## Preparation and nuclear magnetic resonance characterization of N-bonded complexes of platinum(II) with phosphorus-nitrogen rings containing three-coordinate chalcogens: X-ray structure of [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Et<sub>2</sub>)

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The reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Ph<sub>2</sub> with [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> in chloroform at 60°C produces the 1:1 adduct *trans*-PtCl<sub>2</sub>(PEt<sub>3</sub>)(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Ph<sub>2</sub>) in which the platinum is attached to a nitrogen atom on the basis of <sup>31</sup>P nmr spectroscopy. By contrast, the corresponding reactions of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub> (R = Me, Et, Ph) produce the 2:1 adducts [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub>) (7*a*, R = Me; 7*b*, R = Et; 7*c*, R = Ph) which have been characterized by <sup>1</sup>H, <sup>31</sup>P and <sup>77</sup>Se nmr spectroscopy and, in the case of 7*b*, by X-ray crystallography. Crystals of 7*b* are monoclinic, space group C2/*c*, with *a* = 27.803(7) Å, *b* = 12.378(7) Å, *c* = 15.752(8) Å,  $\beta$  = 115.49(2)°, *V* = 4893(3) Å<sup>3</sup>, and *Z* = 4. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at *R* = 0.037 and *R<sub>w</sub>* = 0.022. The platinum centres in 7*b* are attached to distal nitrogen atoms of the disordered P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub> ring. The reaction of the six-membered ring Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SPh with [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> in dichloromethane at 23°C occurs in a regiospecific manner to give the 1:1 adduct PtCl<sub>2</sub>(PEt<sub>3</sub>)(Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SPh) in which, on the basis of <sup>31</sup>P nmr spectroscopy, the platinum is coordinated to a nitrogen atom between phosphorus and sulfur.

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La réaction du 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Ph<sub>2</sub> avec le [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>, dans le chloroforme à 60°C conduit à un adduit 1:1, le *trans*-PtCl<sub>2</sub>(PEt<sub>3</sub>)(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Ph<sub>2</sub>), dans lequel le platine est attaché à l'atome d'azote d'après la rmn du <sup>31</sup>P. Par opposition, les réactions correspondantes des 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub> (R = Me, Et et Ph) conduisent à des adduits 2:1, les [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub>) (7*a*, R = Me; 7*b*, R = Et; 7*c*, R = Ph), qui ont été caractérisés par rmn du <sup>1</sup>H, du <sup>31</sup>P et du <sup>77</sup>Se et, dans le cas du composé 7*b*, par diffraction des rayons X. Les cristaux du composé 7*b* sont monocliniques, groupe d'espace C2/*c*, avec *a* = 27,803(7), *b* = 12,378(7) et *c* = 15,752(8) Å,  $\beta$  = 115,49(2)°, *V* = 4893(3) Å<sup>3</sup> et *Z* = 4. L'affinement par la méthode des moindres carrés pour les paramètres thermiques anisotropiques pour tous les atomes différents de l'hydrogène convergent à *R* = 0,037 et *R<sub>w</sub>* = 0,022. Les centres de platine du composè 7*b* sont attachés aux atomes d'azote distales du cycle P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub> désordonné. La réaction du cycle à six chainons Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SPh avec le [PtCl<sub>2</sub>(PEt<sub>3</sub>)], dans le dichlorométhane à 23°C, se produit d'une facon régiospécifique pour donner l'adduit 1:1 PtCl<sub>2</sub>(PEt<sub>3</sub>)(Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SPh) dans lequel, d'après la rmn du <sup>31</sup>P, le platine est coordiné à un atome d'azote entre le phosphore et le soufre.

[Traduit par la rédaction]

#### Introduction

The coordination chemistry of unsaturated sulfur-nitrogen and selenium-nitrogen rings has been an active area of investigation recently (1). We have been particularly interested in exploring the range of metal complexes that can be formed by the folded  $P_2N_4E_2$  rings 1 and 2 (2-4). The presence of the NPR<sub>2</sub> units in 1 and 2 provides a brace that serves to maintain the integrity of the ring and yields structural information through <sup>31</sup>P nmr spectroscopy. To date the following bonding modes have been established for 1 and 2:  $\eta^{1}$ -N (2, 4),  $\eta^{2}$ -E,E' (3–6) and  $\eta^{2}$ -E,N- $\mu_{2}\eta^{1}$ -E' (3, 4, 7). The combination of  $\eta^1\mathchar`-N$  and  $\eta^2\mathchar`-E,E',$  i.e.  $\mu^2,\eta^3\mathchar`-E,E',N$  has also been observed for both 1 and 2 (2, 4). The  $P_2N_4E_2$  ring can accommodate three (E = S) (2) or two (E = Se) (4) N-bonded PtCl<sub>2</sub>(PEt<sub>3</sub>) groups. In addition, the organolithium derivatives Li[Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R] form  $\eta^1$ -S bonded complexes with platinum(II) or palladium(II) (8).

The S,S'- and Se,Se'-diorgano derivatives of these eightmembered rings, **3** and **4**, are readily prepared (9, 10). The  $P_2N_4E_2$  ring in **3** and **4** adopts a chair conformation with the two chalcogen atoms disposed on either side of the  $P_2N_4$  plane and the exocyclic substituents on S or Se occupying axial positions (9, 10). These ring systems are potential precursors of hybrid inorganic polymers containing alternating PN and EN (E = S, Se) units. Polymers containing two PN and one SN groups in a repeating unit have been prepared from cyclic precursors (*six*-membered rings) (11, 12).

We report here the formation of platinum(II) complexes of **3** and **4**, which were prepared in order to compare the ligand behaviour of the open rings **3** and **4** with that of the corresponding folded rings **1** and **2** and, in particular, to determine (*a*) the site of coordination, (*b*) the effect of coordination on the structure of the  $P_2N_4E_2$  ring, (*c*) the number of Pt(II) groups that can be attached to the  $P_2N_4E_2$  ring, and (*d*) any differences between the coordinating ability of the sulfur and selenium systems. A platinum(II) complex of the related six-membered ring **5** was also characterized.



#### Experimental

Reagents and general procedures

Manipulations of air-sensitive reagents and products were per-

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formed under an atmosphere of prepurified nitrogen or argon using standard Schlenk or dry box techniques. Solvents (acetonitrile, chloroform, dichloromethane, hexanes, diethyl ether) were dried with the appropriate desiccant and purged with N<sub>2</sub> or argon. The compounds 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub> (R = Me, Et, Ph) (9), Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SPh (13), and [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> (14) were prepared by the literature procedures. The compound 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Ph<sub>2</sub> was obtained in 59% yield from Ph<sub>2</sub>PN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> and three molar equivalents of PhSCl by a modification of the literature method (10) in which acetonitrile was used as a solvent instead of CH<sub>2</sub>Cl<sub>2</sub>. The solubility of the Ph<sub>2</sub>S<sub>2</sub> by-product in acetonitrile facilitates the purification of the product by obviating the need to wash it with n-pentane.

#### Instrumentation

<sup>31</sup>P nmr spectra were obtained on a Bruker AM-400 MHz spectrometer operating at 161.978 MHz. <sup>31</sup>P chemical shifts are reported in ppm relative to external 85% H<sub>3</sub>PO<sub>4</sub>. Proton nmr spectra were recorded on a Bruker ACE-200 MHz spectrometer at 200.1 MHz. <sup>77</sup>Se nmr spectra were recorded at 76.311 MHz on the Bruker AM-400 instrument. The lock signal for the <sup>31</sup>P and <sup>77</sup>Se nmr spectra was provided by sealed D<sub>2</sub>O inserts. <sup>77</sup>Se chemical shifts are referenced to external Ph<sub>2</sub>Se<sub>2</sub> [δ<sup>77</sup>Se + 461 ppm relative to SeMe<sub>2</sub> (0 ppm)]. Elemental analyses were performed by the microanalytical service within the Chemistry Department at The University of Calgary.

## Preparation of trans-[ $PtCl_2(PEt_3)(Ph_4P_2N_4S_2Ph_2)$ ], 6

A solution of  $1,5-Ph_4P_2N_4S_2Ph_2$  (0.200 g, 0.31 mmol) in CHCl<sub>3</sub> (20 mL) was added by cannula to a solution of  $[PtCl_2(PEt_3)]_2$ (0.118 g, 0.154 mmol) in CHCl<sub>3</sub> (20 mL). The resulting pale yellow solution was heated at 60°C for 1 h and then stirred for 1 h at 23°C. The solvent was removed under vacuum and the yellow residue was recrystallized from chloroform – diethyl ether at –18°C to give **6** · Et<sub>2</sub>O as pale yellow needles (0.107 g, 0.097 mmol, 31%). Anal. calcd. for C<sub>46</sub>H<sub>55</sub>Cl<sub>2</sub>N<sub>4</sub>OP<sub>3</sub>PtS<sub>2</sub>: C 50.09, H 5.03, N 5.08; found: C 50.83, H 4.44, N 5.71. <sup>1</sup>H nmr (CDCl<sub>3</sub>),  $\delta$ (ppm): 7.22– 8.48 (m, PC<sub>6</sub>H<sub>5</sub> and SC<sub>6</sub>H<sub>5</sub>, 30H), 3.34 (q, O[CH<sub>2</sub>CH<sub>3</sub>]<sub>2</sub>, 4H, <sup>3</sup>J(H—H) = 7.5 Hz, 1.07 (t, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 6H, <sup>3</sup>J(H—H) = 7.5 Hz), 1.51 (dq, PCH<sub>2</sub>CH<sub>3</sub>, 6H, <sup>2</sup>J(P—H) = 12 Hz, <sup>3</sup>J(H—H) = 7.5 Hz), 0.76 (dt, PCH<sub>2</sub>CH<sub>3</sub>, 9H, <sup>2</sup>J(P—H) = 17 Hz, <sup>3</sup>J(H—H) = 7.5 Hz). <sup>31</sup>P nmr (CH<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (ppm): 41.5 (dd, <sup>3</sup>J(P—P) = 5 Hz, <sup>4</sup>J(P—P) = 6 Hz, <sup>2</sup>J(Pt—P) = 30 Hz), 31.3 (d, <sup>4</sup>J(P—P) = 7 Hz), -1.4 (d, <sup>3</sup>J(P—P) = 5 Hz, <sup>1</sup>J(Pt—P) = 3696 Hz).

## Preparation of $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2Me_2)$ , 7a

A cold ( $-78^{\circ}$ C) solution of [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> (0.309 g, 0.402 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added dropwise by cannula to a slurry of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Me<sub>2</sub> (0.247 g, 0.402 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at  $-78^{\circ}$ C. The mixture was allowed to reach room temperature and stirred for 45 min to give a yellow solution. The volume of the solution was reduced under vacuum to ca. 10 mL and the addition of hexanes (5 mL) produced a yellow precipitate of [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> (1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Me<sub>2</sub>) (0.538 g, 0.389 mmol, 97%). Yellow crystals of  $7a \cdot CH_2Cl_2$  were obtained from CH<sub>2</sub>Cl<sub>2</sub> solutions layered with hexanes at 0°C. Anal. calcd. for C<sub>39</sub>H<sub>58</sub>Cl<sub>6</sub>N<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>Se<sub>2</sub>: C 31.92, H 3.98, N 3.82; found: C 32.35, H 4.04, N 4.07. <sup>1</sup>H nmr (CD<sub>2</sub>Cl<sub>2</sub>, 23°C),  $\delta$ (ppm): 7.1–8.4 (m, C<sub>6</sub>H<sub>5</sub>, 20H), 5.32 (s, CH<sub>2</sub>Cl<sub>2</sub>, 2H), 1.5–2.0 (m, CH<sub>2</sub>CH<sub>3</sub>, 12H), 0.6–1.2 (m, CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>Se, 24H). <sup>31</sup>P nmr (CH<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (ppm): 44.3 (s, Ph<sub>2</sub>P), -0.2 (s, Et<sub>3</sub>P, <sup>1</sup>J(P—Pt) = 3620 Hz).

# Preparation of $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2Et_2)$ , 7b, and $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2Ph_2)$ , 7c

Compounds 7*b* and 7*c* were obtained as yellow crystals in ca. 95% yield from  $[PtCl_2(PEt_3)]_2$  and 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Et<sub>2</sub> or 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Ph<sub>2</sub>, respectively, by a procedure similar to that described for the preparation of 7*a*. The products were recrystallized from CH<sub>2</sub>Cl<sub>2</sub> solutions layered with hexanes at 0°C.

7b: Anal. calcd. for  $C_{40}H_{60}Cl_4N_4P_4Pt_2Se_2$ : C 34.05, H 4.30, N 3.97; found: C 33.59, H 4.43, N 3.89. <sup>1</sup>H nmr (CD<sub>2</sub>Cl<sub>2</sub>, 23°C),  $\delta$ (ppm): 7.1–8.4 (m, C<sub>6</sub>H<sub>5</sub>, 20H), 1.5–1.9 (m, PCH<sub>2</sub>CH<sub>3</sub> and

TABLE 1. Crystallographic parameters for  $[PtCl_2(PEt_3)]_2$ - $[Ph_4P_2N_4Se_2Et_2]$ , 7b

Formula	$C_{40}H_{60}Cl_4P_4N_4Se_2Pt_2$
tw	1410.75
Crystal size (mm)	$0.31 \times 0.40 \times 0.10$
Space group <sup>a</sup>	C2/c (No. 15)
<i>a</i> (Å)	27.803(7)
b (Å)	12.378(7)
c (Å)	15.752(8)
β (°)	115.49(2)
$V(Å^3)$	4893(3)
Z	4
$D_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.915
Radiation, Å	Mo $K_{\alpha}$ ( $\lambda = 0.71069$ Å)
	Graphite monochromated
Temperature (K)	170(1)
F(000)	2720
Scan width (°)	$1.31 + 0.35 \tan \theta$
Scan speed (° min <sup>-1</sup> )	4.0
Maximum θ (°)	25
Octants	$hk \pm 1$
Unique reflections	4528
Observed reflections (>3.0 $\sigma$ )	2302
$\mu$ (MoK <sub>a</sub> ) (cm <sup>-1</sup> )	75.59
Minimum-maximum	0.75-0.90
absorption correct	
Parameters refined	261
GOF	1.50
R, R, b	0.037: 0.022
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"Space group Cc or C2/c from systematic absences hkl: h + k = 2n + 1 and h0l: l = 2n + 1; the latter was indicated by the E-statistics and confirmed by successful refinement.

 ${}^{b}R = \Sigma(||F_{o}| - |F_{c}||)/\Sigma|F_{o}|; R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w|F_{o}|^{2}]^{1/2}$ 

SeCH<sub>2</sub>CH<sub>3</sub>, 16H), 0.7–1.2 (m, PCH<sub>2</sub>CH<sub>3</sub>) and SeCH<sub>2</sub>CH<sub>3</sub>, 24H). <sup>31</sup>P nmr (CH<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (ppm): 44.9 (s, Ph<sub>2</sub>P), -0.6 (d, Et<sub>3</sub>P, <sup>1</sup>J(P--Pt) = 3600 Hz, <sup>3</sup>J(P--P) = 3 Hz).

7*c*: Anal. calcd. for C<sub>48</sub>H<sub>60</sub>Cl<sub>4</sub>N<sub>4</sub>P<sub>4</sub>Pt<sub>2</sub>Se<sub>2</sub>: C 38.26, H 4.01, N 3.71; found: C 37.38, H 4.08, N 3.63. <sup>1</sup>H nmr (CD<sub>2</sub>Cl<sub>2</sub>, 23°C),  $\delta$ (ppm): 7.1–8.6 (m, PC<sub>6</sub>H<sub>5</sub> and SeC<sub>6</sub>H<sub>5</sub>, 30H), 1.41 (q, CH<sub>2</sub>CH<sub>3</sub>, 12H), 0.74 (t, CH<sub>2</sub>CH<sub>3</sub>, 18H). <sup>31</sup>P nmr (CH<sub>2</sub>Cl<sub>2</sub>),  $\delta$ (ppm): 43.3 (s, Ph<sub>2</sub>P), -1.4 (d, Et<sub>3</sub>P, <sup>1</sup>J(P—Pt) = 3646 Hz, <sup>3</sup>J(P—P) = 5 Hz).

## Preparation of trans- $[PtCl_2(PEt_3)(Ph_4P_2N_3SPh)]$ , 8

A solution of  $[PtCl_2(PEt_3)]_2$  (0.200 g, 0.26 mmol) in  $CH_2Cl_2$  (20 mL) at 23°C was added dropwise by cannula (10 min) to a solution of  $Ph_4P_2N_3SPh$  (0.272 g, 0.52 mmol) in  $CH_2Cl_2$  (20 mL) at 23°C. The resulting yellow solution was stirred for 1 h and then solvent was removed under vacuum. Recrystallization of the residue from diethyl ether at 23°C afforded yellow crystals of *trans*-[PtCl\_2(PEt\_3)(Ph\_4P\_2N\_3SPh)] (0.211 g, 0.233 mmol, 45%). Anal. calcd. for  $C_{36}H_{40}Cl_2N_3P_3PtS$ : C 47.74, H 4.45, N 4.64; found: C 46.81, H 4.73, N 4.53. <sup>1</sup>H nmr (CDCl\_3),  $\delta$ (ppm): 6.85–8.3 (m, PC<sub>6</sub>H<sub>5</sub> and SC<sub>6</sub>H<sub>5</sub>, 25H), 1.72 (dq, PCH<sub>2</sub>CH<sub>3</sub>, 6H, <sup>2</sup>J(P—H) = 12 Hz, <sup>3</sup>J(H—H) = 8 Hz), 0.98 (dt, PCH<sub>2</sub>CH<sub>3</sub>, 9H, <sup>3</sup>J(P—H) = 17 Hz, <sup>3</sup>J(H—H) = 8 Hz). <sup>31</sup>P nmr (CH<sub>2</sub>Cl\_2),  $\delta$ (ppm): 20.5 (d, <sup>3</sup>J(P—P) = 10 Hz, <sup>2</sup>J(Pt—P) = 40 Hz), 10.0(s), 1.2 (d, <sup>3</sup>J(P—P) = 10 Hz, <sup>1</sup>J(Pt—P) = 3637 Hz).

#### X-ray crystallographic analysis of 7b

Yellow crystals of 7*b* were obtained from a  $CH_2Cl_2$  solution layered with hexane. The crystal was attached to a glass fibre with epoxy. Pertinent crystallographic data are listed in Table 1.

The unit cell constants were determined from the setting angles of 25 reflections with  $18.76^{\circ} < 2\theta < 21.29^{\circ}$ . All measurements were made on a Rigaku AFC6S diffractometer with the  $\omega$ -2 $\theta$  scan technique and calculations were done using the teXsan programs (15). An empirical absorption correction using the program DIFABS

(16) was applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (17) and expanded using Fourier techniques (18). All non-H atoms, except the methylene carbon atom attached to Se which was disordered over two sites, were refined anisotropically and were allowed isotropic temperature factors; the Se atom was also disordered over two sites. All H atoms except those on the ethyl group attached to Se were included in the refinement at geometrically idealized positions. In the full-matrix least-squares refinement, the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$ . Conventional atomic scattering factors (19), corrected for anomalous dispersion (20), were used. Positional parameters are given in Table 2 and selected bond distances and bond angles are summarized in Table 3.

Hydrogen atom parameters, anisotropic thermal parameters, torsion angles, complete tables of bond lengths and bond angles, and structure factors have been deposited.<sup>2</sup>

## **Results and discussion**

## Synthesis and ${}^{31}P$ nmr characterization of **6**

The reaction of two molar equivalents of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>-S<sub>2</sub>Ph<sub>2</sub>, **3**, with [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> in chloroform at 60°C produces the 1:1 adduct **6** in about 30% yield. On the basis of the <sup>31</sup>P nmr spectra of the reaction mixture, the low yield of **6** is attributed to the equilibrium shown in reaction [1]. Unlike the selenium-containing rings 4a-c, a 2:1 adduct could not be obtained either by the reaction of **6** with [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub> or by treatment of **3** with an excess of [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>.

$$[1] \quad 2Ph_4P_2N_4S_2Ph_2 + [PtCl_2(PEt_3)]_2$$

 $\approx 2 trans-PtCl_2(PEt_3)(\eta^1-N-Ph_4P_2N_4S_2Ph_2)$ 

The composition and structure of **6** were established on the basis of the <sup>1</sup>H and <sup>31</sup>P nmr spectra. The <sup>31</sup>P nmr spectrum of **6** shows three equally intense resonances at -1.4, +31.3, and +41.5 ppm consistent with the proposed N-bonded structure. The resonance at -1.4 ppm is a doublet  $({}^{3}J(P_{A}-P_{B}) = 5 \text{ Hz})$  with platinum satellites  $({}^{1}J(Pt-P_{A}) = 3696 \text{ Hz})$  and is attributed to the PEt<sub>3</sub> ligand. The value of the  ${}^{195}Pt-{}^{31}P$  coupling constant is typical for complexes of the type *trans*-PtCl<sub>2</sub>(PEt<sub>3</sub>)L, where L is an N-bonded unsatu-



rated PNS ring (2, 21). The resonances at 31.3 and 41.5 Hz are assigned to the inequivalent ring phosphorus atoms  $P_c$  and

 $P_B$ , respectively, which exhibit a mutual coupling of 7 Hz. The resonance at 41.5 ppm appears as a doublet of doublets and so is readily attributed to  $P_B$ .

Synthesis and nmr characterization of 7a-c

In contrast to the behaviour of **3**, the reaction of two molar equivalents of 4a-c with the dimer  $[PtCl_2(PEt_3)]_2$  yielded only the 2:1 adducts 7a-c. These adducts could be obtained as yellow, air-sensitive solids in essentially quantitative yields by using the stoichiometry shown in reaction [2].

$$[2] Ph_4P_2N_4Se_2R_2 + [PtCl_2(PEt_3)]_2$$

 $\rightarrow$  [PtCl<sub>2</sub>(PEt<sub>3</sub>)]<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>R<sub>2</sub>)

$$7a, R = Me; 7b, R = Et; 7c, R = Ph$$

The composition of the 2:1 adducts 7a-c was established by elemental analyses and by the integrated <sup>1</sup>H nmr spectra (see Experimental section). The <sup>31</sup>P nmr spectra of 7a-c all exhibit a singlet at 43-45 ppm (cf.  $\delta({}^{31}P) = 32-34$ ppm for 4a-c (9)) for the heterocyclic phosphorus atoms in addition to a resonance at 0 to  $-2 \text{ ppm}(^{1}J(\text{Pt}-\text{P}) = 3600 - 100 \text{ ppm})$ 3650 Hz) for the PEt<sub>3</sub> ligand. The  $J(PEt_3 - PPh_2)$  coupling of 3-5 Hz is observed (as a doublet) in the PEt<sub>3</sub> resonance of 7b and 7c, but it was not resolved in the case of 7a. Thus the <sup>31</sup>P nmr data rule out a structure for 7a-c in which the two  $PtCl_2(PEt_3)$  groups are attached to nitrogen atoms which are bonded to the same phosphorus atom or a structure in which the platinum atoms are coordinated to selenium, but do not distinguish between "distal" or "vicinal" N-bonded arrangements (see Fig. 1). The <sup>77</sup>Se nmr spectrum of 7a, however, consists of a virtual triplet, centered at 944 ppm, characteristic of an AA'X spin system (where X is <sup>77</sup>Se (natural abundance = 7.7%) for the most abundant isotopomer and the phosphorus atoms (represented by A and A') are magnetically inequivalent). The "averaged" value of 40 Hz for  ${}^{2}J(P-Se)$  obtained from the  ${}^{77}Se$  nmr spectrum of 7a is smaller than the value of 86 Hz found for the ligands 4a-c (9b). These <sup>77</sup>Se nmr data rule out the "vicinal" N-bonded structure for 7a (see Fig. 1(b)), since this isomer should exhibit two resonances for the inequivalent selenium atoms. In support of the inference based on the <sup>31</sup>P nmr spectra of 7a-c, the Se-coordinated structure (an A<sub>2</sub>X spin system, see Fig. 1(c)) which should give rise to a 1:2:1 triplet, may also be discounted on the basis of the <sup>77</sup>Se nmr data. Thus the <sup>77</sup>Se nmr spectrum of 7a is only consistent with the "distal" N-bonded structure (see Fig. 1(a)). This conclusion has been confirmed by an X-ray crystal structure determination of 7b.

## X-ray crystal structure of $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2Me_2)$ , 7b

The X-ray analysis of 7*b* establishes that the two  $PtCl_2(PEt_3)$  groups are attached to opposite (distal) nitrogen atoms of the  $P_2N_4Se_2$  ring with the  $PEt_3$  ligands *trans* to nitrogen. An ORTEP drawing of the structure with the atomic numbering scheme is displayed in Fig. 2.

In the solid state, the complex lies on a twofold axis with the SeC<sub>2</sub>H<sub>5</sub> group disordered in such a way that the Se and methylene carbon atoms lie over two sites (Se(1), Se(2) and C(191), C(192), respectively) with half-occupancy factors; the thermal parameters of the methyl carbon atom C(20) indicate a large degree of thermal motion. For clarity, Fig. 2 depicts one long chair conformation of the disordered  $P_2N_4Se_2$ ring. There are three possible conformations of the  $P_2N_4Se_2$ 

<sup>&</sup>lt;sup>2</sup>Supplementary material mentioned in the text may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada, K1A 0S2.

Tables of hydrogen atom parameters and bond lengths and angles have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 IEZ, U.K.

TABLE 2. Positional parameters and B(eq) for 7b

Atom <sup>a</sup>	x	y	Z	$\overline{B(\text{eq})^b}$
Pt(1)	0.34861(2)	0.11466(4)	0.71832(3)	2.91(2)
Se(1)'	0.45425(8)	0.13125(16)	0.66747(13)	2.31(8)
Se(2)'	0.42507(9)	0.27215(18)	0.63623(14)	2.9(1)
Cl(1)	0.2992(1)	0.2724(2)	0.6675(2)	4.2(1)
C1(2)	0.4010(1)	-0.0347(2)	0.7781(2)	5.0(2)
P(1)	0.4609(1)	0.2571(3)	0.8348(2)	3.2(1)
P(2)	0.2723(1)	0.0280(2)	0.6862(2)	3.8(1)
N(1)	0.4182(3)	0.2034(6)	0.7373(5)	3.3(4)
N(2)	0.4788(4)	0.2250(8)	0.6334(6)	5.3(5)
C(1)	0.4414(4)	0.2173(8)	0.9258(7)	2.5(4)
C(2)	0.4745(4)	0.1529(8)	0.9980(7)	3.8(5)
C(3)	0.4620(5)	0.1265(11)	1.0735(7)	5.3(6)
C(4)	0.4172(5)	0.1648(10)	1.0741(7)	5.6(7)
C(5)	0.3827(5)	0.2267(10)	1.0021(8)	4.6(6)
C(6)	0.3953(4)	0.2545(8)	0.9291(7)	3.3(5)
C(7)	0.4555(4)	0.4036(9)	0.8268(7)	3.3(5)
C(8)	0.4955(6)	0.4690(11)	0.8843(9)	7.3(8)
C(9)	0.4901(7)	0.5800(11)	0.8766(10)	8(1)
C(10)	0.4448(6)	0.6239(12)	0.8112(10)	6.4(8)
C(11)	0.4065(6)	0.5652(13)	0.7571(13)	11(1)
C(12)	0.4118(6)	0.4498(12)	0.7619(11)	11(1)
C(13)	0.2748(4)	-0.1168(10)	0.6919(7)	5.0(6)
C(14)	0.2871(5)	-0.1699(9)	0.6165(8)	6.6(7)
C(15)	0.2408(5)	0.0660(9)	0.7605(10)	6.4(7)
C(16)	0.2755(6)	0.0394(11)	0.8625(8)	7.0(8)
C(17)	0.2236(5)	0.0582(9)	0.5643(8)	6.7(7)
C(18)	0.1682(6)	0.0063(12)	0.5349(12)	12(1)
C(191)'	0.3894(7)	0.1005(17)	0.5487(12)	4.6(7)
C(192)'	0.3658(7)	0.1999(14)	0.5288(11)	6.7(6)
C(20)	0.3726(7)	0.2117(15)	0.4516(11)	14(1)

<sup>*a*</sup>Primed atoms were disordered over two sites with equal site occupancy factors; C(191) and C(192) were allowed isotropic temperature factors.

 ${}^{b}B_{cq} = \frac{8}{3}\pi^{2}(U_{11}(aa^{*})^{2} + U_{22}(bb^{*})^{2} + U_{33}(bb^{*})^{2} + 2U_{12}aa^{*}bb^{*}\cos\gamma + 2U_{13}aa^{*}cc^{*}\cos\beta + 2U_{23}bb^{*}cc^{*}\cos\alpha).$ 

ring which could contribute to the disordered structure, viz. boat–boat (BB), crown (CR), or long chair (LC) (see Fig. 3).<sup>3</sup> Three combinations of these ring conformations could give rise to the observed disorder. These are (*i*) equal contributions of BB and CR, (*ii*) equal contributions of two LC conformations, or (*iii*) equal contributions of BB, CR, and two LC conformations. Although it is not possible to distinguish between these alternatives on the basis of the crystallographic data, option (*ii*) (two LC conformations involved in a rotational disorder) seems the most likely explanation since the other combinations require equal contributions of energetically different species.

As a result of the disorder the P—N bond distances fall within the range 1.57(1)-1.65(1) Å with a mean value of 1.61 Å, and the Se—N bond distances vary from 1.56(1) to 1.99(1) with a mean value of 1.77 Å. These distances can be compared with the values of 1.605(3) and 1.773(1) Å found for the P—N and Se—N bonds, respectively, in the uncomplexed ligand 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Me<sub>2</sub>, 4a (9). The geometry of the rest of the molecule is not affected by the disorder. The Pt—N bond length of 2.130(8) Å is indicative of a weak interaction. For comparison, the Pt—N bond length in  $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2)$ , a closely related "distal" platinum(II) complex of **2** is 2.162(9) Å (4), while values of 2.02–2.03 Å are found for complexes of chelating, anionic Se—N ligands (22).

## Preparation and ${}^{31}P$ nmr characterization of 8

Investigations of the Lewis base properties of the sixmembered ring 5 have shown that the interaction of the  $P_2N_3S$ ring with Lewis or Brønsted acids is not regiospecific. Whereas methylation occurs at a nitrogen between phosphorus and sulfur, protonation takes place at the unique nitrogen atom (23). Furthermore, the 1:1 boron trihalide adducts of 5 are mixtures of symmetrical and unsymmetrical *N*-bonded isomers and the formation of a 2:1 BCl<sub>3</sub> adduct is indicated on the basis of <sup>31</sup>P nmr investigations. It was of interest, therefore, to include an examination of the ligand behaviour of 5 towards platinum(II) in the current investigation.

The six-membered ring **5** reacts with  $[PtCl_2(PEt_3)]_2$  in dichloromethane at room temperature to give the 1:1 adduct **8** in essentially quantitative yield according to the <sup>31</sup>P nmr spectrum of the reaction mixture. Attempts to attach a second platinum to the P<sub>2</sub>N<sub>3</sub>S ring by heating **8** with  $[PtCl_2(PEt_3)]_2$  in boiling dichloromethane or chloroform were unsuccessful.

The composition of **8** was established by elemental analyses and the  ${}^{1}$ H nmr spectrum (see Experimental section).

<sup>&</sup>lt;sup>3</sup>This terminology for the conformation of eight-membered rings is taken from ref. 21.

1825

TABLE 3. Selected bond lengths (Å) and bond angles (deg) for  $[PtCl_2(PEt_3)]_2$ - $[Ph_4P_2N_4Se_2Et_2], 7b$ 

Length	Bond <sup>a</sup>	Length
2.323(3)	Pt(1)-Cl(2)	2.291(3)
2.231(3)	Pt(1)-N(1)	2.130(8)
1.991(8)	Se(1)-N(2)	1.554(9)
2.00(2)	Se(2)-N(1)	1.887(7)
1.622(9)	Se(2)-C(192)	1.99(2)
1.625(7)	P(1)-N(2)'	1.580(9)
1.804(9)	P(1)-C(7)	1.82(1)
1.79(1)	P(2)-C(15)	1.80(1)
1.85(1)	Se(1)Se(1)'	2.746(4)
Angle	Bonds	Angle
176.0(1)	Cl(1)-Pt(1)-P(2)	87.8(1)
89.0(2)	Cl(2)-Pt(1)-P(2)	94.6(1)
88.9(2)	P(2)-Pt(1)-N(1)	175.1(2)
97.9(6)	N(1)-Se(1)-N(2)	104.9(4)
99.6(5)	N(2)-Se(1)-C(191)	99.9(6)
116.2(5)	N(1)-Se(2)-N(2)	106.9(4)
109.7(5)	N(2)-Se(2)-C(192)	104.5(6)
108.5(5)	N(1)-P(1)-C(1)	106.9(4)
117.1(4)	N(2)-P(1)-C(1)	108.7(5)
109.8(4)	Pt(1)-P(2)-C(15)	114.1(4)
109.5(4)	Pt(1)-N(1)-Se(2)	122.0(4)
126.4(4)	Se(2)-N(1)-P(1)	108.3(4)
111.6(5)	Se(1)-N(2)-P(1)'	129.9(6)
139.9(7)		
	Length 2.323(3) 2.231(3) 1.991(8) 2.00(2) 1.622(9) 1.625(7) 1.804(9) 1.79(1) 1.85(1) Angle 176.0(1) 89.0(2) 88.9(2) 97.9(6) 99.6(5) 116.2(5) 108.5(5) 117.1(4) 109.8(4) 109.5(4) 126.4(4) 111.6(5) 139.9(7)	LengthBond"2.323(3) $Pt(1)$ - $Cl(2)$ 2.231(3) $Pt(1)$ - $N(1)$ 1.991(8) $Se(1)$ - $N(2)$ 2.00(2) $Se(2)$ - $N(1)$ 1.622(9) $Se(2)$ - $C(192)$ 1.625(7) $P(1)$ - $N(2)'$ 1.804(9) $P(1)$ - $C(7)$ 1.79(1) $P(2)$ - $C(15)$ 1.85(1) $Se(1)$ $Se(1)'$ AngleBonds176.0(1) $Cl(1)$ - $Pt(1)$ - $P(2)$ 88.9(2) $P(2)$ - $Pt(1)$ - $N(1)$ 97.9(6) $N(1)$ - $Se(1)$ - $N(2)$ 99.6(5) $N(2)$ - $Se(1)$ - $C(191)$ 116.2(5) $N(1)$ - $Se(2)$ - $N(2)$ 109.7(5) $N(2)$ - $Se(2)$ - $C(192)$ 108.5(5) $N(1)$ - $P(1)$ - $C(1)$ 117.1(4) $N(2)$ - $P(1)$ - $C(1)$ 109.8(4) $Pt(1)$ - $P(2)$ - $C(15)$ 109.5(4) $Pt(1)$ - $N(2)$ - $P(1)'$ 111.6(5) $Se(1)$ - $N(2)$ - $P(1)'$ 139.9(7) $V$

"Primed atoms are related to the unprimed atoms by the symmetry: 1 - x, y,  $1\frac{1}{2} - z$ .





PEt,

`CI



(c)



FIG. 2. ORTEP drawing for one long chair conformation of  $[PtCl_2(PEt_3)]_2[Ph_4P_2N_4Se_2Et_2]$ , 7*b*, showing the atomic numbering scheme.



FIG. 3. ORTEP drawings of three conformations of the  $P_2N_4Se_2$  ring in 7b; (a) boat-boat (BB), (b) crown (CR), (c) long chair (LC). Only one of the LC conformations is shown.

The <sup>31</sup>P nmr spectrum of **8** is uniquely consistent with a structure in which the  $PtCl_2(PEt_3)$  group is attached to one of the sulfur-bonded nitrogen atoms and the  $PEt_3$  ligand

is *trans* to nitrogen. Three equally intense resonances are observed at 1.2, 10.0, and 20.5 ppm. The resonance at 1.2 ppm, which appears as a doublet ( ${}^{3}J(P--P) = 10$  Hz) with platinum satellites ( ${}^{1}J(Pt--P) = 3637$  Hz), is readily attributed to the PEt<sub>3</sub> ligand, while the signals at 10.0 and 20.5 ppm are assigned to the inequivalent ring phosphorus atoms P<sub>c</sub> and P<sub>B</sub>, respectively. The former appears as a singlet while the latter is a doublet ( ${}^{3}J(P--P) = 10$  Hz) with platinum satellites ( ${}^{2}J(Pt--P)\sim 40$  Hz). The two-bond coupling between the inequivalent heterocyclic phosphorus atoms, P<sub>B</sub> and P<sub>c</sub>, could not be resolved. In the *N*-methylated derivative of **5** this coupling is *ca*. 6 Hz, but it was not resolved in the unsymmetrical 1:1 adducts of **5** with BX<sub>3</sub> (X = Cl, F) (23).



Previous studies of the interaction of PNS rings with electrophiles, have shown that the site of electrophilic attack is governed by electrostatic effects (24, 25). In the specific case of the  $P_2N_3S$  ring, however, the interaction with  $BCl_3$  or methyl triflate is not regiospecific whereas protonation occurs exclusively at the unique nitrogen atom. It is possible, therefore, that the observed regiospecific adduct formation with the electrophile  $PtCl_2(PEt_3)$  is controlled by steric effects.

## Conclusions

The eight-membered rings 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>E<sub>2</sub>R<sub>2</sub> (E = S, Se) form either 1:1 (E = S) or 2:1 (E = Se) adducts with platinum(II). By contrast, the folded eight-membered ring  $Ph_4P_2N_4S_2$  (1) forms the 1:1, 2:1, and 3:1 adducts  $[PtCl_2(PEt_3)]_n(Ph_4P_2N_4S_2)$  (n = 1-3) (2). An X-ray structure of the 2:1 adduct of the open ring  $1,5-Ph_4P_2N_4Se_2Et_2$  (4b) reveals features similar to those found for the corresponding adduct of the folded ring (4). In both cases the platinum atoms are attached to "distal" nitrogen sites of the P2N4Se2 rings and the Pt-N distances are indicative of a weak interaction. The  $P_2N_4Se_2$  ring in the 2:1 adduct of 4b exists as a mixture of at least two conformations but, as a result of the disorder, it is not possible to assess the effect of adduct formation on the geometrical parameters of the heterocyclic ring. In contrast to the behavior of Lewis and Brønsted acids, adduct formation between the six-membered ring  $Ph_4P_2N_3SPh$ and platinum(II) occurs in a regiospecific manner to give the isomer in which the metal is attached to a nitrogen between the phosphorus and sulfur atoms.

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