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Preparation and ^{31}P and ^{77}Se NMR Spectra of Platinum and Palladium Complexes of a $P_2N_4Se_2$ Ring

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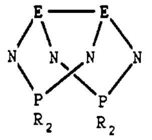
The reaction of 1,5-$Ph_4P_2N_4Se_2$ with $Pt(PPh_3)_2(CH_2{=}CH_2)$ or $Pd(PPh_3)_4$ in toluene at 0 °C produces the η^2-Se,Se′-bonded complexes $M(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$) (**2a**, M = Pt; **2b**, M = Pd) characterized by their ^{31}P and ^{77}Se NMR spectra. Simulation of the ^{77}Se NMR spectra gave detailed coupling information for **2a** and **2b**. Heating **2a** or **2b** in boiling toluene produces the corresponding η^2-Se,N-μ,η^1-Se′-bonded dimers $[M(PPh_3)$(1,5-$Ph_4P_2N_4Se_2)]_2$ (**3a**, M = Pt; **3b**, M = Pd). Variable-temperature ^{31}P NMR spectra of **3a** reveal a fluxional process which is proposed to involve a [1,3]-metallotropic shift. The reaction of 1,5-$Ph_4P_2N_4Se_2$ with $[PtCl_2(PEt_3)]_2$ in CH_2Cl_2 produces the η^1-N-bonded adducts $[PtCl_2(PEt_3)]_n$(1,5-$Ph_4P_2N_4Se_2$) (**4a**, $n = 1$; **5**, $n = 2$). The two $PtCl_2(PEt_3)$ groups in **5** are attached to distal nitrogen atoms of the $P_2N_4Se_2$ ring, which retains a folded structure with d(Se–Se) = 2.594 Å. Treatment of **4a** with $Pt(PPh_3)_2(CH_2{=}CH_2)$ produces the μ^2,η^3-Se,Se′,N-bonded complex $Pt(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$)$[PtCl_2(PEt_3)]$ identified by ^{31}P NMR spectroscopy. Reaction of $[Li[Ph_4P_2N_4Se_2Ph](THF)]_2$, generated from the combination of 1,5-$Ph_4P_2N_4Se_2$ and phenyllithium in THF, with *cis*-$PtCl_2(PEt_3)_2$ yields the η^1-Se-bonded complex *trans*-$PtCl(PEt_3)_2(Ph_4P_2N_4Se_2Ph)$ (**7a**). Variable temperature ^{31}P NMR spectra of **7a** reveal a two-site exchange process involving the two PEt_3 ligands, which is proposed to occur via rotation about the Pt–Se bond. Line-fitting analysis yielded the thermodynamic parameters for this process.

Introduction

Recent investigations of the coordination chemistry of the unsaturated $P^V{}_2N_4S_2$ ring **1a** have revealed it to be a multifaceted ligand for which the following bonding modes have been established (see Figure 1): η^1-N,[1] η^2-S,S′,[2] η^2-S,N-μ,η^1-S′,[2b,3] and μ^2,η^3-S,S′,N.[1] In addition, the reaction of 1,5-$Ph_4P_2N_4S_2$ with organolithium reagents generates the organolithium derivatives $[Li[Ph_4P_2N_4S_2R](THF)]_2$, which form η^1-S-bonded complexes with platinum(II) or palladium(II).[4]



1a, E = S
1b, E = Se

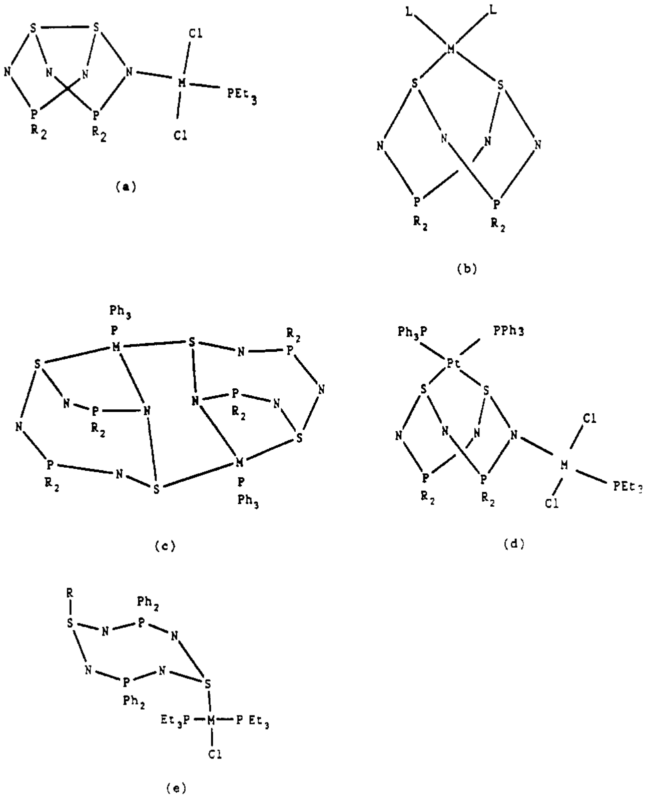


Figure 1. Known coordination modes for 1,5-$R_4P_2N_4S_2$: (a) η^1-N (R = Me, Et, Ph; M = Pt, Pd[1]); (b) η^2-S,S′ (R = Me, Et, Ph; L = PPh_3; M = Pt, Pd;[2b] R = Ph, L = PEt_3, M = Pt;[2c] R = Ph, L_2 = diphos, M = Ni[2c]); (c) η^2-S,N-μ,η^1-S′ (R = Me, Et, Ph; M = Pt, Pd[2b]); (d) μ^2,η^3-S,S′,N[1]; (e) η^1-S complexes of the $Ph_4P_2N_4S_2R^-$ anion (R = Me, Bu^t, Ph, CH_2PPh_2; M = Pt;[4b] R = Me; M = Pd[4b]).

The recent discovery of a high-yield synthesis of the $P_2N_4Se_2$ ring **1b** (R = Ph)[5] has paved the way for a comparison of the ligand behavior of this Se–N heterocycle with that of **1a**. In addition, the $P_2N_4Se_2$ ring can be expected to behave as a model for reactions of the hazardous compound Se_4N_4,[6] which invariably result in fragmentation of the eight-membered cage.[7] In contrast to the case of Se_4N_4, which has two transannular Se- -Se interactions,[6] attention can be focused on the unique Se- -Se cross-ring bond in $P_2N_4Se_2$. Furthermore, the NPN units in **1b**, by analogy with $P_2N_4S_2$ chemistry,[1-4] should provide an informative structural probe (^{31}P NMR spectroscopy) and should act as a

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brace that will serve to maintain the integrity of the eight-membered ring. ^{77}Se NMR spectroscopy is likely to be a source of additional structural insights that are not accessible for the corresponding sulfur compounds.

In this paper we describe the preparation and spectroscopic characterizaton of (a) the η^2-Se,Se′-bonded complexes $M(PPh_3)_2(Ph_4P_2N_4Se_2)$ (M = Pt, Pd), (b) the η^2-Se,N-μ,η^1-Se′-bonded dimers $[M(PPh_3)(Ph_4P_2N_4Se_2)]_2$ (M = Pt, Pd), (c) the η^1-N-bonded complexes $[PtCl_2(PEt_3)]_n(Ph_4P_2N_4Se_2)$ (n = 1, 2), (d) the μ^2,η^3-Se,Se′,N complex $Pt(PPh_3)_2(Ph_4P_2N_4Se_2)[PtCl_2(PEt_3)]$, and (e) the η^1-Se-bonded complex $PtCl(PEt_3)_2(Ph_4P_2N_4Se_2Ph)$. A preliminary account of this work, including the X-ray structure of $[PtCl_2(PEt_3)]_2(Ph_4P_2N_4Se_2)$ has been published.[5a]

Experimental Section

Reagents and General Procedures. The compounds 1,5-$Ph_4P_2N_4Se_2$,[5b] $Pt(PPh_3)_2(CH_2{=}CH_2)$,[8] $[PtCl_2(PEt_3)]_2$,[9] $[PdCl_2(PEt_3)]_2$,[10] and *cis*-$PtCl_2(PEt_3)_2$[11] were prepared by the literature procedures. The commercial reagents $PtCl_2$, K_2PtCl_4, $Pd(PPh_3)_4$, PEt_3, PPh_3, and PhLi (all from Aldrich) were used as received.

All manipulations were carried out under a dry atmosphere of nitrogen (Ridox, P_4O_{10}, and silica). Toluene, hexanes and THF were freshly distilled over Na/benzophenone. Dichloromethane and hexanes were distilled from P_4O_{10}. Distillations were performed under nitrogen. Chemical analyses were performed by Analytical Services of the Department of Chemistry, The University of Calgary, and by the Canadian Microanalytical Service, Vancouver, BC.

Instrumentation. Infrared spectra were recorded as Nujol mulls with KBr plates on a Nicolet 5DX FT-IR spectrometer. ^{1}H NMR spectra were obtained on a Bruker ACE200 spectrometer using various deuterated solvents as internal references. ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker AM400 spectrometer using 85% H_3PO_4 or Ph_2Se_2 in $CDCl_3$ (+461 ppm relative to Me_2Se) as the external reference.

Preparation of $Pt(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$). A solution of $Pt(PPh_3)_2(CH_2{=}CH_2)$ (0.310 g, 0.415 mmol) in toluene (20 mL) at 0 °C was added dropwise, via cannula, to a stirred solution of 1,5-$Ph_4P_2N_4Se_2$ (0.243 g, 0.415 mmol) in toluene (20 mL) at 0 °C. The yellow solution became orange and then golden yellow. After 30 min at 0 °C, the reaction mixture was stored at −20 °C for 1 day to give a bright yellow precipitate, which was isolated via filter cannula, dried under vacuum, and identified as $Pt(PPh_3)_2$(1,5-$Ph_4P_2P_2N_4Se_2$) (0.38 g, 0.29 mmol, 70% yield). Analytically pure yellow crystals were obtained by layering a CH_2Cl_2 solution with hexanes at 0 °C. Anal. Calcd for $C_{60}H_{50}N_4P_4PtSe_2$: C, 55.26; H, 3.87; N, 4.30. Found: C, 55.50; H, 3.98; N, 4.57. ^{31}P NMR (in CH_2Cl_2): δ 17.6 [s, Ph_3P, ^1J(P–Pt) = 2980 Hz, ^2J(P–Se) = 140 Hz], 46.8 ppm [s, Ph_2P, ^3J(P–Pt) = 424 Hz, ^2J(P–Se) = 71 Hz]. ^{77}Se NMR (in CH_2Cl_2): δ 833 ppm [$A_2BB'M$ multiplet, ^2J(Ph_2P–Se) = 71 Hz, ^2J(Ph_3P–Se) = 137 Hz, ^2J(Ph_3P–Se) = 28 Hz]. IR (cm^{-1}): 1437 (s), 1114 (m), 1104 (m), 1057 (w), 1039 (m), 1005 (m), 974 (s), 948 (s), 755 (w), 749 (w), 693 (s), 580 (w), 533 (s), 510 (s).

Preparation of $Pd(PPh_3)_2$(1,5-$Ph_4P_2N_2Se_2$). A solution of 1,5-$Ph_4P_2N_4Se_2$ (0.530 g, 0.907 mmol) in toluene (35 mL) at 0 °C was added dropwise, via cannula, to a stirred slurry of $Pd(PPh_3)_4$ (1.048 g, 0.907 mmol) in toluene (35 mL) at 0 °C. The solution changed color from yellow to red after 30 min at 0 °C. After 1 day at −20 °C, the red precipitate was isolated via filter cannula, dried under vacuum, and identified as $Pd(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$) (1.00 g, 0.823 mmol, 91% yield). Anal. Calcd for $C_{60}H_{50}N_4P_4PdSe_2$: C, 59.29; H, 4.16; N, 4.61. Found: C, 59.13; H, 4.21; N, 4.50. ^{31}P NMR (in CH_2Cl_2): δ 25.1 [t, Ph_3P, ^4J(Ph_3P–PPh_2) = 24 Hz, ^2J(P–Se) = 88 Hz], 59.1 ppm [t, Ph_2P, ^4J(Ph_2P–PPh_3) = 24 Hz, ^2J(P–Se) = 81 Hz]. ^{77}Se NMR (in CH_2Cl_2): δ 855 ppm [$A_2BB'M$ multiplet, ^2J(Ph_2P–Se) = 78 Hz, ^2J(Ph_3P–Se) = 90 Hz]. Not all ^{31}P–^{77}Se couplings were resolved in the ^{77}Se resonance.

Preparation of $[Pt(PPh_3)$(1,5-$Ph_4P_2N_4Se_2)]_2$. A slurry of $Pt(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$) (0.122 g, 0.094 mmol) was heated at reflux in toluene (30 mL) for 2 h. The yellow slurry slowly dissolved (40 min) to give an orange solution, which deposited a yellow precipitate after 2 h. The product was isolated via filter cannula at room temperature, recrystallized from CH_2Cl_2, and dried under vacuum to give $[Pt(PPh_3)$(1,5-$Ph_4P_2N_4Se_2)]_2\cdot CH_2Cl_2$ (0.095 g, 0.044 mmol, 94% yield). Anal. Calcd for $C_{84}H_{70}N_8P_6Pt_2Se_4\cdot CH_2Cl_2$: C, 47.68; H, 3.35; N, 5.17. Found: C, 47.31; H, 3.36; N, 4.89. ^{31}P NMR (in THF): at −89 °C, δ 5.8 [s, Ph_3P, ^1J(P–Pt) = 3789 Hz], 64.5 [s, Ph_2P], 27.4 ppm [s, Ph_2P]; at +15 °C, δ 5.8 [s, Ph_3P, ^1J(P–Pt) = 3789 Hz], 45.7 ppm [s, Ph_2P]. IR (cm^{-1}): 1305 (s), 1110 (m), 1099 (m), 1036 (m), 1026 (m), 970 (s), 955 (s), 871 (m), 740 (m), 697 (m), 691 (m), 652 (w), 622 (w), 592 (w), 535 (w), 523 (w), 517 (w).

Preparation of $[Pd(PPh_3)$(1,5-$Ph_4P_2N_4Se_2)]_2$. A slurry of $Pd(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$) (0.881 g, 0.725 mmol) in toluene (50 mL) was heated at reflux for 2 h. The red slurry dissolved slowly (25 min) to give a bright red solution, which deposited a red precipitate after 2 h. The product was isolated via filter cannula at room temperature, recrystallized from CH_2Cl_2, and identified as $[Pd(PPh_3)$(1,5-$Ph_4P_2N_4Se_2)]_2\cdot CH_2Cl_2$ (0.65 g, 0.33 mmol, 91% yield). Anal. Calcd for $C_{84}H_{70}N_8P_6Pd_2Se_2\cdot CH_2Cl_2$: C, 51.27; H, 3.65; N, 5.63. Found: C, 51.09; H, 3.43; N, 5.85. ^{31}P NMR (in CH_2Cl_2): δ 21.0 [s, Ph_3P], 39.3 ppm [s, Ph_2P]. IR (cm^{-1}): 1435 (s), 1111 (m), 1102 (m), 1021 (s), 961 (s), 880 (s), 744 (w), 693 (s), 652 (w), 609 (w), 593 (w), 540 (w), 530 (m), 511 (w).

Preparation of $PtCl_2(PEt_3)$(1,5-$Ph_4P_2N_4Se_2$). A solution of 1,5-$Ph_4P_2N_4Se_2$ (0.517 g, 0.885 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added via cannula to a solution of $[PtCl_2(PEt_3)]_2$ (0.340 g, 0.443 mmol) in CH_2Cl_2 (30 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 20 min. The ^{31}P NMR spectrum of the reaction mixture indicated the presence of both $PtCl_2(PEt_3)$(1,5-$Ph_4P_2N_4Se_2$) and $[PtCl_2(PEt_3)]_2$(1,5-$Ph_4P_2N_4Se_2$) in the approximate molar ratio 3.4:1, together with a small amount of unreacted 1,5-$Ph_4P_2N_4Se_2$. Transparent yellow crystals of $PtCl_2(PEt_3)$(1,5-$Ph_4P_2N_4Se_2$) were obtained from a CH_2Cl_2 solution layered with hexanes after several days at 0 °C. Anal. Calcd for $C_{30}H_{35}Cl_2N_4P_3PtSe_2$: C, 37.20; H, 3.65; N, 5.79. Found: C, 37.93; H, 3.75; N, 5.49. ^{31}P NMR (in CH_2Cl_2): δ 114.3 [dd, ^3J(Ph_2P–PEt_3) = 5 Hz, ^4J(Ph_2P–PPh_2) = 16 Hz, ^2J(Ph_2P–Pt) = 94 Hz], 109.3 [d, ^4J(Ph_2P–PPh_2] = 16 Hz, ^2J(Ph_2P–Se) = 93 Hz], 2.4 ppm [d, ^3J(Et_3P–PPh_2) = 5 Hz, ^1J(Et_3P–Pt) = 3619 Hz]. ^{77}Se NMR (in CH_2Cl_2): δ 1270 [pseudo-t, ^2J(Se–PPh_2) = 93 and 85 Hz], 1258 ppm [dd, ^2J(Se–PPh_2) = 96 Hz, ^2J(Se–PPh_2) = 60 Hz].

Preparation of $[PtCl_2(PEt_3)]_2$(1,5-$Ph_4P_2N_4Se_2$). A solution of 1,5-$Ph_4P_2Se_2$ (0.069 g, 0.118 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added via cannula to a solution of $[PtCl_2(PEt_3)]_2$ (0.091 g, 0.118 mmol) in CH_2Cl_2 (5 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 10 min. The ^{31}P NMR spectrum of this solution revealed the presence of both $[PtCl_2(PEt_3)]_2$(1,5-$Ph_4P_2N_4Se_2$)] and $PtCl_2(PEt_3)$(1,5-$Ph_4P_2N_4Se_2$) in the approximate molar ratio 11.5:1. Transparent yellow crystals of the diadduct were obtained from a CH_2Cl_2 solution layered with hexanes after several days at 0 °C. Anal. Calcd for $C_{36}H_{50}Cl_4N_4P_4Pt_2Se_2$: C, 31.96; H, 3.73; N, 4.14. Found: C, 32.25; H, 3.91; N, 4.03. ^{31}P NMR (in CH_2Cl_2): δ 113.2 [s, ^2J(P–Se) = 89 Hz, ^2J(P–Se) = 69 Hz], 3.0 ppm [s, ^1J(Et_3P–Pt) = 3654 Hz]. ^{77}Se NMR (in CH_2Cl_2): δ 1337 ppm (m).

Preparation of $Pt(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$)$[PtCl_2(PEt_3)]$. A solution of $Pt(PPh_3)_2(CH_2{=}CH_2)$ (0.154 g, 0.206 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added via cannula to a solution of $PtCl_2(PEt_3)$(1,5-$Ph_4P_2N_4Se_2$) (0.200 g, 0.206 mmol) in CH_2CL_2 (10 mL) at −78 °C. The yellow solution immediately became red-brown. The product $Pt(PPh_3)_2$(1,5-$Ph_4P_2N_4Se_2$)$[PtCl_2(PEt_3)]$ was identified by ^{31}P NMR spectroscopy. Details are given under Results and Discussion.

Preparation of $PtCl(PEt_3)_2(Ph_4P_2N_4Se_2Ph)$. A yellow solution of $[Li[Ph_4P_2N_4Se_2Ph](THF)]_2$ was generated by the addition of a 1 M solution of phenyllithium in diethyl ether–cyclohexane (0.627 ml, 0.627 mmol) via syringe to a solution of 1,5-$Ph_4P_2N_4Se_2$ (0.336 g, 0.627 mmol) in THF (30 mL) at −78 °C, followed by warming the solution to room temperature for 15 min. This solution was then recooled to −78 °C and added via cannula to a slurry of *cis*-$PtCl_2(PEt_3)_2$ (0.315 g, 0.627 mmol) in THF (15 mL) at −78 °C. This mixture was allowed to warm to room temperature and stirred for a further 45 min to give an orange solution. The solvents were removed under vacuum, and the residue was extracted with toluene (2 × 20 mL) to remove LiCl. Removal of solvent from the filtered toluene extracts under vacuum gave *trans*-$PtCl(PEt_3)_2(Ph_4P_2N_4Se_2Ph)$ as a yellow-orange solid (0.64 g, 0.60 mmol, 95% yield), which was recrystallized by layering a THF solution with hexanes at 0 °C. Anal. Calcd for $C_{38}H_{45}ClN_4P_4PtSe_2$: C, 42.64; H, 4.25; N, 5.24. Found: C, 42.62; H, 4.49; N, 5.82. The variable-temperature ^{31}P NMR spectra of this product are discussed in the next section.

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Table I. ^{31}P and ^{77}Se NMR Data for $M(PPh_3)_2(1,5\text{-}Ph_4P_2N_4Se_2)$[a]

PPh$_3$		PPh$_2$			
$\delta(^{31}P)$[b]	J	$\delta(^{31}P)$[b]	J	$\delta(^{77}Se)$[c]	J[d]
		2a (M = Pt)			
17.6	$^1J(P_3\text{–}Pt) = 2980$ $^2J(P_4\text{–}Se_5) = 140$	46.8	$^3J(P_1\text{–}Pt) = 424$ $^2J(P_1\text{–}Se_5) = 71$	833[e]	$^2J(P_1\text{–}Se_5) = 71$ $^2J(P_2\text{–}Se_5) = 71$ $^2J(P_3\text{–}Se_3) = 28$ $^2J(P_4\text{–}Se_5) = 137$ $^2J(P_3\text{–}P_4) = 8$
		2b (M = Pd)			
25.1	$^4J(P_1\text{–}P_4) = 24$ $^2J(P_4\text{–}Se_5) = 88$	59.1	$^4J(P_1\text{–}P_4) = 24$ $^2J(P_1\text{–}Se_5) = 81$	855[e,f]	$^2J(P_1\text{–}Se_5) = 78$ $^2J(P_2\text{–}Se_5) = 78$ $^2J(P_4\text{–}Se_5) = 90$ $^4J(P_1\text{–}P_4) = 24$ $^4J(P_1\text{–}P_3) = 24$ $^4J(P_2\text{–}P_3) = 24$ $^4J(P_2\text{–}P_4) = 24$

[a] Chemical shifts are in ppm, and coupling constants are in Hz. [b] Relative to 85% H_3PO_4. [c] Relative to Me_2Se (0 ppm). [d] Obtained from the spin simulation of the ^{77}Se NMR spectra.[13] [e] An $A_2BB'M$ multiplet (see text). [f] The coupling constants $^2J(P_3\text{–}Se_5)$ and $^2J(P_3\text{–}P_4)$ for **2b** could not be obtained unambiguously because the experimental spectrum did not clearly display all the lines of the resonance.

Results and Discussion

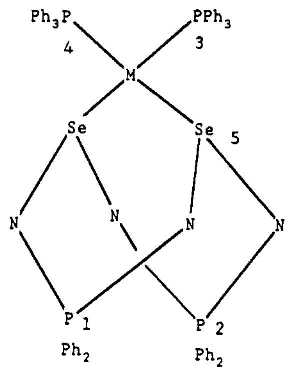
Preparation and Spectroscopic Characterization of $M(PPh_3)_2$-$(1,5\text{-}Ph_4P_2N_4Se_2)$ (2a, M = Pt; 2b, M = Pd). The reaction of $1,5\text{-}Ph_4P_2N_4Se_2$ with either $Pt(PPh_3)_2(CH_2{=}CH_2)$ or $Pd(PPh_3)_4$ proceeds readily in toluene at 0 °C according to eq 1. Compounds

$$1,5\text{-}Ph_4P_2N_4Se_2 + M(PPh_3)_2L \xrightarrow[\text{or } -2PPh_3]{-C_2H_4} M(PPh_3)_2(1,5\text{-}Ph_4P_2N_4Se_2) \qquad (1)$$

$$\begin{array}{ll} (M = Pt,\ L = C_2H_4) & 2a,\ M{=}Pt \\ (M = Pd,\ L = 2PPh_3) & 2b,\ M{=}Pd \end{array}$$

2a and **2b** were isolated as yellow and red solids in 71% and 91% yields, respectively. These complexes are moisture-sensitive, but solid samples can be stored for several months under nitrogen at −20 °C without decomposition.

The η^2-Se,Se′ bonding mode for **2a** and **2b** was established on the basis of ^{31}P and ^{77}Se spectroscopic data (see Table I). The spin-labeling scheme is indicated as follows:



2a, M = Pt
2b, M = Pd

The ^{31}P NMR spectrum of the platinum complex **2a** consists of two equally intense signals at 17.6 and 46.8 ppm, each with ^{195}Pt and ^{77}Se satellites, which can be assigned to the PPh$_3$ ligands and PPh$_2$ groups, respectively, from the magnitude of the ^{195}Pt–^{31}P coupling constants [*cf.* ^1J(Pt–P) = 2861 and ^3J(Pt–P) = 572 Hz for the sulfur analogue of **2a**].[2b] The four-bond *P*Ph$_3$–*P*Ph$_2$ coupling is not resolved. By contrast, the ^{31}P NMR spectrum of the palladium complex **2b** consists of two equally intense 1:2:1 triplets at 25.1 and 59.1 ppm, each with ^{77}Se satellites. The triplets arise from the four-bond PPh$_3$–PPh$_2$ coupling of 24 Hz. Thus the ^{31}P NMR data for **2a** and **2b** clearly indicate that the heterocyclic ligand is symmetrically bonded to the metal. The large shift of the resonance of the ring phosphorus atoms from 113.4 ppm in the ligand[5b] to 46.8 (**2a**) and 59.1 ppm (**2b**) in the complexes is indicative of insertion of the $M(PPh_3)_2$ fragment into the Se–Se bond.

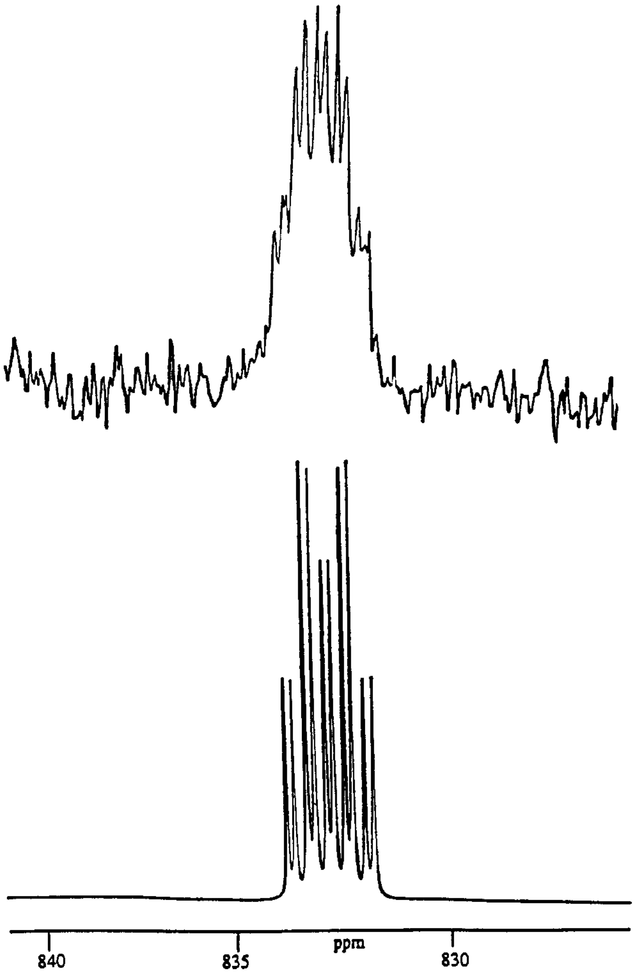


Figure 2. (a) Experimental (top) and (b) simulated (bottom) ^{77}Se NMR spectra of $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4Se_2)$ (**2a**).

As indicated in Figure 2a, the ^{77}Se NMR spectrum of **2a** displays a multiplet centered at 833 ppm characteristic of an $A_2BB'M$ spin system [where M is a ^{77}Se atom (natural abundance 7.7%) in the most abundant isotopomer for which the two PPh$_3$ phosphorus atoms are magnetically *inequivalent* but the two ring (Ph$_2$P) phosphorus atoms are magnetically *equivalent*]. The simulation of this spectrum[13] yielded the coupling constants listed

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(13) PANIC NMR simulation program supplied by Bruker.

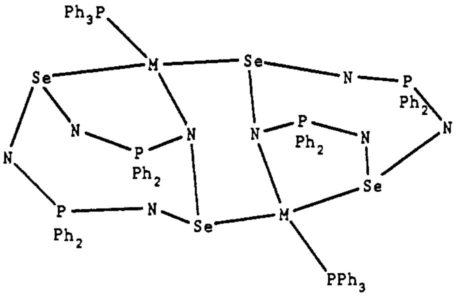
in Table I, and the simulated spectrum (Figure 2b) is in good agreement with the observed ^{77}Se NMR spectrum (Figure 2a). Furthermore, the coupling constants derived from the simulated ^{77}Se NMR spectrum are consistent with those obtained from the ^{31}P NMR spectrum. The ^{77}Se NMR spectrum of **2b** also displays a multiplet characteristic of an $A_2BB'M$ spin system, which was successfully simulated to give the coupling constants listed in Table I.[13] Thus the NMR data for **2a** and **2b** are consistent with an η^2-Se,Se′ bonding mode analogous to that established by X-ray crystallography for the corresponding η^2-S,S′ complex $Pt(PPh_3)_2$-$(1,5\text{-}Ph_4P_2N_4S_2)$.[2b] Although X-ray-quality crystals of **2a** were obtained and a data collection was completed, the structure could not be solved.[14]

Preparation and Spectroscopic Characterization of $[M(PPh_3)(1,5\text{-}Ph_4P_2N_4Se_2)]_2$ (3a, M = Pt; 3b, M = Pd). When the monometallic complexes **2a** and **2b** are heated at reflux in toluene for 2 h, the dimeric complexes **3a** and **3b** are obtained as yellow and red solids, respectively, via the loss of a triphenylphosphine ligand. The process can be reversed by the addition of triphenylphosphine to a CH_2Cl_2 solution of **3a** or **3b** (eq 2).

$$2M(PPh_3)_2(1,5\text{-}Ph_4P_2N_4Se_2) \underset{+2PPh_3}{\overset{-2PPh_3}{\rightleftarrows}} [M(PPh_3)(1,5\text{-}Ph_4P_2N_4Se_2)]_2 \qquad (2)$$

3a, M = Pt
3b, M = Pd

The ^{31}P NMR spectroscopic data for **3a** and **3b** suggest that they have structures similar to that of the sulfur analogue $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$;[3] *i.e.*, each $P_2N_4Se_2$ ring acts as a chelating (N, Se) ligand toward one metal and as a bridging ligand through the other selenium atom toward the second metal.



3a, M = Pt
3b, M = Pd

The ^{31}P NMR spectrum of **3a** in CH_2Cl_2 at -89 °C exhibits two equally intense singlets at 27.4 and 64.5 ppm, as expected for the inequivalent PPh_2 groups of the $P_2N_4Se_2$ rings and a singlet with ^{195}Pt satellites for the PPh_3 ligands. As the temperature of the solution is increased, the two PPh_2 singlets broaden, coalesce, and eventually give rise to a new singlet at 45.7 ppm at +15 °C. These changes are reversible upon recooling the solution to -89 °C. The coalescence temperature is -31 °C, which corresponds to an interconversion barrier of 9.5 ± 0.2 kcal mol^{-1};[15] *cf.* 10.2 ± 0.2 kcal mol^{-1} for $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$.[3] It is proposed that a [1,3]-metallotropic rearrangement involving a pendular movement of the Ph_3P–Pt pivot between vicinal nitrogen atoms and across a selenium atom of a $P_2N_4Se_2$ ring accounts for the observed dynamic exchange of PPh_2 groups on the NMR time scale.[16] The resonance for the Ph_3P ligand in **3a** is essentially invariant over the temperature range -90 to +15 °C. The $^1J(^{195}Pt\text{–}^{31}P)$ value of 3789 Hz in **3a** is much larger than the value of 2980 Hz observed for the same interaction in the η^2-Se,Se′ complex **2a**, probably due to the weaker *trans* influence of nitrogen in the dimer **3a** compared to selenium in **2a**.

The ^{31}P NMR spectrum of **3b** at +23 °C showed a singlet at 21.0 ppm for the rapidly exchanging PPh_2 groups and a singlet at 39.3 ppm for the PPh_3 ligands. However, the slow-exchange limit for **3b** was not reached at -90 °C, indicating that the energy barrier for the [1,3]-metallotropic rearrangement is significantly lower when platinum is replaced by palladium, as was found for the corresponding complexes of $1,5\text{-}Ph_4P_2N_4S_2$.[2b]

η^1-N Platinum and Palladium Complexes of $1,5\text{-}Ph_4P_2N_4Se_2$. The addition of $1,5\text{-}Ph_4P_2N_4Se_2$ to the chloro-bridged dimers $[MCl_2(PEt_3)]_2$ (M = Pt, Pd) in a 2:1 molar ratio in CH_2Cl_2 results in cleavage of the chloro bridges and the production of 1:1 adducts. The 1:2 adduct can also be obtained for M = Pt by appropriate adjustment of the stoichiometry (eq 3).

$$x\,1,5\text{-}Ph_4P_2N_4Se_2 + [MCl_2(PEt_3)]_2 \longrightarrow [MCl_2(PEt_3)]_n(1,5\text{-}Ph_4P_2N_4Se_2) \qquad (3)$$

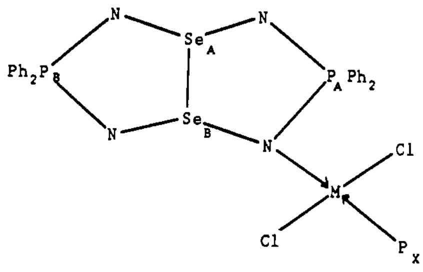
(*x* = 1 or 2) (M = Pt,Pd)

(*x* = 1, *n* = 2)
(*x* = 2, *n* = 1)

4a, M = Pt, *n* = 1
4b, M = Pd, *n* = 1
5, M = Pt, *n* = 2

Both platinum adducts **4a** and **5** are air-sensitive, yellow solids which, in common with $1,5\text{-}Ph_4P_2N_4Se_2$ itself,[5b] dissolve readily in CH_2Cl_2 at 23 °C to yield deep lime green solutions that become yellow at -20 °C.

The ^{31}P and ^{77}Se NMR spectra of **4a** are consistent with a structure in which the platinum(II) atom is attached to one of the nitrogen atoms of the $P_2N_4Se_2$ ring with retention of the cross-ring Se–Se bond.



4a, M = Pt
4b, M = Pd

The ^{31}P NMR spectrum of **4a** displays three resonances at 2.4, 109.3, and 114.3 ppm, which appear as a doublet $[^3J(P_X\text{–}P_A) = 5\ \text{Hz}]$, a doublet $[^3J(P_B\text{–}P_A) = 16\ \text{Hz}]$, and a doublet of doublets $[^4J(P_A\text{–}P_B) = 16\ \text{Hz};\ ^3J(P_A\text{–}P_X) = 5\ \text{Hz}]$, respectively. The low-frequency doublet is readily assigned to the PEt_3 ligand since it exhibits a large coupling to Pt $[^1J(P_X\text{–}Pt) = 3619\ \text{Hz}]$. In view of the mutual four-bond coupling of 16 Hz observed for P_A and P_B, the doublet of doublets at 114.3 ppm must be attributable to P_A while the doublet at 109.3 ppm is assigned to P_B. The fact that the chemical shifts of these two resonances are close to that of the free ligand ($\delta(^{31}P)$ 113.4 ppm) is strong evidence for the retention of the cross-ring Se–Se bond in the adduct **4a**. The ^{77}Se NMR spectrum of **4a** displays two resonances at 1270 and 1258 ppm for the inequivalent selenium atoms Se_A and Se_B, respectively. The former appears as a pseudotriplet (overlapping doublet of doublets) due to the near equality of the coupling to inequivalent heterocyclic phosphorus atoms $[^2J(^{31}P\text{–}^{77}Se) = 93$ and 85 Hz]. The signal at 1258 ppm is a well-resolved doublet of doublets with $^2J(^{31}P\text{–}^{77}Se) = 96$ and 60 Hz. The smaller coupling may be due to the interaction with P_A which occurs through the nitrogen atom bonded to platinum. Thus the ^{31}P and ^{77}Se NMR data for **4a** are consistent with the proposed η^1-N-bonded structure.

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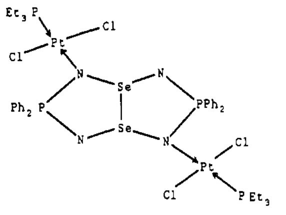
(14) Yellow hexagonal crystals of **1a** were obtained by layering a dichloromethane solution with hexane at 0 °C in a crystallization tube (25 cm long; 0.5-cm inner diameter, narrowing to 0.2 cm at the midpoint).

(15) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

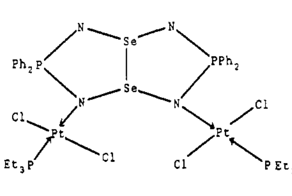
(16) For a pictorial representation of this [1,3]-metallotropic rearrangement, see Scheme I in ref 3.

The palladium adduct **4b** decomposes slowly in solution and could only be characterized by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **4b** also displays three signals. A doublet at 37.9 ppm [$^{3}J(P_X\text{–}P_A) = 6$ Hz] due to the PEt_3 ligand, a second doublet a 109.5 ppm [$^{4}J(P_B\text{–}P_A) = 12$ Hz, $^{2}J(P_B\text{–}Se) = 89$ Hz] attributed to the remote heterocyclic ring phosphorus atom P_B, and a doublet of doublets at 115.3 ppm [$^{3}J(P_A\text{–}P_X) = 6$ Hz, $^{4}J(P_A\text{–}P_B) = 12$ Hz] assigned to the ring phosphorus atom P_A adjacent to the coordinated palladium. These data suggest that **4b** has a structure similar to that of **4a**.

The ^{31}P NMR spectrum of the diadduct **5** exhibits two singlets at 3.0 and 113.2 ppm. The former exhibits platinum satellites with $^{1}J(^{31}P\text{–}^{195}Pt) = 3654$ Hz and is readily assigned to the equivalent PEt_3 ligands. The resonance at 113.2 ppm displays two sets of selenium satellites with $^{2}J(^{31}P\text{–}^{77}Se) = 69$ and 89 Hz and is attributed to the equivalent PPh_2 groups of the $P_2N_4Se_2$ ring. The high frequency of this resonance strongly implies the retention of the Se–Se bond. Thus the ^{31}P NMR data rule out a structure in which the two $PtCl_2(PEt_3)$ groups of **5** are attached to nitrogens which are bonded to the same ring phosphorus atom, but they do not distinguish between a distal arrangement of $PtCl_2(PEt_3)$ groups and the "vicinal" isomer.



5 (distal isomer)



5 ('vicinal' isomer)

The ^{77}Se NMR spectrum of the vicinal isomer should exhibit two resonances for the inequivalent selenium atoms. However, the ^{77}Se NMR spectrum of **5** displays one resonance with a five-line pattern, centered at 1337 ppm, characteristic of an AA′X spin system, as expected for the most abundant isotopomer with one ^{77}Se nucleus. The sum of the two phosphorus–selenium coupling constants, as obtained from the separation of the two outer lines of the resonance, is $|^{2}J(P_A\text{–}Se) + {}^{2}J(P_{A'}\text{–}Se)| = 160$ Hz, which is in good agreement with the sum of the $^{2}J(P\text{–}Se)$ values of 69 and 89 Hz observed in the ^{31}P NMR spectrum.

Thus the NMR data for **5** indicate a distal structure with retention of the Se–Se bond, and these conclusions have been confirmed by an X-ray structural determination. The structural parameters have been reported in the preliminary communication of this work, and only the main conclusions will be repeated here.[5a] The $PtCl_2(PEt_3)$ groups are attached to the $P_2N_4Se_2$ ring by relatively weak Pt–N bonds of 2.162(9) Å [*cf.* *d*(Pt–N) = 2.005(8) and 2.062(7) Å in $[Pt(Se_2N_2)(PPh_3)]_2$.[17]] Consistently, the $P_2N_4Se_2$ ligand in **5** or **4a** is readily displaced by THF to give *trans*-$[PtCl_2(PEt_3)(\eta^1\text{-THF-}O)]$. The Se–Se distance in **5** is 2.594(2) Å. On the basis of the observation that the formation of the N-bonded adduct $PtCl_2(PEt_3)(1,5\text{-}Ph_4P_2N_4S_2)$ results in a contraction of the S–S distance from 2.528(1) Å in 1,5-$Ph_4P_2N_4S_2$[18] to *ca.* 2.46(1) Å in the platinum(II) adduct,[1,19] we tentatively estimate a value of 2.65–2.70 Å for the Se–Se interaction in **5**. This can be compared with the values of 2.748(9) and 2.84(1) Å found for the corresponding interactions in Se_4N_4[20] and Se_8^{2+}[21] and a calculated value of 2.88 Å.[22]

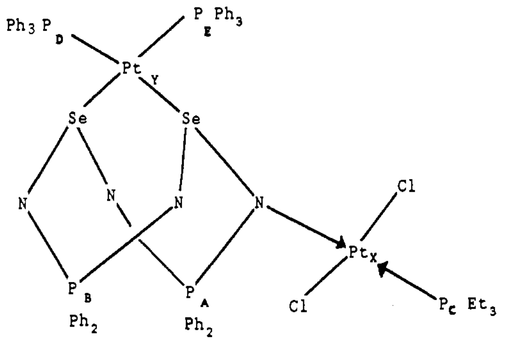
Table II. ^{31}P NMR Data for $Pt(PPh_3)_2(1,5\text{-}R_4P_2N_4E_2)[PtCl_2(PEt_3)]$

NMR param[a]	E = S, R = Me[b]	E = S, R = Et[b]	E = Se, R = Ph (6)[c]
$\delta(P_A)$	47.7	58.2	43.8 (ddd)
$\delta(P_B)$	50.1	60.3	48.0 (d)
$\delta(P_C)$	−3.6	−1.6	−2.9 (d)
$\delta(P_D)$	14.4	16.8	15.3[d]
$\delta(P_E)$	12.3	14.2	17.0[d]
$^{4}J(P_A\text{–}P_B)$	34	30	16
$^{3}J(P_A\text{–}P_C)$	9	11	8
$^{4}J(P_A\text{–}P_E)$	7	6	8
$^{2}J(P_D\text{–}P_E)$	27	25	29
$^{3}J(P_A\text{–}Pt_Y)$	388	377	242
$^{3}J(P_B\text{–}Pt_Y)$	569	594	523
$^{1}J(P_D\text{–}Pt_Y)$	3057	3008	3022
$^{1}J(P_E\text{–}Pt_Y)$	2816	2800	3005
$^{1}J(P_C\text{–}Pt_X)$	3478	3501	3481

[a] Chemical shifts are in ppm, and coupling constants are in Hz; the atom-labeling scheme for **6** is given in the text. [b] Data taken from ref 1. [c] This work; d = doublet; ddd = doublet of doublets of doublets. [d] See text for description of these resonances.

In a related study of platinum(II) adducts of 1,5-$Ph_4P_2N_4S_2$ (**1a**), ^{31}P NMR evidence for the formation of the triadduct $[PtCl_2(PEt_3)]_3(Ph_4P_2N_4S_2)$ was obtained.[1] However, attempts to generate a triadduct from the reaction of **5** with $[PtCl_2(PEt_3)]_2$ were unsuccessful.

Preparation and ^{31}P NMR Spectrum of the μ^2,η^3-Se,Se′,N Complex $Pt(PPh_3)_2(1,5\text{-}Ph_4P_2N_4Se_2)[PtCl_2(PEt_3)]$ (6). In view of the established presence of the Se–Se bond in **4a** and **5a**, it was of interest to determine whether η^2-Se,Se′ and η^1-N bonding modes can coexist in the same molecule. A solution of the monoadduct **4a** reacts with an equimolar amount of $Pt(PPh_3)_2(C_2H_4)$ in CH_2Cl_2 at −78 °C to give a red-brown product identified as **6** on the basis of ^{31}P NMR spectroscopy. This complex decomposes in solution after *ca.* 1 h. An attempt to prepare a μ^3,η^4-Se,Se′,N,N′ trimetallic complex by the reaction of **5a** with $Pt(PPh_3)_2(C_2H_4)$ was unsuccessful.



The ^{31}P NMR parameters for **6** are compared to those of related sulfur systems in Table II. The ^{31}P NMR spectrum displays five resonances as expected for the five chemically unique phosphorus atoms of **6**. The assignments of individual resonances were made by inspection of the coupling patterns. Two pairs of resonances are observed at 43.8 and 48.0 ppm and at 15.3 and 17.0 ppm, all of which exhibit platinum satellites. These resonances are readily assigned to PPh_2 and PPh_3 groups, respectively, on the basis of the magnitude of the $^{195}Pt\text{–}^{31}P$ coupling constants. The values of $^{3}J(^{195}Pt\text{–}^{31}P)$ are 242 and 523 Hz, while the $^{1}J(^{195}Pt\text{–}^{31}P)$ couplings are 3022 and 3005 Hz. The PPh_2 resonances at 43.8 and 48.0 ppm are assigned to P_A and P_B, respectively. The former

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(17) Kelly, P. F.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1990**, *9*, 1567.

(18) Burford, N.; Chivers, T.; Richardson, J. F. *Inorg. Chem.* **1983**, *22*, 1482.

(19) Parvez, M. Private communication.

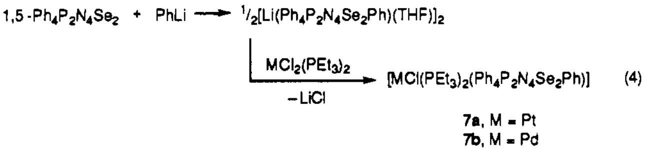
(20) Bärnighausen, H.; Volkman, T.; Jander, J. *Acta Crystallogr.* **1966**, *21*, 571.

(21) McMullen, R. K.; Prince, D. J.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 1749.

(22) A restricted Hartree–Fock (RHF) geometry optimization, at the 6-21* level, utilizing the Gaussian 92 program, was performed for the model compound 1,5-$H_4P_2N_4Se_2$. While the calculated P–N (1.601 Å) and Se–N (1.752 Å) distances are as expected for an unsaturated P–N–Se system, the computed transannular Se–Se distance of 2.881 Å is somewhat longer than predicted from the structural data for **5a**.

consists of a doublet of doublets of doublets [$^4J(P_A–P_B)$ = 16 Hz, $^3J(P_A–P_C)$ = 8 Hz, $^4J(P_A–P_E)$ = 8 Hz] while the latter is a doublet [$^4J(P_B–P_A)$ = 16 Hz]. The P_B signal also displays two sets of ^{77}Se satellites [$^2J(P_B–^{77}Se)$ = 73 and 78 Hz], but these couplings cannot be assigned to individual Se atoms. The two PPh_3 resonances give rise to an AB pattern [$^2J(P_D–P_E)$ = 29 Hz] distorted by the coupling $^4J(P_E–P_A)$ = 8 Hz.

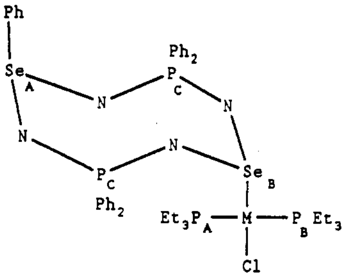
Preparation, Spectroscopic Characterization, and Fluxional Behavior of $PtCl(PEt_3)_2(1,5\text{-}Ph_4P_2N_4Se_2Ph)$ (7a). When a solution of 1,5-$Ph_4P_2N_4Se_2$ (**1b** (R = Ph)), in THF at –78 °C is treated with an equimolar amount of phenyllithium and the mixture is allowed to react at 23 °C for 15 min, the ^{31}P NMR singlet at 113.4 ppm for **1b** (R = Ph) disappears completely and is replaced by a broad singlet at 28.8 ppm. This behavior is analogous to that observed for the corresponding sulfur system **1a** (R = Ph), for which variable-temperature ^{31}P NMR spectra indicate the formation of $[Li(Ph_4P_2N_4S_2Ph)(THF)]_2$, which exhibits fluxional behavior.[4b] Thus it is reasonable to assume that the reaction of phenyllithium with **1b** (R = Ph) produces a solution of $[Li(Ph_4P_2N_4Se_2Ph)(THF)]_2$.[23] The reaction of this solution with $MCl_2(PEt_3)_2$ (M = Pt, Pd) in THF at –78 °C yields **7a** and **7b** (eq 4).



$$1{,}5\text{-}Ph_4P_2N_4Se_2 + PhLi \longrightarrow {}^1/_2[Li(Ph_4P_2N_4Se_2Ph)(THF)]_2 \xrightarrow[-LiCl]{MCl_2(PEt_3)_2} [MCl(PEt_3)_2(Ph_4P_2N_4Se_2Ph)] \quad (4)$$

7a, M = Pt
7b, M = Pd

Complexes **7a** and **7b** are obtained as yellow-orange, moisture-sensitive solids in essentially quantitative yields. The platinum complex **7a** can be recrystallized from THF–hexane at 0 °C, but the palladium compound **7b** decomposes in solution after 30 min and thus could only be identified by ^{31}P NMR spectroscopy.[24]



7a, M = Pt
7b, M = Pd

The ^{31}P NMR spectrum of **7a** in toluene-d_8 at –84 °C shows three resonances at 14.2, 20.3, and 36.0 ppm. The last resonance is a singlet with ^{195}Pt satellites [$J(^{31}P–^{195}Pt)$ = 362 Hz] and couplings to the inequivalent selenium atoms of $J(^{31}P–^{77}Se)$ = 57 and 41 Hz. Thus this signal is attributed to the two equivalent phosphorus atoms, P_C, of the heterocyclic ring. The two resonances at 14.2 and 20.3 ppm appear as an AB quartet with a mutual two-bond coupling of 387 Hz and platinum satellites with $^1J(^{31}P–^{195}Pt)$ = 2726 and 2540 Hz typical for PR_3 ligands *trans* to each other in a platinum(II) complex.[25] Thus these two resonances are assigned to the inequivalent phosphorus atoms, P_A and P_B, respectively, assuming a structure similar to that established by X-ray crystallography for the sulfur analogue *trans*-$PdCl(PEt_3)_2(Ph_4P_2N_4S_2Me)$.[4a] When the temperature of the solution of **7a** in toluene-d_8 is raised gradually, the AB quartet collapses, with a coalescence temperature of *ca.* –14 °C, until at 31 °C a sharp singlet is observed at 16.8 ppm with $^1J(^{31}P–^{195}Pt)$ = 2636 Hz. These changes in the ^{31}P NMR spectra of **7a** with temperature were found to be reversible. Thus the PEt_3 ligands must be involved in a two-site exchange process which is rapid on the NMR time scale at room temperature. We propose that this process involves a simple rotation of the $P_2N_4Se_2$ ligand about the Pt–Se bond. A similar mechanism has been suggested to explain the fluxional behavior of the sulfur analogues depicted in structure e of Figure 1.[4b]

The ^{77}Se NMR spectrum of **7a** at 0 °C displays two resonances, one of which appears as a 1:2:1 triplet at 894 ppm with $^2J(^{77}Se–^{31}P)$ = 57 Hz. This resonance is assigned to Se_A. The second signal is a multiplet at 879 ppm, which is assigned to Se_B. The coupling constants of this resonance could not be resolved, presumably due to the rapid exchange of PEt_3 ligands that is occurring at 0 °C. Unfortunately, **7a** was not sufficiently soluble to obtain a ^{77}Se NMR spectrum at the slow-exchange limit.

In order to determine the thermodynamic parameters for the fluxional process exhibited by **7a**, the rate constants k_r were determined at a series of temperatures by computer line shape fitting of the variable-temperature ^{31}P NMR spectra using the DNMR program of Kleier and Binsch.[26] The energy of activation for the dynamic exchange of phosphorus nuclei, E_a, was obtained from the slope of an Arrhenius plot [$\ln(k_r)$ vs $1/T$] while an Eyring plot [$\ln(k_r/T)$ vs $1/T$] enabled $\Delta H^{\circ *}$ and $\Delta S^{\circ *}$ to be calculated. Finally, the $\Delta G^{\circ *}$ value was determined from the Gibbs equation. The E_a for rotation about the Pt–Se bond in **7a** was found to be 39 kJ mol^{-1}, which is comparable to the values of 41–46 kJ mol^{-1} determined for the analogous sulfur systems.[4] The restricted rotation about the metal–chalcogen bond in these complexes at low temperatures is likely due to a combination of steric and π-bonding effects. Since the Pt–Se bond is probably longer than a Pt–S bond, steric effects should be less pronounced in **7a**. Thus the similar E_a values for the sulfur and selenium complexes may reflect stronger π-bonding for Pt–Se versus Pt–S. The values of the other thermodynamic parameters were $\Delta H^{\circ *}$ = 37 kJ mol^{-1}, $\Delta G^{\circ *}$ = 4.69 kJ mol^{-1}, and $\Delta S^{\circ *}$ = –33.1 J mol^{-1} K^{-1}. The inherent error in each thermodynamic parameter is at least ±10%.

Conclusions. The diphosphadiselenatetrazocine 1,5-$Ph_4P_2N_4Se_2$ exhibits all the coordination modes known for the corresponding sulfur system in platinum and palladium complexes, *viz.* η^1-N, η^2-Se,Se′, η^2-Se,N-μ,η^1-Se′, and μ^2,η^3-Se,Se′,N. In contrast to that of Se_4N_4, the integrity of the $P_2N_4Se_2$ ring is maintained in all cases and the structure of the initial product of the interaction of the heterocyclic ring with metallic reagents can be determined. In combination with ^{31}P NMR spectroscopy, ^{77}Se NMR spectroscopy provides useful structural information especially for the η^2-Se,Se′- and η^1-N-bonded complexes. The structural determination of a bis-η^1-N-bonded platinum(II) complex has confirmed the presence of a transannular Se–Se bond for the $P_2N_4Se_2$ ring, which had been inferred from ^{31}P NMR chemical shifts. The aryllithium derivative $[Li(Ph_4P_2N_4Se_2Ph)(THF)]_2$ which is readily generated as the lithium salt from 1,5-$Ph_4P_2N_4Se_2$ and phenyllithium, should be a versatile source of both metallic and nonmetallic derivatives of the $P_2N_4Se_2$ ring.

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Supplementary Material Available: A table of computer-generated rate constants and Eyring and Arrhenius plots for the ^{31}P exchange in **7a** (3 pages). Ordering information is given on any current masthead page.

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(23) In contrast to the behavior of 1,5-$Ph_4P_2N_4S_2$,[4b] the reactions of 1,5-$Ph_4P_2N_4Se_2$ with other organolithium reagents, *e.g.* MeLi and Bu^{t}Li, did not proceed cleanly as determined by ^{31}P NMR spectroscopy.

(24) **7b** $\delta(^{31}P)$ (in toluene-d_8, 23 °C): 17.5 (s) and 33.2 ppm (s), assigned to PEt_3 ligands, which are equivalent on the NMR time scale at this temperature, and the equivalent PPh_2 groups of the heterocyclic ring, respectively.

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