of π bonding interactions throughout the coplanar atoms. In this respect unsaturated diphosphines such as *cis*-dppen have different properties when compared with analogous saturated ligands such as dppe. In the case of sulfide-bridged species the presence of chelating terminal ligands destabilizes the orbitals of the metallic fragment that can interact with sulfur p orbitals and thus decreases the tendency to folding [8]. However, in contrast to dppe, *cis*-dppen is capable of stabilizing metallic fragments by π bonding. Thus the actual geometries of *cis*-dppen containing sulfide-bridged complexes could deviate from the analogous compounds with dppe. A possible consequence of this difference is the unique occurrence of $[Pt_2(\mu_2\text{-}S)_2(\textit{cis}\text{-dppen})_2]$ (**4**) and $[Pt_2(\mu_2\text{-}S)(\mu_2\text{-}S_2CPCy_3)(\textit{cis}\text{-dppen})_2](BF_4)_2$ (**5**). Further work on this is in progress.

5. Supplementary material

Tables of bond lengths and bond angles, thermal parameters, H atom coordinates (15 pages) and structure factors (38 pages) are available from the author on request.

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