Preparation, Spectroscopic and Structural Characterization of η^1-N and η^2-Se,Se′ Complexes of a $P_2N_4Se_2$ Ring

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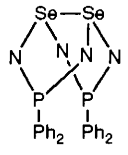
The reaction of 1,5-$Ph_4P_2N_4Se_2$, **1**, prepared by the treatment of $Ph_2PN_2(SiMe_3)_3$ with a mixture of $SeCl_4$ and Se_2Cl_2 in acetonitrile, with $[PtCl_2(PEt_3)]_2$ gives the adducts $[PtCl_2(PEt_3)]_n[\eta^1\text{-N-}Ph_4P_2N_4Se_2]$ (**2**, *n* = 1; **3**, *n* = 2) in which the $P_2N_4Se_2$ ring is shown by an X-ray structural determination of **3** to contain a transannular Se–Se interaction; the oxidative addition of **1** or **2** to $Pt(C_2H_4)(PPh_3)_2$ produces the corresponding η^2-Se,Se′ complexes.

Several interesting reactions of Se_4N_4 have been reported recently.[1–5] Without exception these reactions result in breakdown of the heterocyclic ring. For example, the treatment of Se_4N_4 with $[PtCl_2(PMe_2Ph)]_2$ or $Pt(PPh_3)_3$ produces the complexes $Pt(Se_3N)Cl(PMe_2Ph)$[4] or $[Pt(Se_2N_2)(PPh_3)]_2$,[5] which contain the chelating ligands Se_3N^- and $Se_2N_2^{2-}$, respectively. Furthermore, Se_4N_4 is difficult to handle owing to its explosive nature and insolubility in organic solvents. By contrast, the 1,5-diphosphadiselenatetrazocine **1** is non-explosive, soluble in organic solvents, and contains a structurally informative ^{31}P NMR probe.[6] By analogy with the chemistry of the sulfur analogue,[7,8] the hybrid inorganic heterocycle **1** should provide a good model for investigating reactions of unsaturated selenium–nitrogen systems. However, **1** has only been obtained in very low yields and the existence of the cross-ring bond has not been unequivocally established owing to the tendency of this compound to deposit red selenium in the solid state or in solution.[6]

We report here a high yield synthesis of **1** and the reaction of **1** with $[PtCl_2(PEt_3)]_2$ to give the *N*-bonded 1:1 and 1:2 adducts, **2** and **3**. We also establish the presence of a transannular Se–Se interaction in **3** by X-ray crystallography. The oxidative addition of $Pt(PPh_3)_2(C_2H_4)$ to **1** or **2** produces the corresponding η^2-Se,Se′ adducts **4** and **5**, respectively.

The eight-membered ring **1** is readily obtained by the cyclocondensation reaction between $Ph_2PN_2(SiMe_3)_3$ and a mixture of selenium halides designed to imitate '$SeCl_3$' [eqn. (1)]. The slow addition of $Ph_2PN_2(SiMe_3)_3$ (21.5 mmol) in acetonitrile (100 ml) to a mixture of $SeCl_4$ (14.3 mmol) and Se_2Cl_2 (3.6 mmol) suspended in acetonitrile (150 ml) at 23 °C produced (after 16 h) a yellow–brown precipitate and a yellow solution. The volume of the solution was reduced to 50 ml and



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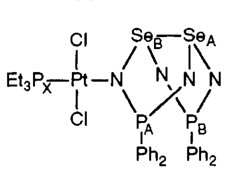

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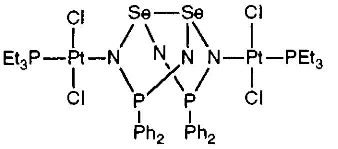

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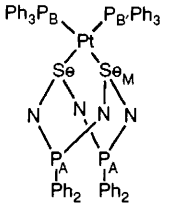

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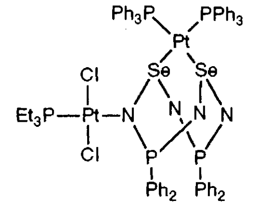

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the precipitate was dried under vacuum. Extraction of this precipitate with dichloromethane (3 × 40 ml) gave **1** in 85% yield (9.1 mmol) as a yellow solid identified by ^{31}P and ^{77}Se NMR spectra.[6]†

$$2Ph_2PN_2(SiMe_3)_3 + 4/3\ SeCl_4 + 1/3\ Se_2Cl_2 \rightarrow 1,5\text{-}Ph_4P_2N_4Se_2 + 6Me_3SiCl \quad (1)$$

The addition of **1** to the dimer $[PtCl_2(PEt_3)]_2$ in a 2 : 1 molar ratio in CH_2Cl_2 at −78 °C, followed by warming to room temp. for 20 min, produces a mixture of the 1 : 1 adduct, **2**, and the 2 : 1 adduct, **3**, in the approximate molar ratio 7 : 2 as determined by ^{31}P NMR spectroscopy. A pure sample of the monoadduct was obtained by layering hexane on to a solution of the mixture of **2** and **3** in dichloromethane.† The $^{31}P\{^1H\}$ NMR spectrum of **2** shows three resonances at δ 2.4 (d, $^3J_{P_X-P_A}$ 5, $^1J_{P_X-Pt}$ 3619 Hz), 109.3 (d, $^4J_{P_A-P_B}$ 16, $^2J_{P_B-Se_A}$ 93 Hz) and 114.3 (dd, $^4J_{P_A-P_B}$ 16, $^3J_{P_A-P_X}$ 5, $^2J_{P_A-Pt}$ 94 Hz). The low-frequency resonance is readily assigned to the Et_3P ligand (P_X) on the basis of the large P–Pt coupling constant, whereas the two high-frequency resonances can be attributed to the inequivalent phosphorus atoms, P_A and P_B of the heterocyclic ring, [*cf.* δ(^{31}P) 113.4 for **1**].[6] The ^{77}Se NMR spectrum of **2** shows two resonances for the inequivalent Se atoms at δ 1270 ($^2J_{Se_A-P_B}$ 93, $^2J_{Se_A-P_A}$ 85 Hz) and 1258 ($^2J_{Se_B-P}$ 96, $^2J_{Se_B-P}$ 60 Hz) (ref. $SeMe_2$ δ 0), which appear as a pseudotriplet and a doublet of doublets, respectively.

The diadduct **3** can be obtained in virtually quantitative yield by carrying out the reaction of **1** with $[PtCl_2(PEt_3)]_2$ in a 1 : 1 molar ratio.† The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits two singlets at δ 3.0 ($^1J_{P-Pt}$ 3654 Hz) and 113.2 ($^2J_{P-Se}$ 69 and 89 Hz) attributable to the Et_3P ligands and equivalent PPh_2 groups, respectively. The ^{77}Se NMR spectrum of **3** exhibits a five line AA′X pattern (where X is ^{77}Se for the most abundant isotopomer) centred at δ 1337 with $|(J_{P_A-Se} + J_{P_{A'}-Se})|$ 160 Hz. These NMR data are uniquely consistent with a distal arrangement for the $PtCl_2(PEt_3)$ groups in the 2 : 1 adduct. Furthermore, the anomalously high-frequency ^{31}P NMR chemical shifts of the PPh_2 groups observed for **2** and **3** suggests strongly that *N*-coordination does not disrupt the Se–Se transannular interaction in these adducts.[9,10]

The structure of **3** was established by X-ray crystallography. Yellow crystals of **3** were obtained by recrystallization from CH_2Cl_2–hexane at 0 °C.‡ The molecular geometry and atomic numbering scheme are shown in Fig. 1. The structural determination confirms that the equivalent $PtCl_2(PEt_3)$ groups are η^1-N bonded to the $P_2N_4Se_2$ ring in distal positions. The most interesting feature of the structure of **3** is the transannular Se–Se interaction. The Se–Se distance is 2.594(2) Å (*cf.* 2.34 Å for the Se–Se single bond in Se_8).[11] Based on the observation that the formation of *N*-bonded adducts results in a small contraction of the S–S distance for the sulfur analogue of **1**,[9,10] we tentatively estimate a value of 2.65–2.70 Å for the Se–Se interaction in **1**. This can be compared with the values of 2.748(9) and 2.84(1) Å found for the analogous intramolecular π*–π* interactions[12] in S_4N_4[13] and Se_8^{2+},[14] respectively. The Se–N and P–N bonds involving the coordinated nitrogen atom N(1) in **3** are slightly longer than the corresponding bonds to N(2). The Se(1)–N(2) distance of 1.717(8) Å is significantly shorter than the average value of 1.777(3) Å observed for d(Se^{IV}-N) in 1,5-$Ph_4P_2N_4Se_2Me_2$[6] (*cf.* 1.64 Å predicted for Se^{IV}=N double bond).[13] The coordinated nitrogen atom N(1) is removed significantly from the Se_2N_2 plane as indicated by the dihedral angles N(1)–Se(1)–Se(1)*–N(1)* = 129.0(6), N(2)*–Se(1)–Se(1)–N(2)* = −83.0(6), and N(1)–Se(1)–Se(1)*–N(2) = 23.0(4)°. The sum of the angles at N(1) is 344°. The geometry at the platinum(II) centres is approximately square planar with bond angles in the range 86.9(3)–94.2(1)°.

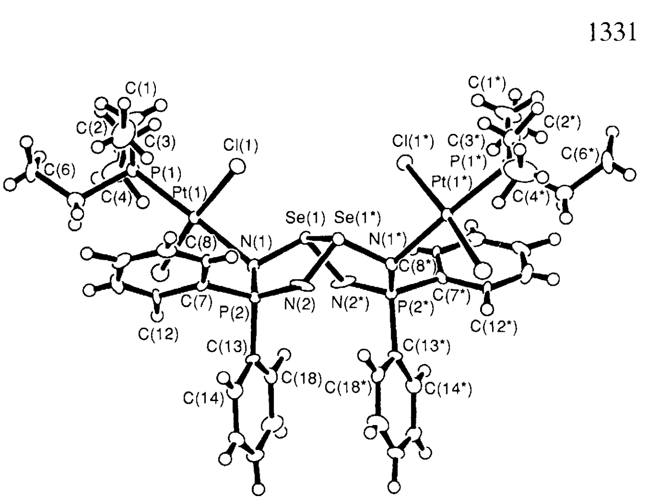

Fig. 1 ORTEP plot (50% probability ellipsoids) for $[\eta^1\text{-N-}PtCl_2(PEt_3)]_2(1,5\text{-}Ph_4P_2N_4Se_2)$, **3**; selected bond lengths (Å) and bond angles (°): Pt(1)–P(1) 2.229(3), Pt(1)–Cl(1) 2.319(3), Pt(1)–Cl(2) 2.301(3), Pt(1)–N(1) 2.162(9), Se(1)–Se(1)* 2.594(2), Se(1)–N(1) 1.753(9), Se(1)–N(2)* 1.717(8), P(2)–N(1) 1.673(9), P(2)–N(2) 1.64(1), Cl(2)–Pt(1)–P(1) 91.5(1), Cl(2)–Pt(1)–N(1) 87.5(3), Cl(1)–Pt(1)–P(1) 94.2(1), Cl(1)–Pt(1)–N(1) 86.9(3), Se(1)*–Se(1)–N(1) 91.7(3), Se(1)–Se(1)*–N(2) 89.9(3), N(1)–Se(1)–N(2)* 106.0(4), N(1)–P(2)–N(2) 110.9(4), Pt(1)–N(1)–Se(1) 108.7(4), Pt(1)–N(1)–P(2) 117.2(5), Se(1)–N(1)–P(2) 118.1(6), Se(1)*–N(2)–P(2) 122.4(5). The asterisks indicate symmetry-related atoms.

The eight-membered ring **1** readily undergoes oxidative-addition with $Pt(C_2H_4)(PPh_3)_2$ at 0 °C in toluene to give **4** in 70% yield.† The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of two singlets (with ^{195}Pt and ^{77}Se satellites) at δ 17.6 ($^1J_{P-Pt}$ 2980,

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† Satisfactory C, H, N analyses were obtained for **1**, **2**, **3** and **4**.

‡ *Crystal data* for $C_{36}H_{50}Cl_4P_4N_4Se_2Pt_2$ **3**: *M* = 1352.62, monoclinic, space group *C*2/*c*; at 150(1) K, *a* = 25.150(10), *b* = 12.090(3), *c* = 14.597(5) Å, β = 96.73(4)°, *V* = 4407(3) Å³, *Z* = 4, μ(Mo-Kα) = 8.464 mm⁻¹, *F*(000) = 2584, D_c = 2.038 g cm⁻³. Intensity data were collected at 150(1) K on a Rigaku AFC6S diffractometer operating in the ω–2θ mode and using Mo-Kα radiation (λ = 0.71069 Å, graphite monochromator) and were corrected for absorption. Total number of unique reflections 4121, of which 2915 had *I* > 3σ(*I*). Crystal dimensions 0.45 × 0.55 × 0.15 mm. The structure was solved by direct methods and was refined by full-matrix least-squares calculations to *R* 0.037 and R_w 0.034. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$^2J_{\text{P–Se}}$ 140 Hz) and 46.8 ($^3J_{\text{P–Pt}}$ 424, $^2J_{\text{P–Se}}$ 71 Hz) attributable to the equivalent Ph_3P ligands and Ph_2P groups, respectively. The ^{77}Se NMR spectrum of **4** is characteristic of an $A_2BB'M$ spin system (where M is ^{77}Se in the most abundant isotopomer for which the $Ph_3\mathit{P}$ phosphorus atoms are magnetically inequivalent). The simulation of this spectrum provides the following coupling constants: $^2J_{\text{P}_\text{A}\text{–Se}}$ 71, $^2J_{\text{P}_\text{B}\text{–Se}}$ 137 $^2J_{\text{P}_{\text{B}'}\text{–Se}}$ 28, and $^2J_{\text{P}_\text{B}\text{–P}_{\text{B}'}}$ 8 Hz.[15] Thus, the NMR data are consistent with an η^2-Se,Se′ bonding mode for **4** analogous to that established by X-ray crystallography for the corresponding η^2-S,S′ complex.[8b] Finally we note that **2** also undergoes oxidative-addition with $Pt(C_2H_4)(PPh_3)_2$ to give complex **5** in which the $P_2N_4Se_2$ ring acts as a μ^2,η^3-N,Se,Se′ ligands on the basis of ^{31}P NMR spectroscopy. Details will be given in the full account of this work.

In summary, the high-yield synthesis of **1** has facilitated studies of the chemistry of this heterocycle. Initial investigations indicate multimode coordination behaviour for this interesting ligand and the combination of ^{31}P and ^{77}Se NMR spectroscopy provides a powerful structural probe for metal complexes. The presence of a transannular Se–Se interaction in *N*-bonded platinum(II) adducts of **1** has been established.

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