J. CHEM. SOC. DALTON TRANS. 1990

Preparation and Characterisation of $[Pt(SeSN_2)(PR_3)_2]$, $[Pt(Se_2N_2)(PR_3)_2]$, $[Pt(SeSN_2H)(PR_3)_2]BF_4$, and $[Pt(Se_2N_2H)(PR_3)_2]BF_4$

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Reaction of $[Se_2N_2S]_2Cl_2$, or $SeCl_4$–$[S_4N_3]Cl$, with $[PtCl_2(PR_3)_2]$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) in liquid ammonia gives complexes of the type $[Pt(SeSN_2)(PR_3)_2]$ (*ca.* 70% yield). Reaction of $SeCl_4$ with $[PtCl_2(PR_3)_2]$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) in liquid ammonia produces $[Pt(Se_2N_2)(PR_3)_2]$ in variable yield (*ca.* 24—74%). Treatment of $[Pt(SeSN_2)(PR_3)_2]$ or $[Pt(Se_2N_2)(PR_3)_2]$ with HBF_4 in tetrahydrofuran–benzene produces $[Pt(SeSN_2H)(PR_3)_2]BF_4$ or $[Pt(Se_2N_2H)(PR_3)_2]BF_4$ quantitatively according to ^{31}P n.m.r. spectroscopy (*ca.* 75% isolated). The identity of the complexes was established by ^{31}P n.m.r., i.r., mass spectra, and microanalyses. Proton-exchange reactions reveal increasing basicity in the series $[Pt(S_2N_2)(PR_3)_2] \approx [Pt(SeSN_2)(PR_3)_2]$, $[Pd(S_2N_2)(PR_3)_2]$, $[Pt(Se_2N_2)(PR_3)_2]$.

We have recently been studying the reactions of various sulphur nitrogen compounds with bis(phosphine) platinum dichlorides in liquid ammonia, and have synthesised a range of metal–sulphur–nitrogen heterocycles.[1–4] Ammonia is a useful solvent for these reactions because of the generation of soluble sulphur–nitrogen anions and the thermodynamically favourable loss of chlorine as ammonium chloride.

The synthesis and properties of $[Pt(S_2N_2)(PR_3)_2]$ (**1**) and $[Pt(S_2N_2H)(PR_3)_2]X$ (**2**) (PR_3 = PMe_3, PEt_3, $PPr^n{}_3$, PMe_2Ph, $PMePh_2$, PPh_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$; X = PF_6 or BF_4) are well established.[5,6] In the solid state (**2**) stacks into channels of anions and cations with significant intercation close contacts.[6] Partial substitution to form a selenium-substituted analogue of (**1**) and (**2**) has proved difficult by conventional 'wet' chemistry because of the limited number of Se–N[7] or Se–N–S[8] heterocycles known and the insolubility of the best characterised species the highly explosive Se_4N_4.[9] Equally, very few metal–selenium–nitrogen compounds have been made, largely due to the paucity of starting materials and their low solubility. However in a parallel study to this one involving a high-temperature reaction of Se_4N_4 with $[\{PtCl_2(PR_3)\}_2]$ small yields of $[Pt(Se_3N)Cl(PR_3)]$ and $[Pt(Se_2N_2H)Cl(PR_3)]$ have been obtained.[10] The only other report of a co-ordinated naked Se–N fragment is the reaction of Se_4N_4 with WCl_6 which produced $[\{WCl_4(NSeCl)\}_2]$ in moderate yield.[11]

The synthesis of sulphur/selenium–nitrogen heterocycles has proved difficult and only a handful are fully structurally characterised.[12,13] In this study we have used $[SeS_3N_3]_2[SeCl_6]$ which has also been formulated[8,14] as $[S_4N_3][Cl_2SeN-SeCl_2]$. To incorporate selenium into a metallocyclic ring, we have investigated the dissolution of various selenium and as well as the above selenium/sulphur–nitrogen compound in liquid ammonia and the subsequent reactivity of these solutions with $[PtCl_2(PR_3)_2]$. Here, we report the preparation of partially and fully selenated analogues of previously reported Pt–S–N compounds (**1**) and (**2**).

Experimental

All manipulations were performed under an inert atmosphere (N_2, Ar) in pre-dried solvents. The compounds $[PtCl_2(PR_3)_2]$, $[S_4N_3]Cl$, $[SeS_3N_3]_2[SeCl_6]$, and $[Se_2N_2S]_2Cl_2$ were prepared by literature methods.[14–16] Ammonia (B.O.C.), $SeCl_4$ (Fluka) and $HBF_4 \cdot 2Et_2O$ (Aldrich) were used as supplied. ^{31}P-$\{^1H\}$ N.m.r. spectra were obtained in $CDCl_3$ using a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to external 85% H_3PO_4 (some ^{31}P n.m.r. spectra were obtained on a Bruker 250 WM spectrometer at 101.2 MHz). I.r. spectra were recorded as pressed KBr discs using a Perkin-Elmer 1720X instrument, mass spectra on a Varian VG 2020 spectrometer in the electron impact (e.i.) and fast atom bombardment modes (f.a.b.). Elemental analyses were provided by the microanalytical service at Imperial College.

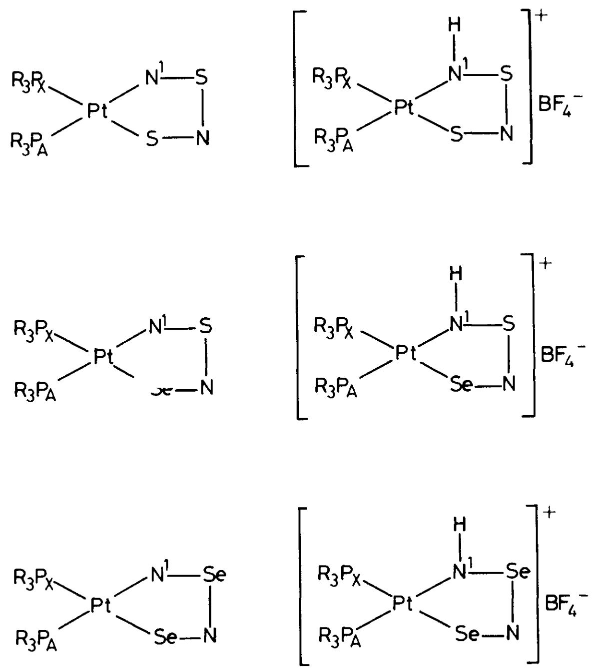
CAUTION: reactions involving $SeCl_4$ in liquid ammonia have been known to explode on evaporation of the ammonia either by the addition of water or by heating.

Preparations.—$[Pt(SeSN_2)(PR_3)_2]$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$). The same general procedures were carried out throughout, illustrated here for $[Pt(SeSN_2)(PEt_3)_2]$.

Method 1. The compound $[Se_2N_2S]_2Cl_2$ (0.049 g, 0.096 mmol) was added to liquid ammonia (5 cm^3) at −78 °C to generate a red-purple solution. The complex $[PtCl_2(PEt_3)_2]$ (0.050 g, 0.096 mmol) was added and the suspension stirred for 1 h at −78 °C. The solution was allowed to warm slowly to room temperature (*ca.* 0.5 h) with the ammonia being blown off under a stream of argon to leave a red-brown solid. Extraction into CH_2Cl_2 followed by filtration through a glass wool–Celite plug afforded a red solution which on layering with n-hexane (10 cm^3) gave red brown crystals of $[Pt(SeSN_2)(PEt_3)_2]$ (**3**) (0.040 g, 0.07 mmol, 73% yield). Alternatively, the product could also be obtained by preparative t.l.c. on silica gel using 95% CH_2Cl_2–5% MeOH as the eluant. The product was obtained from the red band at R_f = 0.15 by back extraction with CH_2Cl_2–MeOH and removal of the solvent *in vacuo*.

Method 2. The salt $[S_4N_3]Cl$ (0.040 g, 0.195 mmol) and $SeCl_4$ (0.200 g, 0.0910 mmol) were added as solids to liquid ammonia (15 cm^3) at −78 °C and the slurry stirred for 0.5 h. Solid $[PtCl_2(PR_3)_2]$ (0.15 mmol) was added and the mixture stirred for 0.5 h at −78 °C. The reaction was allowed to warm to room temperature (*ca.* 0.5 h) with the ammonia being blown off by a stream of nitrogen. Extraction with $CHCl_3$ (15 cm^3) afforded a red solution which was filtered through Celite and the product precipitated by the addition of hexane (30 cm^3), $[Pt(SeSN_2)(PR_3)_2]$ (0.011 mmol, *ca.* 70%).

Reaction of an equimolar mixture of $[S_4N_3]Cl$ and Se_2Cl_2 as above yielded *ca.* 60% $[Pt(S_2N_2)(PR_3)_2]$ and 40% $[Pt(SeSN_2)$-



$(PR_3)_2]$ according to ^{31}P n.m.r. spectroscopy. Similarly an equimolar mixture of $[S_4N_3]Cl$ and $SeOCl_2$ gave *ca.* 80% $[Pt(S_2N_2)(PR_3)_2]$ and 20% $[Pt(SeSN_2)(PR_3)_2]$.

$[Pt(SeSN_2H)(PR_3)_2]BF_4$ ($PR_3 = PEt_3, PMe_2Ph, PMePh_2, PPh_3$, *or* $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$). The general procedure is illustrated for $PR_3 = PMe_2Ph$.

To $[Pt(SeSN_2)(PMe_2Ph)_2]$ (0.035 g, 0.057 mmol) dissolved in tetrahydrofuran (thf)–benzene (5 cm^3 of each) was added three drops of $HBF_4 \cdot 2Et_2O$ (85% in ether, Aldrich). This solution was stirred at room temperature for 2 h by which time the solution had darkened from light orange to green-brown. The solution was reduced in volume *in vacuo*, dissolved in CH_2Cl_2 (5 cm^3), and layered with n-hexane to produce green crystals of $[Pt(SeSN_2)(PMe_2Ph)_2]$ by slow diffusion (0.028 g, 0.040 mmol, 71%, quantitative according to ^{31}P n.m.r. spectroscopy.

$[Pt(Se_2N_2)(PR_3)_2]$ ($PR_3 = PPh_3$ *or* $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$). The same general procedure was carried out for both phosphines, and is illustrated here for $PR_3 = \frac{1}{2}Ph_2PCH_2CH_2PPh_2$.

The compound $SeCl_4$ (0.60 g, 19.8 mmol) was carefully added in small amounts to liquid ammonia (30 cm^3) at −78 °C to produce a green solid and a pale orange solution. The complex $PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ (0.21 g, 3.15 mmol) was added and the suspension stirred for 2 h at −78 °C. The solution was allowed to warm to room temperature (*ca.* 0.5 h) with the ammonia being blown off under a stream of nitrogen to leave a green-orange solid. Extraction with CH_2Cl_2 (50 cm^3) and filtering through a Celite–glass wool plug afforded an orange solution which on layering with light petroleum (b.p. 60—80 °C (50 cm^3) produced orange crystals of compound (**15**) (0.184 g, 74%).

In the case of $PR_3 = PMe_2Ph, PMePh_2$, and PEt_3 the reaction was carried out on the same scale and procedure as above except the $SeCl_4$ was left in ammonia for 0.5 h at −35 °C before the $[PtCl_2(PR_3)_2]$ was added.

$[Pt(Se_2N_2H)(PR_3)_2]BF_4$. The same scale and procedure was used as above on $[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ (**15**) and on $[Pt(Se_2N_2)(PPh_3)_2]$ (**18**) to convert them into $[Pt(Se_2N_2H)(Ph_2PCH_2CH_2PPh_2)]BF_4$ (**20**) and $[Pt(Se_2N_2H)(PPh_3)_2]BF_4$ (**19**) respectively.

Reaction of $[SeS_3N_3]_2[SeCl_6]$ *with* $[PtCl_2(PMe_2Ph)_2]$.—The salt $[SeS_3N_3]_2[SeCl_6]$ (0.057 g, 0.078 mmol) was dissolved in liquid ammonia at −78 °C to generate a red solution. The complex $[PtCl_2(PMe_2Ph)_2]$ (0.06 g, 0.112 mmol) was added and the suspension stirred for 0.5 h at −78 °C. The ammonia was then allowed to evaporate as the reaction warmed to room temperature to leave a brown-red solid. The residue was extracted with $CDCl_3$ (3 cm^3), filtered through a Celite–glass wool plug and the ^{31}P n.m.r. spectrum obtained.

^{31}P *N.M.R. Exchange Reactions.*—All ^{31}P n.m.r. spectra were collected at room temperature in $CDCl_3$ for between 4 and 12 h in 10-mm n.m.r. tubes: (*a*) $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ (0.0140 g, 0.0215 mmol) and $[Pt(SeSN_2)(PMe_2Ph)_2]$ (0.0088 g, 0.0144 mmol); (*b*) $[Pt(SeSN_2H)(PMe_2Ph)_2]BF_4$ (0.0071 g, 0.0126 mmol) and $[Pt(S_2N_2)(PMe_2Ph)_2]$ (0.0079 g, 0.014 mmol); (*c*) $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ (0.0100 g, 0.0161 mmol) and $[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ (0.0126 g, 0.0160 mmol) (Figure 4); (*d*) $[Pt(Se_2N_2H)(PPh_3)_2]BF_4$ (0.0050 g, 0.005 mmol) and $[Pd(S_2N_2)(PMe_2Ph)_2]$ (0.0048 g, 0.010 mmol); (*e*) $[Pt(Se_2N_2)(PPh_3)_2]$ (0.006 95 g, 0.0077 mmol) and $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ (0.0050 g, 0.0077 mmol); and (*f*) $[Pt(SeSN_2H)(PPh_3)_2]$ (0.0040 g, 0.004 26 mmol) and $[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ (0.0050 g, 0.0064 mmol).

To the equilibrium (*a*) was added excess (five drops) of MeOD and the spectrum remeasured. To the equilibrium (*b*) was added excess of NEt_3 (three drops) and the spectrum remeasured.

Results and Discussion

Reaction of $[Se_2N_2S]_2Cl_2$ with *cis*-$[PtCl_2(PR_3)_2]$ in liquid ammonia produces $[Pt(SeSN_2)(PR_3)_2]$ (**3**)—(**7**) in high yield, *ca.* 70% [equation (1)]. Alternatively $[Pt(SeSN_2)(PR_3)_2]$ can

$$[PtCl_2(PR_3)_2] + \tfrac{1}{2}[Se_2N_2S]_2Cl_2 + NH_3 \longrightarrow [Pt(SeSN_2)(PR_3)_2] + SeCl_2 + NH_4Cl \quad (1)$$

be made by reaction of a mixture of $[S_4N_3]Cl$–$SeCl_4$ (or Se_2Cl_2) in ammonia with $[PtCl_2(PR_3)_2]$. This reaction is dependent on the $[S_4N_3]Cl$–$SeCl_4$ ratio. With lower amounts of $SeCl_4$ (ratio 1:1) a mixture of (**1**) and the monoselenated complex is obtained. With excess of $SeCl_4$ (ratio 1:5 or higher) the monoselenated compound is obtained with less than 3% of (**1**) and no diselenated compounds are formed. This may suggest that the reactive species is of the type $SeSN_2^{2-}$. In the case of $[PtCl_2(PMePh_2)_2]$, we have carried out the above reaction using 99% ^{15}N-labelled $[S_4N_3]Cl$ (with excess of $SeCl_4$ and a reaction time of 3 h) and observe 33% ^{15}N enrichment of the final product. In a similar reaction[3,17] to form $[Pt(S_2N_2)(PR_3)_2]$ from $[S_4N_3]Cl$ equivalent behaviour was observed. We hypothesise that in the $[S_4N_3]Cl$–$SeCl_4$ reactions the initial step is formation of a SN anion such as $S_3N_3^-$ which can exchange its nitrogen atoms for those of the ammonia. The SN anion is in equilibrium with short-chain species such as N_2S^{2-} and S_2N^+ which can themselves react to form mixed Se–S–N anions and cations (*e.g.* $SeSN_2^{2-}$ and $Se_2SN_2^{2+}$) which finally react to form (**3**)—(**7**). An important feature of the final products which has to be reconciled in any mechanism is that in the $SeSN_2^{2-}$ ligand we have only observed the isomer with metal-bound selenium. The formation of either an anion formed by chain lengthening of the N_2S^{2-} or the $Se_2SN_2^{2+}$ cation (made up of a Se–Se bond and an N_2S group) would be consistent with our observations. ^{14}N N.m.r. studies of this system are in progress.

Complexes (**3**)—(**7**) are easily protonated on the metal-bound nitrogen (N^1) by reaction of a slight excess of $HBF_4 \cdot 2Et_2O$ in thf–benzene [equation (2)].

Table 1. ^{31}P N.m.r. data *

	Compound	δ_X	δ_A	^1J_X	^1J_A	^2J	R
(1a)	$[Pt(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$	43.7	41.1	2 756	2 784	12	1.010
(1b)	$[Pt(S_2N_2)(PPh_3)_2]$	23.6	11.4	2 827	2 994	22	1.060
(2a)	$[Pt(S_2N_2H)(Ph_2PCH_2CH_2PPh_2)]BF_4$	44.6	38.6	2 734	3 162	10	1.157
(2b)	$[Pt(S_2N_2H)(PPh_3)_2]BF_4$	12.9	6.0	2 683	3 433	22	1.280
(3)	$[Pt(SeSN_2)(PEt_3)_2]$	18.2	0.7	2 800	2 799	22	1.000
(4)	$[Pt(SeSN_2)(PMe_2Ph)_2]$	−6.7	−27.1	2 837	2 799	24	0.987
(5)	$[Pt(SeSN_2)(PMePh_2)_2]$	9.4	−14.4	2 898	2 872	24	0.991
(6)	$[Pt(SeSN_2)(PPh_3)_2]$	22.5	7.0	2 948	2 996	22	1.016
(7)	$[Pt(SeSN_2)(Ph_2PCH_2CH_2PPh_2)]$	42.7	40.0	2 868	2 787	12	0.972
(8)	$[Pt(SeSN_2H)(PMe_2Ph)_2]BF_4$	−12.4	−30.1	2 687	3 227	24	1.201
(9)	$[Pt(SeSN_2H)(PMePh_2)_2]BF_4$	0.6	−18.3	2 719	3 277	24	1.205
(10)	$[Pt(SeSN_2H)(PPh_3)_2]BF_4$	15.0	1.4	2 697	3 300	22	1.224
(11)	$[Pt(SeSN_2H)(PEt_3)_2]BF_4$	12.0	−0.7	2 664	3 130	20	1.175
(12)	$[Pt(SeSN_2H)(Ph_2PCH_2CH_2PPh_2)]BF_4$	46.1	38.1	2 718	3 212	7	1.182
(13)	$[Pt(Se_2N_2)(PEt_3)_2]$	17.2	−2.9	2 801	2 685	22	0.958
(14)	$[Pt(Se_2N_2)(PMePh_2)_2]$	12.3	−15.8	2 842	2 709	24	0.953
(15)	$[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$	45.7	37.1	2 817	2 627	10	0.933
(16)	$[Pt(Se_2N_2)(PMe_2Ph)_2]$	−9.6	−31.0	2 822	2 690	24	0.953
(17)	$[Pd(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$	55.7	54.7			21	
(18)	$[Pt(Se_2N_2)(PPh_3)_2]$	26.8	6.2	2 963	2 778	24	0.938
(19)	$[Pt(Se_2N_2H)(PPh_3)_2]BF_4$	18.2	1.9	2 698	3 300	20	1.223
(20)	$[Pt(Se_2N_2H)(Ph_2PCH_2CH_2PPh_2)]BF_4$	48.9	36.2	2 698	3 094	10	1.156

* δ/p.p.m., J in Hz. Complexes **(1a)**, **(1b)** and **(2a)**, **(2b)** are included for comparison. $R = J_A/J_X$.

$$[Pt(SeSN_2)(PR_3)_2] + HBF_4 \longrightarrow [Pt(SeSN_2H)(PR_3)_2]BF_4 \quad (2)$$

Treatment of a liquid ammonia solution of $[SeS_3N_3]_2[SeCl_6]$ with $[PtCl_2(PR_3)_2]$ produces a mixture of two main products $[Pt(S_2N_2)(PR_3)_2]$ (*ca.* 80%) and $[Pt(SeSN_2)(PR_3)_2]$ (*ca.* 20%). This is consistent with the proposed structure[14] of $[SeS_3N_3]_2[SeCl_6]$ rather than $[S_4N_3][Cl_2SeNSeCl_2]$. The latter structure would be expected to give rise to complexes containing the $PtSe_2N_2$ ring as a result of reaction of the $Cl_2SeNSeCl_2^-$ anion with ammonia. Alternatively, we propose that the $[SeS_3N_3]^+$ reacts with ammonia analogously to $[S_4N_3]Cl$ (which forms $[S_3N_3]^-$) to give $[SeS_2N_3]^-$. This intermediate then reacts with $[PtCl_2(PR_3)_2]$ to form the observed products. The actual amount of selenium incorporation in the product is about half that expected on a simple statistical basis, thus the formation of the PtS_2N_2 is more facile than that of $PtSeSN_2$, or the selenium undergoes a competitive side reaction. Further, in this case, like the reaction of $[Se_2N_2S]Cl_2$ with $[PtCl_2(PR_3)_2]$, none of the potential isomers with sulphur and nitrogen bound to the metal in the $PtSeSN_2$ ring is observed.

Reaction of $SeCl_4$ in liquid ammonia with $[PtCl_2(PR_3)_2]$ produces $[Pt(Se_2N_2)(PR_3)_2]$ in variable yield [equation (3)].

$$[PtCl_2(PR_3)_2] + 2SeCl_4 + 8NH_3 \longrightarrow 6NH_4Cl + [Pt(Se_2N_2)(PR_3)_2] + 2Cl_2 \quad (3)$$

The reaction works best for bulky bidentate phosphines; with small phosphines a variety of compounds are formed such as $SePR_3$, $HNPR_3$, and $[Pt(Se_4)(PR_3)_2]$ {identified by mass spectrometry and comparison with an authentic sample prepared from reaction of red selenium with $[PtCl_2(PR_3)_2]$ in liquid ammonia} along with the desired product. A longer reaction time of 2 h was required for completion of the reaction in the case of complex **(15)** which was obtained in the best yield (74%). This suggests that the active Se–N species ($Se_3N_3^-$?) requires time for generation; the low solubility of $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ in liquid ammonia limits side-reactions unlike in **(16)**. The bidentate nature of the ligand discourages displacement from the inner co-ordination sphere and the formation of species such as $SePh_2PCH_2CH_2PPh_2$.

Compounds **(3)**—**(20)** were characterised by i.r., n.m.r., mass spectra, and microanalyses (Tables 1—3). In the case of PMe_2Ph a crystal structure has already been reported.[17] The side product, NH_4Cl, was readily detected by its i.r. spectrum in the CH_2Cl_2-insoluble portion. {The $SeCl_2$ formed could react further eventually to form $[Pt(Se_4)(PR_3)_2]$, as this species is detected in small amounts in the ^{31}P n.m.r. spectrum of the crude reaction mixture.}

The ^{31}P n.m.r. spectra of complexes **(3)**—**(20)** are of the AX type with the appropriate platinum satellites, and $^2J(^{31}P-^{31}P)$ couplings which are typical of *cis* square-planar Pt^{II}.[5,6]

The assignment of the individual phosphorus resonances δ_A and δ_X as *trans* to nitrogen and *trans* to selenium respectively is based on the chemical shifts reported for similar compounds[3,5,6] and upon the observed effect on the ^1J coupling constants upon protonation. In Table 1 the data for $[Pt(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ **(1a)**, $[Pt(S_2N_2H)(Ph_2PCH_2CH_2PPh_2)]^+$ **(2a)**, their monoselenated analogues **(7)** and **(12)**, and their fully selenated analogues **(15)** and **(20)** are shown. As would be expected, replacing the co-ordinating sulphur in the PtS_2N_2 ring by a selenium has the most marked effect on the resonances associated with P_X (*trans* to S/Se) with the ^1J coupling constant increasing by *ca.* 100 Hz. On going to the fully selenated compound, P_A is also affected being reduced by *ca.* 150 Hz relative to the sulphur analogue.

For complexes **(1a)**, **(7)**, and **(15)** the $^1J(^{31}P_A-^{195}Pt)$ coupling constant increases markedly (*ca.* 400 Hz) whilst $^1J(^{31}P_X-^{195}Pt)$ decreases upon protonation. This indicates that on protonation N^1 is a poorer electron donor to the platinum enabling the *trans* phosphorus to bond more strongly. The corresponding P_X–Pt coupling constant decreases as the selenium/sulphur is slightly more electron donating than before and the P_X–Pt distance has increased.

In general the larger the $^1J(^{195}Pt-^{31}P)$ coupling constant of the *trans* phosphine [square-planar *cis* phosphine platinum(II) complexes] the weaker is the Pt–X (X = N, S, or Se) bond. Increasing Se substitution into $[Pt(S_2N_2)(PR_3)_2]$ decreases the ratio $R(^1J_A/^1J_X)$ thus indicating selenium is a weaker donor to platinum than nitrogen.

Table 2. Infra-red (cm^{-1}) and mass spectral data

							m/z		
Compound	ν(NH)	ν(NS)	ν(NS/SeN)	ν(NSe)	δ(SN)	δ(SeN)	M^+	M^+–NS	M^+–NSe
(3)		1 075vs	638s, 541s, 401m		356m		570	524	476
(4)		1 071vs	642s, 546m, 403m		356m		610	565	
(5)		1 071vs	639s, 549m, 403m		360m		736		
(6)		1 067vs	638s, 541m, 400w		360w		858	812	
(7)		1 070vs	637s, 538m, 405w		360w		732	686	622
(8)	3 299s	1 071s	645m, 519m, 447m		331/323m		611		
(8a)	2 449ms		628m, 520m		328/309m				
(9)	3 255s	1 072s	640s, 540m, 451w		330w				
(10)	3 191s	1 072vs	632w, 548m, 456w		330w		859	814	780
(10a)	2 368m		622w		335w				
(13)				808m, 606s, 374m					
(14)				807m, 596s, 362m					
(15)				806m, 598s, 366m					
(16)				806m, 604s, 370m		658	564		
(18)				810s, 598s, 370w					
(19)	3 280s			852m, 608m			903		
(20)	3 270s			827m, 604m					

Compounds **(8a)** and **(10a)** are deuteriated compounds. For **(1)**, **(2)**, and **(13)** the mass spectra were measured by e.i., the rest by f.a.b. in a thiodiethanol matrix.

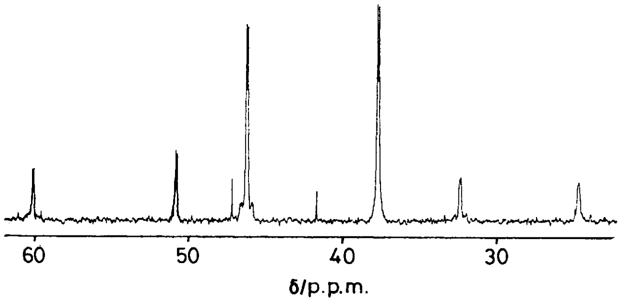


Figure 1. ^{31}P-{^{1}H} N.m.r. spectrum of [Pt(Se$_2$N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] **(15)**

Further small $^2J(^{77}\text{Se}-^{31}\text{P})$ (^{77}Se = 7% abundant, $I = \frac{1}{2}$) coupling constants of 30 Hz are observable for the higher-frequency resonance of complex **(3)** confirming its assignment as the phosphorus *trans* to selenium. For **(15)** (Figure 1) this coupling is much higher in magnitude at 72 Hz, and for the protonated derivative, **(20)**, this has decreased to 60 Hz. We cannot rationalise the difference in ^2J between **(3)** and **(15)** but the decrease on going from **(15)** to **(20)** could be because of a weaker P–Pt bond on protonation as indicated by a decrease in the $^1J(^{195}\text{Pt}-^{31}\text{P})$ coupling constant from 2 817 to 2 698 Hz.

The i.r. spectra of complexes **(3)**—**(7)** show five vibrations not attributable to the phosphine ligand at *ca.* 1 070vs, 638s, 540m, 400m, and 360m cm^{-1}. The highest-frequency vibration at 1 070 cm^{-1} is assigned to a ν(NS) and is higher in energy than that normally observed for **(1)** at 1 046 cm^{-1}. The co-ordinated species (SeSN$_2$) behaves largely as a sulphur di-imide moiety with an attached selenium. The vibration at *ca.* 640 cm^{-1} of **(3)**—**(5)** is typical of the N=S=N–S fragment and that at 541 cm^{-1} is assigned as an ν(SeN) vibration and the lower-frequency vibrations as δ(SN) as for **(1)**.[5,6]

The i.r. spectra of the protonated species **(8)**—**(12)** have the same bands as their non-protonated parents with the addition of an ν(NH) stretch at 3 299 cm^{-1}. The two highest-frequency bands attributable to ν(NS) vibrations at *ca.* 1 071 and 640 cm^{-1} remain unaltered. However the band at 550 decreases to 520 cm^{-1} and the band at 404 increases to 447 cm^{-1}. The ν(NH) stretch at 3 299 cm^{-1} is similar to those observed for [Pd(S$_2$N$_2$H)(L–L′)] and [Pt(S$_2$N$_2$H)(PR$_3$)$_2$] at 3 250 and 3 200 cm^{-1} respectively.[3,6] Stirring complex **(8)** in CH$_2$Cl$_2$ with excess of MeOD results in ready proton–deuterium exchange and allows [Pt(SeSN$_2$D)(PMe$_2$Ph)$_2$] to be made. This compound has a ν(ND) stretch at 2 449 cm^{-1} and two identifiable ν(NS/NSe) vibrations at 628 and 520 cm^{-1}. The other ν(NS/NSe) vibrations shift on deuteriation but cannot be unambiguously assigned due to overlapping phosphine vibrations.

The i.r. spectra of complexes **(13)**—**(18)** contain two vibrations not associated with the phosphine ligands at *ca.* 810 and 600 cm^{-1}. A shoulder at 586 cm^{-1} is also observed. These bands are assigned as ν(NSe) vibrations. In PtSeSN$_2$, four, and in MS$_2$N$_2$, three, vibrations are associated with the metallacycle. On protonation to form the Se$_2$N$_2$H derivatives a ν(NH) vibration at 3 280 cm^{-1} is observed and the ν(NSe) modes increase slightly in frequency.

The mass spectra (Table 2) show peaks due to the parent molecular ion in the e.i. mode and the protonated molecular ion in the f.a.b. spectra. The isotopic correlation of the parent ion is shown together with the calculated values in Figure 2. There is a characteristic fragmentation pattern dependent on the number of selenium atoms present.

Table 3. Microanalytical data (calculated values in parentheses) and yields

	Analysis/%			
Compound	C	H	N	Yield/%
(3)	25.4 (25.3)	5.3 (5.3)	4.9 (4.9)	73
(4)	31.0 (31.4)	3.5 (3.5)	4.8 (4.6)	76
(5)[a]	41.1 (41.2)	3.3 (3.3)	3.7 (3.7)	64
(6)[b]	44.7 (45.3)	3.2 (3.1)	2.7 (2.9)	51
(7)[b]	40.5 (40.1)	3.4 (3.0)	3.8 (3.5)	55
(8)	27.2 (27.5)	3.1 (3.3)	3.9 (4.0)	71
(10)[a]	43.0 (43.0)	2.9 (3.2)	2.5 (2.7)	74
(14)	39.3 (39.8)	3.1 (3.3)	3.5 (3.6)	38
(15)	40.1 (40.0)	3.0 (3.1)	2.9 (3.5)	74
(16)	28.9 (29.1)	3.1 (3.3)	3.9 (4.2)	28
(18)[a]	42.8 (43.2)	3.1 (3.1)	2.7 (2.8)	38
(19)[a]	41.3 (41.1)	3.0 (2.9)	2.6 (2.5)	78
(20)	35.5 (35.9)	3.0 (2.7)	2.9 (3.2)	80

[a] CH$_2$Cl$_2$ of crystallisation. [b] CDCl$_3$ of crystallisation.

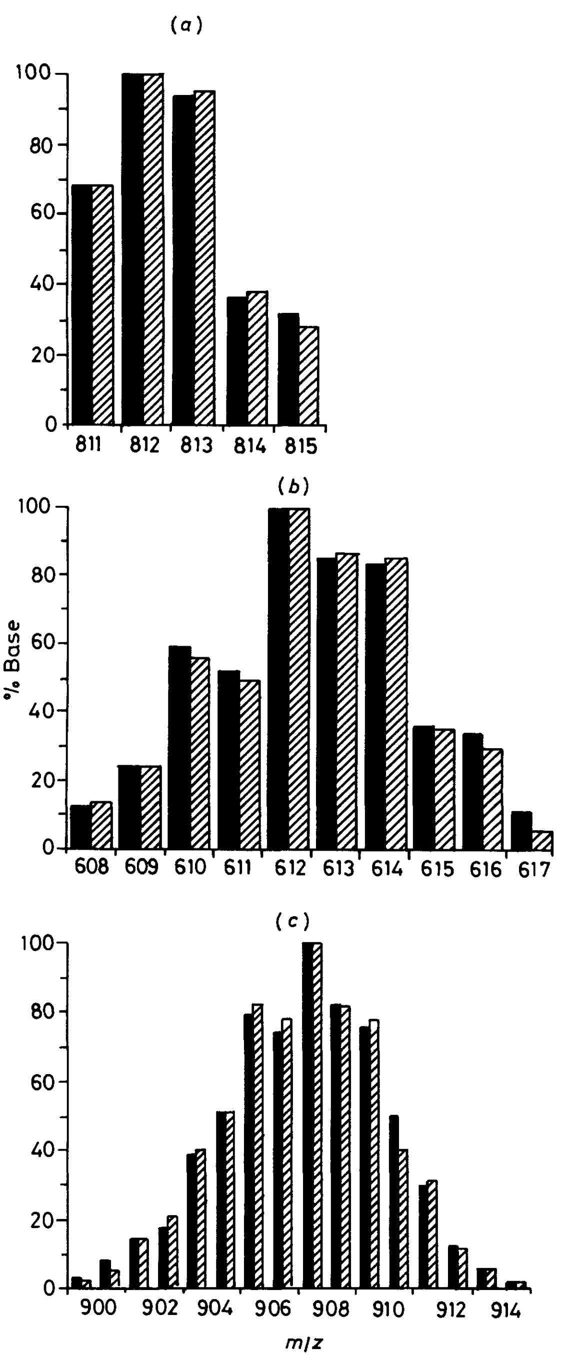


Figure 2. Observed (solid) and calculated (cross-hatched) isotopic distribution of the parent ions in complexes (*a*) (**1b**), (*b*) (**4**), and (*c*) (**19**). Compound (**19**) was measured in the f.a.b. mode.

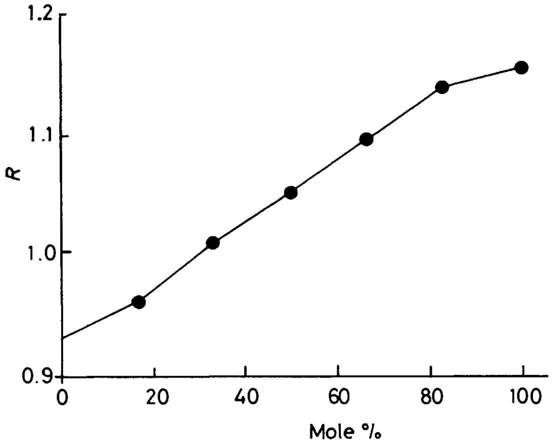


Figure 3. Plot of R (ratio of $^1J_A/^1J_X$) *versus* mole % of HBF_4 added to a solution of $[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ (**15**)

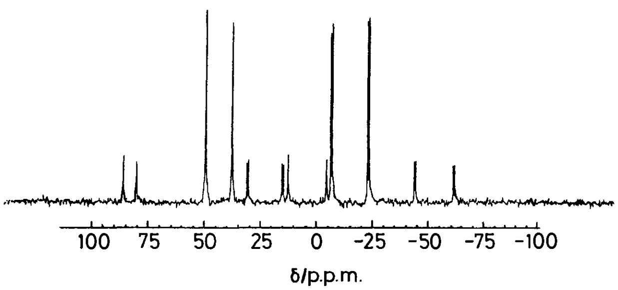


Figure 4. ^{31}P N.m.r. spectrum of the exchange reaction between $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ and $[Pt(Se_2N_2)(Ph_2PCH_2CH_2PPh_2)]$

Table 4. ^{31}P N.m.r. spectra from proton-exchange reactions

Reaction and ligand	δ_X	δ_A	^1J_X	^1J_A	^2J	$R = J_A/J_X$	% ^1H*
(a) ($SeSN_2$)	−8.8	−28.3	2 764	2 940	24	1.062	35
(S_2N_2)	−12.5	−25.9	2 607	3 082	24	1.182	70
(b) ($SeSN_2$)	−8.1	−27.9	2 790	2 912	24	1.044	30
(S_2N_2)	−11.6	−25.6	2 654	3 025	24	1.140	55
(c) (Se_2N_2)	48.4	36.7	2 676	3 087	10	1.154	100
(S_2N_2)	−7.9	−24.6	2 733	2 795	24	1.023	0
(d) (Se_2N_2)	19.2	2.6	2 724	3 236	24	1.188	90
(S_2N_2)	−3.9	−9.1			41		
(e) (Se_2N_2)	18.3	2.2	2 694	3 298	22	1.224	100
(S_2N_2)	−8.0	−24.6	2 732	2 797	24	1.024	0
(f) ($SeSN_2$)	22.5	6.9	2 948	2 996	22	1.016	0
(Se_2N_2)	48.1	36.8	2 783	3 027	10	1.088	70

For reaction details refer to Experimental section. Chemical shifts (p.p.m.) coupling constants (Hz), and R values are for the partially protonated rings. * Percentage protonation calculated assuming a linear relationship between R and degree of protonation, $10^2(R_o - R_n)/(R_f - R_n)$, where R_o = observed R ($^1J_A/^1J_X$) value in the Table, R_n = value for unprotonated complex, and R_f = value for fully protonated complex. The % values are not scaled to adjust for the non-stoicheiometric quantities used in the experiment.

It has been shown that the proton-exchange reaction between $[Pt(S_2N_2)(PR'_3)_2]$ and $[Pt(S_2N_2H)(PR_3)_2]BF_4$ is rapid on the n.m.r. time-scale such that even when cooled to −78 °C only a mixed intermediate species is observed (when $PR_3' = PR_3$) and not the individual resonances due to the unprotonated and protonated species. When PR'_3 and PR_3 are different the individual resonances due to two partly protonated complexes are discernible with the relative R ($^1J_A/^1J_X$) values of each giving the degree of protonation. Indeed the large difference in R value between protonated and unprotonated complexes [*e.g.* 1.06 for (**1b**) to 1.28 for (**2b**)] and the linear relationship between R and the degree of protonation (Figure 3) allows an accurate calculation of protonation in an equimolar mixture. Furthermore, the proton exchange is independent of the phosphines {*i.e.* exchange between $[Pt(S_2N_2)(PPh_3)_2]$ and $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ gave R values intermediate between fully protonated and fully deprotonated} but dependent on the metal used with the corresponding palladium compounds being much more basic than their platinum analogues.[18]

In this present study (Table 4) when the phosphines were the same the sulphur/selenium nitrogen ligands were different (*i.e.* S_2N_2 with $SeSN_2$ or Se_2N_2) such that the spectrum was resolvable into two different sets of resonances (Figure 4), the individual R values of each allowing the determination of the relative degree of protonation. From these equilibria it can be seen that the $SeSN_2^{2-}$ and $S_2N_2^{2-}$ derivatives have approximately the same basicity.

The addition of excess of MeOD to a mixture of $[Pt(S_2N_2H)(PMe_2Ph)_2]^+$ and $[Pt(SeSN_2)(PMe_2Ph)_2]$ had no effect on the spectrum, whilst addition of excess of NEt_3 to the equilibrium resulted in complete deprotonation of both species, thus indicating that the S_2N_2 and $SeSN_2$ derivatives are weak bases in general terms.

The reaction in equation (4) ($PR_3 = PMe_2Ph$, $PR'_3 =$

$$[Pt(Se_2N_2)(PR'_3)_2] + [Pt(S_2N_2H)(PR_3)_2]BF_4 \longrightarrow [Pt(Se_2N_2H)(PR'_3)_2]BF_4 + [Pt(S_2N_2)(PR_3)_2] \quad (4)$$

$\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) shows that the $PtSe_2N_2$ ring is a much better base than the PtS_2N_2 ring, with almost complete protonation of the Se_2N_2 species [$R = 1.150$ for the Se_2N_2 derivative compared to 1.156 for (**20**)]. Proton exchange in reaction (f) indicates that the Se_2N_2 derivative is a better base than the $SeSN_2$ species.

In reaction (d) the palladium compound although in two-fold molar excess is essentially unprotonated, with $[Pt(Se_2N_2H)(PPh_3)_2]^+$ remaining *ca.* 90% protonated. This indicates the $PtSe_2N_2$ rings are better bases than the PdS_2N_2 species. Overall the basicity of the rings is in the order $Pt(S_2N_2) \approx Pt(SeSN_2) < Pd(S_2N_2) < Pt(Se_2N_2)$.

Acknowledgements

We are grateful to Johnson Matthey for loans of precious metals.

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Received 30*th May* 1989; *Paper* 9/02238D