

Pyridine-2-selenolate complexes of palladium(II) and platinum(II): crystal structure of $[(Pr^n_3P)Cl_2Pd(NC_5H_4Se)PdCl(PPr^n_3)]$

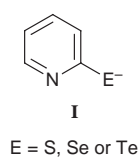
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Reactions of sodium pyridine-2-selenolate with several palladium(II) and platinum(II) complexes were carried out and a variety of products isolated and characterized. Treatment of $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ with $NaSeC_5H_4N$ readily afforded complexes of the type $[MCl(NC_5H_4Se)(PR_3)]$ **1** ($M = Pd$ or Pt ; $PR_3 = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, PMePh_2$ or PPh_3). Some of the complexes containing trialkylphosphine existed as binuclear species, $[M_2Cl_2(\mu-NC_5H_4Se)_2(PR_3)_2]$ **2** in $\approx 5\%$ concentration in solution. Reaction of $[MCl(NC_5H_4Se)(PR_3)]$ with $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ gave an unusual series of binuclear complexes, $[(R_3P)Cl_2M(NC_5H_4Se)MCl(PR_3)]$ **3**, in which NC_5H_4Se acts simultaneously as a Se bridging and Se,N chelating ligand. Reactions of $[PtCl_2(cod)]$ or $Na_2[PdCl_4]$ with $NaSeC_5H_4N$ afforded $[M(NC_5H_4Se)_2]_n$. Similar reactions with $[MCl_2(L-L)]$ and $[MCl_2(PPh_3)_2]$ ($L-L = dppe$ or $dppp$) gave $[M(NC_5H_4Se)_2(L-L)]$ and $[M(NC_5H_4Se)_2(PPh_3)_2]$, respectively. The latter complex exists in a dynamic equilibrium with $[M(NC_5H_4Se)(NC_5H_4Se-N,Se)(PPh_3)_2]$ and PPh_3 . All the complexes were characterized by elemental analyses and NMR ($^1H, ^{31}P, ^{77}Se, ^{195}Pt$) spectral data. The crystal structure of $[(Pr^n_3P)Cl_2Pd(NC_5H_4Se)PdCl(PPr^n_3)]$ revealed that NC_5H_4Se acts as a triply bridging ligand. One of the palladium atoms is co-ordinated to two *trans* chlorine atoms, one Pr^n_3 , and a Se atom, while the second is bound to a chelating NC_5H_4Se ligand, a chlorine atom and a PPr^n_3 ligand.

The chemistry of mono- and bi-nuclear complexes of platinum group metals with organochalcogenide ligands has attracted considerable attention in recent years.¹⁻⁴ The area of platinum group organochalcogenolates has been dominated by molecules containing the M-SR linkage. Several strategies have been adopted to isolate these molecules. The mononuclear *cis* complexes, *cis*- $[Pt(RS)_2L_2]$, useful synthons for the preparation of bi- and poly-nuclear derivatives,⁵ tend to isomerize (to the *trans* form) and polymerize when L and SR are monodentate ligands.⁶ However, with chelating organochalcogenides^{7,8} or bidentate L-L,^{8,9} stable *cis* complexes are formed. Alternatively, small bite bidentate anionic hybrid ligands containing both soft chalcogen and hard O/N atoms have also been employed in building bi- and poly-nuclear complexes.¹⁰⁻¹² One of the families of this class of ligands is the pyridine-2-chalcogenolate ion **I**. The ligand chemistry of $NC_5H_4S^-$ is well developed.¹¹⁻¹⁶ However, the co-ordination chemistry of the higher homologs, *viz.* $NC_5H_4Se^-$ and $NC_5H_4Te^-$, remained unexplored until recently,¹⁷ although these have been known for some time.¹⁸ The complexes of Zn, Cd and Hg with pyridine-2-selenolate are useful single-source precursors for the preparation of semiconductor materials.¹⁷ The complexes of higher homologs have an additional advantage of being amenable to investigation by $^{77}Se/^{125}Te$ NMR spectroscopy (both nuclides have nuclear spin $\frac{1}{2}$ and their natural abundances are 7.58 and 6.99%, respectively). Here, we report the chemistry of platinum and palladium complexes with the $NC_5H_4Se^-$ ligand.



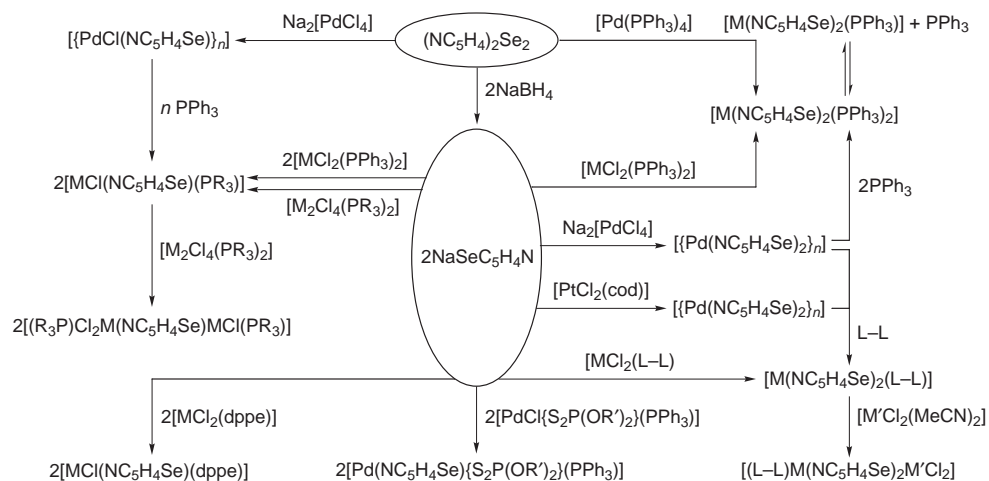
Results and Discussion

Reactions of $NaSeC_5H_4N$ with $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$

Treatment of $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ with 2 equivalents of

$NaSeC_5H_4N$ prepared by reductive cleavage of the Se-Se bond in di-2-pyridyl diselenide with $NaBH_4$, afforded pyridine-2-selenolate complexes of the type $[MCl(NC_5H_4Se)(PR_3)]$ **1** ($M = Pd$ or Pt ; $PR_3 = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, PMePh_2$ or PPh_3) (Scheme 1). When trialkylphosphine was one of the ligands, dimeric species $[M_2Cl_2(\mu-NC_5H_4Se)_2(PR_3)_2]$ **2** were also formed in small amounts ($\approx 5\%$ as revealed by the integration of 1H NMR spectra) in some cases. Recently, reactions of $[Pd_2Cl_2(\mu-Cl)_2(PR_3)_2]$ ($PR_3 = PMe_3, PMe_2Ph, PMePh_2$ or PPh_3) with pyridine-2-thiol have been studied.^{14,15} When $PR_3 = PPh_3$ a mononuclear complex $[MCl(NC_5H_4S)(PR_3)]$ formed exclusively with a chelating thiolate ligand.^{14,15c} However, when $PR_3 = PMe_3, PMe_2Ph$ or $PMePh_2$, binuclear complexes have been isolated with bridging NC_5H_4S ligands as shown by X-ray diffraction studies.^{15a,c} However, in solution a dimer \rightleftharpoons monomer equilibrium was established with the dimer predominating.^{15a,c} Subtle energetic factors shift the equilibrium to either side. The ^{31}P NMR signal for the dimer appears at a higher frequency than that of the corresponding monomeric species.^{14,15c} A similar behavior was observed for the analogous platinum complexes.^{15d}

The pyridine-2-selenolate complexes of platinum are yellow while the palladium derivatives are maroon-red crystalline solids. Both sets of complexes **1** have similar NMR data and it is likely that the two series have similar structures. Their ^{31}P NMR spectra exhibited a single resonance except for some of those containing trialkylphosphine. The latter displayed an additional resonance at higher frequency integrating to $\approx 5\%$ which can be attributed to a binuclear species $[M_2Cl_2(\mu-NC_5H_4Se)_2(PR_3)_2]$ on comparison with the spectra of complexes containing the $NC_5H_4S^-$ ligand.^{14,15} The signals of the platinum complexes were flanked with platinum satellites (Table 1). The magnitude of $^1J(^{195}Pt-^{31}P)$ is consistent with the phosphine being *trans* to the nitrogen atom of the chelated $NC_5H_4Se^-$ ligand (**II**).¹⁹ This conclusion is further substantiated by the recently reported crystal structure of $[PdCl(NC_5H_4S)(PPh_3)]$.^{14,15c} The 1H NMR spectra of **1** showed the expected integration and peak multiplicities. The spectra of the complexes containing trialkylphosphine displayed resonances due



Scheme 1 M = Pd or Pt; PR₃ = PEt₃, PPrⁿ₃, PBuⁿ₃, PMe₂Ph, PMePh₂ or PPh₃; L-L = dpmm or dppe; R' = Prⁿ or Prⁱ

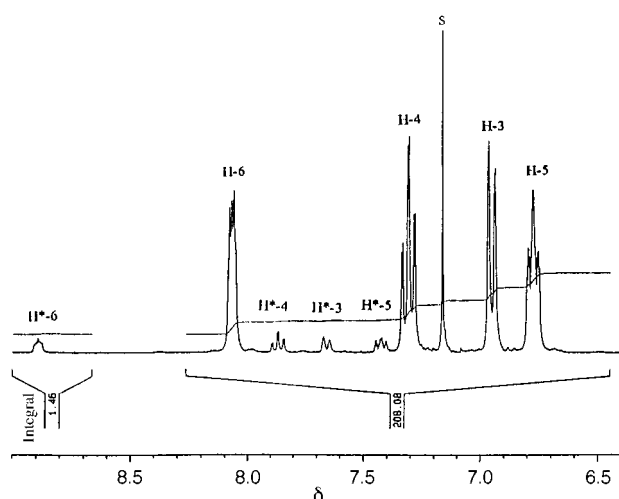
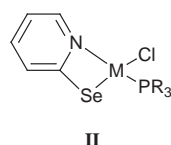


Fig. 1 Aromatic region of the ¹H NMR spectrum of [PdCl(NC₅H₄Se)(PEt₃)] **1a** in CDCl₃. Protons indicated H* are due to [Pd₂Cl₂(μ-NC₅H₄Se)₂(PEt₃)₂], s indicates a solvent peak



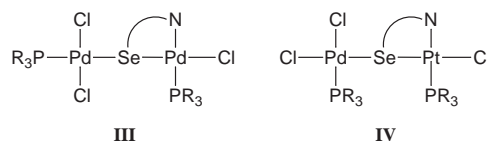
to the dimeric species. The signals assignable to the bridging NC₅H₄Se ligand in the dimeric species are deshielded from the corresponding resonances for the monomeric complex containing chelating NC₅H₄Se (Fig. 1).

Unlike NC₅H₄S⁻, NC₅H₄Se⁻ preferentially yields monomeric complexes and the concentration of binuclear species, when formed, is always ≈5%. For example, **1j** exists exclusively as a monomer while, the binuclear species predominates for [PtCl(NC₅H₄S)(PMe₂Ph)]_n (*n* = 2, 87; *n* = 1, 13%).^{15d} Seemingly, the larger size of the selenium atom increases the M–Se distance (*e.g.* Pd–S ≈ 2.28, Pd–Se ≈ 2.45 Å) and consequently facilitates the M–N interaction to a single metal centre.

The ⁷⁷Se–{¹H} and ¹⁹⁵Pt–{¹H} NMR spectra of a few representative complexes were recorded in CDCl₃. The ⁷⁷Se resonances appeared as singlets in the region δ –1159.1 to –1216.8. The signal is deshielded for platinum compared to the corresponding palladium analogues. The spectra of platinum complexes were flanked with platinum satellites. The magnitude of ¹J(¹⁹⁵Pt–⁷⁷Se) is comparable to the values reported for mononuclear platinum selenolato complexes.³ The appearance of singlets in the ⁷⁷Se NMR spectra further suggests that the phosphine is *cis* to the selenium atom [²J(⁷⁷Se–³¹P)_{cis} > 10 Hz].

The ¹⁹⁵Pt NMR spectra displayed a doublet due to coupling with the single phosphorus nucleus.

When [M₂Cl₂(μ-Cl)₂(PR₃)₂] was allowed to react with [MCl(NC₅H₄Se)(PR₃)] in 1 : 2 stoichiometry a new series of binuclear complexes [(R₃P)Cl₂M(NC₅H₄Se)MCl(PR₃)] **3** were formed in which the selenium atom of the chelated NC₅H₄Se ligand is co-ordinated to the 'MCl₂(PR₃)' fragment. It is noteworthy that such reactions have been extensively used to prepare complexes of general formula [M₂Cl₂(μ-Cl)(μ-R'E)(PR₃)₂] (E = S, Se or Te; R' = alkyl or aryl; M = Pd or Pt) in high yield.^{3,19,20} The ³¹P NMR spectra of **3** showed two singlets indicating two different types of phosphine ligands. The signals for the platinum complexes were flanked by platinum satellites. The signal at lower frequency may be attributed to the phosphine attached to the metal atom bound to chelating NC₅H₄Se. The magnitude of ¹J(Pt–P) associated with this signal is reduced as compared to that of the corresponding mononuclear complex. The second resonance at higher frequency can be assigned to the phosphine co-ordinated to the metal atom bound to two chlorides and the selenium atom. Although X-ray analysis of the palladium complex revealed a *trans* chloride configuration (**III**) around palladium, the analogous platinum complexes have been assigned a *cis* chloride configuration (**IV**) based on the ¹J(Pt–P) coupling.²¹ For the *trans* configuration ¹J(Pt–P) would be of the order of ≈3000 Hz due to the strong *trans* influence of the selenolato group.¹⁹ The signal due to the phosphine bound to this platinum also showed ³J(Pt–P) ≈ 50 Hz (Fig. 2) which is in accord with reported values.²⁰



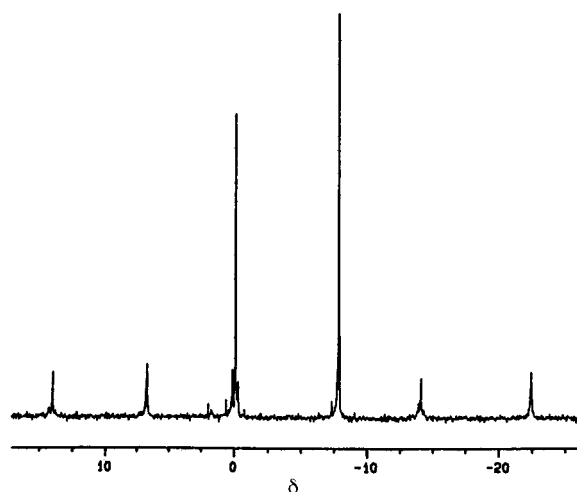
The molecular structure of [(PrⁿP)Cl₂Pd(NC₅H₄Se)PdCl(PPrⁿ)] was established by single-crystal X-ray diffraction studies. The ORTEP²² plot with the numbering scheme of the molecule is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. The structure of the molecule is unique in the sense that the two square-planar palladium atoms are held together by a single bridging atom, *i.e.* selenium. It differs from the reported complexes [M₂Cl₂(μ-Cl)(μ-R'E)(PR₃)₂] (E = S, Se or Te; M = Pd or Pt)^{3,20,21} wherein the metal atoms are bridged by the Cl and R'E ligands.

The co-ordination around each palladium atom is distorted square-planar and the two planes form an open-book structure (dihedral angle 95.82°). Atom Pd(1) is co-ordinated to two mutually *trans* chlorine atoms, one PPrⁿ₃ and the selenium atom; Pd(2) is bound to the chelating NC₅H₄Se ligand, a

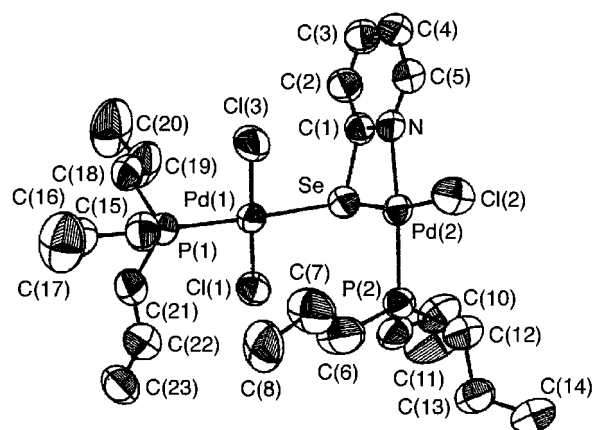
Table 1 The ^{31}P - $\{^1\text{H}\}$ and ^1H NMR data for pyridine-2-selenolate complexes of palladium(II) and platinum(II) in CDCl_3

Complex	^{31}P - $\{^1\text{H}\}$ NMR (δ)	^1H NMR ^a
1a $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PEt}_3)]$	33.5, 38.2 ^b	1.15 [dt, J 17.4 (d), 7.6 (t), PCH_2CH_3], 1.74 (m, PCH_2), 6.77 (m), 6.95 (d, J 8.0), 7.31 [dt, J 1.8 (d), 7.8 (t)], 8.07 (br, m) (each integrated to 1H, py), 7.45 (m), ^b 7.68 (d, J 8.0), ^b 7.92 (dt), ^b 8.91 (br) ^b (py)
1b $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PPr}^n_3)]^c$	24.3, 29.4 ^b	0.98 (t, J 6.3, $\text{PCH}_2\text{CH}_2\text{CH}_3$), 1.65 (br, m, PCH_2CH_2), 6.77 (t, J 6.6), 6.95 (d, J 8.0), 7.30 (t, J 7.8), 8.08 (m) (each integrated to 1H, py), 7.42 (t), ^b 7.65 (d), ^b 7.85 (t), ^b 8.90 (br) ^b (py)
1c $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PBu}^n_3)]^d$	25.4	0.80 (t, J 7.2, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.31 (q, J 7.3, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 1.48 (m, PCH_2CH_2), 1.65 (m, PCH_2), 6.71 (t), 6.90 (d, J 8.0), 7.26 [dt, J 1.7 (d), 8.0 (t)], 8.00 (m) (each integrated to 1H, py)
1d $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PMe}_2\text{Ph})]$	5.2	1.85 (d, 11.6 J , PMe_2), 7.45 (m), 7.74 (m) (PPh), 6.85 (t), 7.01 (d, J 8.0), 7.40 (t), 8.20 (m) (each integrated to 1H, py)
1e $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PMePh}_2)]^e$	18.1	2.07 (d, J 11.5, PMe), 7.36 (m), 7.62 (m) (PPh_2), 6.77 (m), 6.90 (d, J 8.0), 7.32 [dt, J 1.7 (d), 8.0 (t)], 8.17 (m) (each integrated to 1H, py)
1f $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PPh}_3)]$	30.1	6.87 (t, J 6.0), 6.97 (d, J 7.8) (each 1H, py), 6.69 (m) (Ph + 1H, py), 7.44 (m), 8.35 (br, 1H, py)
3a $[(\text{Pr}^n_3\text{P})\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_4\text{Se})\text{PdCl}(\text{PPr}^n_3)]$	25.6, 26.8 (1 : 1) 38.1 (very br, small)	1.06 (t, $\text{PCH}_2\text{CH}_2\text{CH}_3$), 1.71 (br, m, PCH_2CH_2), 7.05 (br), 7.27 (d, J 7.1), 7.55 (t, J 7.7), 8.29 (br) (each integrated to 1H, py)
1g $[\text{PtCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PEt}_3)]$	0.6, $^1J(\text{Pt-P}) = 3622$	1.10 [dt, J 1.7 (d), 7.6 (t), PCH_2Me], 1.74 (m, PCH_2), 6.81 (d, J 8.0), 6.89 (t, J 5.7), 7.33 (t, J 7.8), 8.21 [br s, $^3J(\text{Pt-H}) = 37.5$] (each integrated to 1H, py)
1h $[\text{PtCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PPr}^n_3)]^f$	-8.0, $^1J(\text{Pt-P}) = 3584$ 0.1 (minor product <5%)	0.96 (t, J 7.0, $\text{PCH}_2\text{CH}_2\text{CH}_3$), 1.61 (m, PCH_2CH_2), 6.80 (d, J 8), 6.89 (t, J 6.6), 7.33 [dt, J 1.6 (d), 8.0 (t)], 8.18 [br s, $^3J(\text{Pt-H}) = 38.4$] (each integrated to 1H, py)
1i $[\text{PtCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PBu}^n_3)]$	-7.4, $^1J(\text{Pt-P}) = 3595$	0.82 (t, J 7.2, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.33 (q, J 7.2, $\text{PCH}_2\text{CH}_2\text{CH}_2$), 1.48 (m br, PCH_2CH_2), 1.66 (m, PCH_2), 6.78 (d, J 8.0), 6.90 (br), 7.31 (t), 8.15 [br s, $^3J(\text{Pt-H}) = 44.0$] (each integrated to 1H, py)
1j $[\text{PtCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PMe}_2\text{Ph})]$	-24.9, $^1J(\text{Pt-P}) = 3658$	1.90 [d, J 11.3, $^3J(\text{Pt-H}) = 36.6$, PMe_2], 7.43 (m), 7.77 (m) (Ph + 1H of py), 6.90 (d, J 8.0), 6.99 [dt, J 1.2 (d)], 8.32 [br s, $^3J(\text{Pt-H}) = 44.0$] (each integrated to 1H, py)
1k $[\text{PtCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PMePh}_2)]^g$	-10.4, $^1J(\text{Pt-P}) = 3737$	2.08 [d, J 11.2, $^3J(\text{Pt-H}) = 34$, PMe], 7.33 (br), 7.59 (br) (Ph + 1H of py), 6.90 (t, J 5.5), 7.76 (d, J 8.0), 8.28 [br, $^3J(\text{Pt-H}) = 42.0$] (each integrated to 1H, py)
3b $[(\text{Et}_3\text{P})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_4\text{Se})\text{PtCl}(\text{PEt}_3)]$	1.2, $^1J(\text{Pt-P}) = 3560$; 8.1, $^1J(\text{Pt-P}) = 3426$, $^3J(\text{Pt-P}) = 52$	1.21 (m, PCH_2CH_3), 1.89 (m), 2.07 (m) (each 1 : 1, PCH_2), 7.23 (t, J 8.0, 2H), 7.70 (t, J 7.7, 1H), 8.54 [1H, $^3J(\text{Pt-H}) = 37.0$] (py)
3c $[(\text{Pr}^n_3\text{P})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_4\text{Se})\text{PtCl}(\text{PPr}^n_3)]$	-0.1, $^1J(\text{Pt-P}) = 3410$, $^3J(\text{Pt-P}) = 52$; -7.84, $^1J(\text{Pt-P}) = 3540$	1.05 (m, $\text{PCH}_2\text{CH}_2\text{CH}_3$), 1.51-2.04 (m, PCH_2CH_2), 7.22 (d, J 8.0, 2H), 7.68 [dt, J 1.4 (d), 8.0 (t)], 8.52 [br, $^3J(\text{Pt-H}) = 36.0$] (py)

^a d = Doublet, t = triplet, q = quartet, m = multiplet, dt = doublet of triplets, br = broad; J in Hz. ^b Due to minor species present in approximately 5% concentration. ^c ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1211.0 (s). ^d ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1210.5 (s). ^e ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1159.1 (s). ^f ^{195}Pt - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -3875 [d, $^1J(\text{Pt-P}) = 3578$ Hz]. ^g ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1216.8 [s, $^1J(\text{Pt-Se}) = 120$ Hz]. ^h ^{195}Pt - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -3858 [d, $^1J(\text{Pt-P}) = 3720$ Hz]. ⁱ ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1184.5 [s, $^1J(\text{Pt-Se}) = 197$ Hz].

**Fig. 2** The ^{31}P - $\{^1\text{H}\}$ NMR spectrum of $[(\text{Pr}^n_3\text{P})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_4\text{Se})\text{PtCl}(\text{PPr}^n_3)]$ **3c** in CDCl_3

chlorine and a PPr^n_3 ligand. The Pd(2) square plane and the planar pyridine ring of the chelating $\text{NC}_5\text{H}_4\text{Se}$ ligand are coplanar. The chlorine atom is *trans* to the selenium while the phosphine is *trans* to the nitrogen of the chelate ligand. The two square planes of the palladium atoms are hinged at the selenium atom and are inclined to each other through a Pd(1)-Se-Pd(2) angle of $99.80(3)^\circ$. The Pd-P and Pd-Se

**Fig. 3** Molecular structure of $[(\text{Pr}^n_3\text{P})\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_4\text{Se})\text{PdCl}(\text{PPr}^n_3)]$ **3a** with the crystallographic numbering scheme

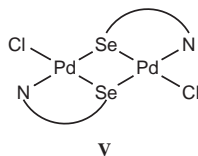
bond distances are sensitive to the *trans* influence of the ligands *trans* to them. Accordingly, the Pd(1)-P(1) [2.255(2) Å] and Pd(1)-Se [2.5077(8) Å] bond distances are longer than Pd(2)-P(2) [2.238(2) Å] and Pd(2)-Se [2.4215(9) Å]. The Pd-Cl, Pd-P, Pd-Se and Pd-N bond distances are in agreement with reported values.^{3,14,15,23,24} Owing to the small bite of the $\text{NC}_5\text{H}_4\text{Se}$ ligand, the angles in the four-membered chelate ring are significantly reduced from their normal values (Table 2).

Table 2 Selected bond lengths (Å) and angles (°) for [(PrⁿP)Cl₂Pd(NC₅H₄Se)PdCl(PPrⁿ)₃] **3a**

Pd(1)–Se	2.5077(8)	Pd(2)–Se	2.4215(9)
Pd(1)–P(1)	2.255(2)	Pd(2)–P(2)	2.238(2)
Pd(1)–Cl(1)	2.300(2)	Pd(2)–Cl(2)	2.306(2)
Pd(1)–Cl(3)	2.289(2)	Pd(2)–N	2.104(4)
Se–C(1)	1.930(6)		
P(1)–Pd(1)–Cl(1)	94.41(6)	P(2)–Pd(2)–Cl(2)	93.50(6)
P(1)–Pd(1)–Cl(3)	86.81(6)	P(2)–Pd(2)–N	169.98(13)
P(1)–Pd(1)–Se	174.16(5)	P(2)–Pd(2)–Se	98.99(5)
Cl(1)–Pd(1)–Cl(3)	177.84(7)	Cl(2)–Pd(2)–N	96.34(13)
Cl(1)–Pd(1)–Se	84.79(5)	Cl(2)–Pd(2)–Se	167.35(5)
Cl(3)–Pd(1)–Se	94.17(5)	N–Pd(2)–Se	71.25(12)
Pd(1)–Se–Pd(2)	99.80(3)	Pd(2)–N–C(1)	103.9(3)
Pd(1)–Se–C(1)	104.0(2)	Pd(2)–Se–C(1)	77.2(2)
Se–C(1)–N	107.6(4)		

Reactions of pyridine-2-selenolate with other palladium and platinum complexes

When a methanolic solution of Na₂[PdCl₄] was refluxed with (NC₅H₄)₂Se₂ an orange insoluble product with empirical formula [₂{PdCl(NC₅H₄Se)}₂] **4** was obtained. The IR spectrum displayed a medium to strong intensity band at 350 cm⁻¹ attributable to terminal ν(Pd–Cl) stretching.²⁵ However, for polynuclear [_n{PdCl(PhE)}_n] (E = S, Se or Te) complexes four ν(Pd–Cl) absorptions in the region 247–300 cm⁻¹ assignable to bridging have been reported.²⁵ Bridge cleavage of **4** with PPh₃ gave a mononuclear complex **1f** containing chelating NC₅H₄Se. These facts indicate that **4** has a dimeric structure (**V**); **1f** and its platinum analogue **1l** can also be prepared by the reaction of [MCl₂(PPh₃)₂] with 1 equivalent of NaSeC₅H₄N.



Treatment of Na₂[PdCl₄] or [PtCl₂(cod)] with 2 mol equivalents of SeC₅H₄N afforded compounds with analytical formula [₂{M(NC₅H₄Se)}₂] (M = Pd **5a** or Pt **5b**). These complexes are insoluble in common organic solvents but react with various neutral donor ligands, such as tertiary phosphines (see later), to give mononuclear complexes. Ooi and co-workers¹³ have prepared palladium and platinum complexes with pyridine-2-thiol of the type [₂{M(NC₅H₄S)}₂] in which the MN₂S₂ square has the *cis* configuration. Since the pyridine-2-selenolate has the same kind of donor atoms as NC₅H₄S⁻ it is likely that **5** has a structure similar to that of [₂{M(NC₅H₄S)}₂].

Treatment of [PdCl₂(dppe)] with 1 equivalent of NaSeC₅H₄N gave a red crystalline solid with composition [PdCl(NC₅H₄Se)(dppe)] **6**. The ³¹P-¹H NMR spectrum showed two broad signals indicating the non-equivalence of the two phosphorus nuclei. The ¹H NMR spectrum displayed a broad resonance due to the methylene protons. The appearance of a broad resonance indicates that there may be a dynamic equilibrium between the ionic (**VI**) and the non-ionic (**VII**) species as shown. This is further substantiated by the low molar conductivity (1.7 ohm⁻¹ cm² mol⁻¹) of the complex in methanol (accepted values for 1:1 electrolytes are 65–90 ohm⁻¹ cm² mol⁻¹).

When [MCl₂(L–L)] was treated with 2 equivalents of NaSeC₅H₄N, bis(pyridine-2-selenolate) complexes, [M(NC₅H₄Se)₂(L–L)] (M/L–L = Pd/dppe **7a**, Pt/dppe **7b** or Pt/dppm **7c**) were formed readily. The ³¹P NMR spectra exhibited single signals with platinum satellites in the case of **7b** and **7c** indicating that all the phosphorus nuclei are equivalent. The negative value of the chemical shift for **7c** can be taken as evidence for

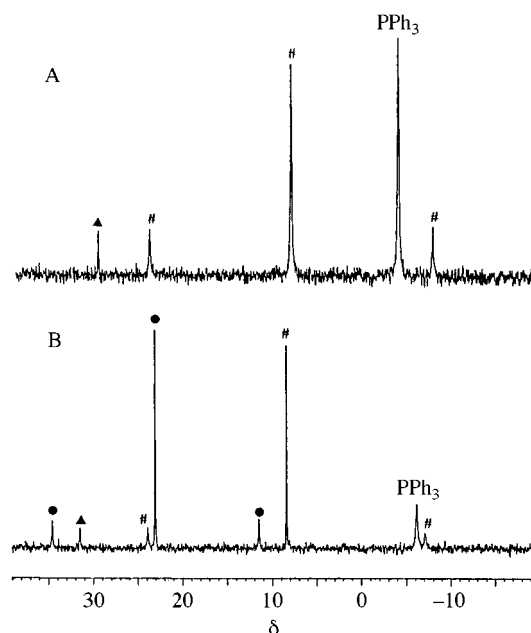
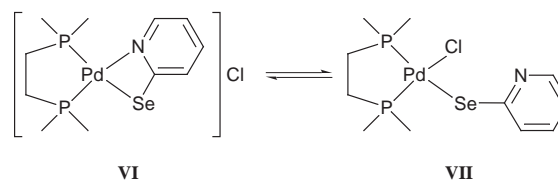


Fig. 4 Variable-temperature ³¹P-¹H NMR spectra of [Pt(NC₅H₄Se)₂(PPh₃)₂] **9c** in CDCl₃. Resonances marked with # and ● are due to [Pt(NC₅H₄Se)₂(PPh₃)₂] and [Pt(NC₅H₄Se)₂(PPh₃)₂], respectively, ▲ to Ph₃PO. (A) Room temperature (25 °C), (B) –30 °C

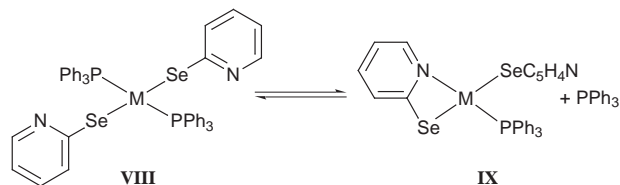


the chelating character of the dppe ligand.^{3,26} Owing to the strong *trans* influence of the NC₅H₄Se ligand, the magnitude of ¹J(Pt–P) for **7b** and **7c** is reduced significantly. The ¹⁹⁵Pt NMR spectrum of **7b** displayed a triplet at δ –4986 with ¹J(Pt–P) 2968 Hz. The ⁷⁷Se-¹H NMR spectrum showed a doublet of doublets at δ –1058.3 with ²J(Se–P)_{trans} 81, ²J(Se–P)_{cis} 12 and ¹J(Pt–Se) 220 Hz. These values are comparable with those reported for analogous complexes containing the PhSe ligand.^{3,27} Preliminary X-ray studies of **7b** revealed that the NC₅H₄Se is bonded to platinum through the Se atoms which are *trans* to the chelating dppe [Pt–Se 2.434(1), 2.498(1); Pt–P 2.244(2), 2.270(2) Å].²⁸

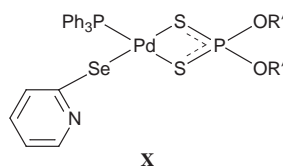
The unco-ordinated nitrogen atoms in complex **7** are available for further ligation. Thus, the reaction of **7** with [M'Cl₂(MeCN)₂] was carried out and products with empirical composition [(dppe)M(NC₅H₄Se)₂M'Cl₂] (M/M' = Pd/Pd **8a**, Pt/Pd **8b** or Pt/Pt **8c**) were isolated. These complexes are insoluble in common organic solvents. The IR spectra showed bands in the region 280–313 cm⁻¹ assignable to ν(M–Cl) absorptions which were absent for **7**.

Reactions of [MCl₂(PPh₃)₂] with 2 equivalents of NaSeC₅H₄N afforded [M(NC₅H₄Se)₂(PPh₃)₂] (M = Pd **9b** or Pt **9c**) which existed in a dynamic equilibrium with [M(NC₅H₄Se)(NC₅H₄Se-*N,Se*)(PPh₃)₂] (M = Pd **9a** or Pt **9d**) and PPh₃ in solution at room temperature. Thus, the elemental analyses for **9b** and **9c** varied between bis- and mono-phosphine complexes from one preparation to another. After several recrystallizations of **9b** pure **9a** could be obtained which showed only one sharp signal in the ³¹P NMR spectrum. This **9a** when treated with 1 equivalent of PPh₃ showed a ³¹P NMR spectrum identical to that of **9b** [δ(³¹P) 33.1, –4.5, both broad]. The repeated crystallization of **9c**, however, did not give pure **9d**. Complex **9c** at room temperature exists exclusively as a mixture of **9d** [δ(³¹P) 7.8, ¹J(Pt–P) 3833 Hz] and PPh₃. However, at lower temper-

atures (-30°C) both **9c** [$\delta(^{31}\text{P})$ 23.1, $^1J(\text{Pt-P})$ 2805 Hz] and **9d** [$\delta(^{31}\text{P})$ 8.4, $^1J(\text{Pt-P})$ 3760 Hz] exist with a small quantity of PPh_3 (Fig. 4). The observed $^1J(\text{Pt-P})$ coupling constant for **9c** is consistent with a *trans* configuration and can be compared with that for $[\text{Pt}(\text{PhSe})_2(\text{PPh}_3)_2]$ [*trans* isomer in C_6D_6 , δ 20.4, $^1J(\text{Pt-P}) = 2831$ Hz; *cis* isomer, δ 18.6, $^1J(\text{Pt-P}) = 2969$ Hz].³ These data indicate that a dynamic equilibrium exists in solution (**VIII** and **IX**). Surprisingly, for $[\text{Pt}(\text{NC}_5\text{H}_4\text{S})_2(\text{PPh}_3)_2]$ and $[\text{Pt}(\text{NC}_5\text{H}_4\text{S})_2(\text{PPh}_3)]$, there is little difference between their chemical shifts and $^1J(\text{Pt-P})$ coupling constants.¹⁴ Complex **9b** can also be prepared either by the reaction of **5a** with PPh_3 or by the oxidative addition of $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ to a palladium(0) complex, $[\text{Pd}(\text{PPh}_3)_4]$.



Reaction of $[\text{PdCl}\{\text{S}_2\text{P}(\text{OR}')_2\}(\text{PPh}_3)]$ with $\text{NaSeC}_5\text{H}_4\text{N}$ afforded complexes of the type $[\text{Pd}(\text{NC}_5\text{H}_4\text{Se})\{\text{S}_2\text{P}(\text{OR}')_2\}(\text{PPh}_3)]$ ($\text{R}' = \text{Pr}^n$ **10a** or Pr^i **10b**). The ^1H NMR spectra were consistent with the proposed formulation (X). The ^{31}P NMR spectra exhibited two signals attributable to PPh_3 and the dithioacid ligand.



From the foregoing discussion it may be concluded that pyridine-2-selenolate is a versatile ligand. It binds in several ways, such as monodentate (as in complex **7**), bidentate bridging (**2**), chelating (**1, 9a**) or even triply bridging (**3**). Complexes **3** and **8** are examples where the unco-ordinated lone pair on selenium or nitrogen can be used for ligation. The pyridine-2-selenolate has a greater tendency to chelation than that of its sulfur counterpart as evident from **1**.

Experimental

The complexes $[\text{MCl}_2(\text{PPh}_3)_2]$, $[\text{MCl}_2(\text{dppm})]$, $[\text{MCl}_2(\text{dppe})]$, $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}$ or Pt ; $\text{PR}_3 = \text{PEt}_3$, PPr^n_3 , PBu^n_3 , PMe_2Ph , PMePh_2 or PPh_3),²⁹ $[\text{PdCl}\{\text{S}_2\text{P}(\text{OR}')_2\}(\text{PPh}_3)]$ ³⁰ ($\text{R}' = \text{Pr}^n$ or Pr^i) and $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ ^{17d} were prepared according to the literature methods. The latter was purified by recrystallization from ethanol, m.p. $48\text{--}50^{\circ}\text{C}$ (^1H NMR in CDCl_3 : δ 7.07 (m), 7.53 [dt, J 7 (t), 1.8 (d)], 7.78 (d, 8.1 Hz) and 8.45 (br). $^{77}\text{Se}\text{-}\{^1\text{H}\}$ NMR in CDCl_3 : δ -852 (lit.,^{17c} -857)). The phosphines were obtained from Strem Chemicals (USA). Reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents. The ^1H , $^{31}\text{P}\text{-}\{^1\text{H}\}$, $^{77}\text{Se}\text{-}\{^1\text{H}\}$ and $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300, 121.49, 57.3 and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform (δ 7.26) for ^1H , external 85% H_3PO_4 for ^{31}P , H_2SeO_3 in water for ^{77}Se and $\text{Na}_2[\text{PtCl}_4]$ in D_2O for ^{195}Pt . A 90° pulse was used in every case. The IR spectra were recorded on a Bomem MB-102 FT spectrometer as Nujol mulls using CsI discs. Microanalyses of the complexes were carried out in the Analytical Chemistry Division of this research centre.

Preparations

[PtCl(NC₅H₄Se)(PEt₃)] 1g. To a methanolic solution (8 cm³)

of $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (48 mg, 0.15 mmol) was added a dilute solution of NaBH_4 (11 mg, 0.30 mmol) with vigorous stirring under a nitrogen atmosphere. After 5 min a dichloromethane solution (10 cm³) of $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$ (117 mg, 0.15 mmol) (in the case of insoluble chloro-bridged complexes a suspension was used) was added with vigorous stirring which was continued for 5 h. The solvents were evaporated in vacuum. The residue was extracted with dichloromethane (5 cm³ \times 3), filtered, concentrated and recrystallized from dichloromethane-hexane mixture as a yellow crystalline solid (80 mg, 52%). All other complexes of this series were prepared similarly and the pertinent data are given in Table 3.

[PdCl(NC₅H₄Se)(PPh₃)] 1f. (i) To a dichloromethane solution (10 cm³) of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (286 mg, 0.41 mmol) was added a methanolic solution (8 cm³) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (78 mg, 0.25 mmol) and NaBH_4 (20 mg, 0.54 mmol)] and the mixture stirred for 5 h. The solvents were evaporated *in vacuo* and the residue was extracted with benzene and filtered. The filtrate was concentrated *in vacuo* and the residue recrystallized from a benzene-hexane mixture as maroon crystals (yield 167 mg, 73%), m.p. $198\text{--}200^{\circ}\text{C}$ (Found: C, 50.0; H, 3.2; N, 2.5. Calc. for $\text{C}_{23}\text{H}_{19}\text{ClNPPdSe}$: C, 49.2; H, 3.4; N, 2.5%).

(ii) To a dichloromethane suspension (20 cm³) of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PPh}_3)_2]$ (350 mg, 0.40 mmol) was added a methanolic solution (10 cm³) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (127 mg, 0.40 mmol) and NaBH_4 (40 mg, 1.07 mmol)] and the mixture was stirred at room temperature for 4 h. The solvents were evaporated in vacuum and the residue was extracted with dichloromethane (5 cm³ \times 3), filtered, concentrated *in vacuo* and recrystallized from dichloromethane-hexane as maroon crystals (162 mg, 37%), m.p. $196\text{--}198^{\circ}\text{C}$ (Found: C, 48.5; H, 3.1; N, 2.9. Calc. for $\text{C}_{23}\text{H}_{19}\text{ClNPPdSe}$: C, 49.2; H, 3.4; N, 2.5%). The NMR data (^1H and ^{31}P) were in agreement with those of the product prepared *via* route (i).

(iii) To a dichloromethane suspension (10 cm³) of complex **4** (98 mg, 0.32 mmol) was added a solution of triphenylphosphine (87.3 mg, 0.33 mmol). The reactants were stirred until a clear solution was obtained (*ca.* 3 h). The solvent was evaporated *in vacuo* and the residue recrystallized from a benzene-hexane mixture (130 mg, 70%). The analytical and spectroscopic data were consistent with those of the product obtained in (i).

[PtCl(NC₅H₄Se)(PPh₃)] 1l. This was prepared in an analogous manner to that for complex **1f** by route (i) from $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $\text{NaSeC}_5\text{H}_4\text{N}$. The complex was recrystallized from acetone-hexane in 82% yield as a yellow crystalline solid, m.p. $180\text{--}182^{\circ}\text{C}$ (Found: C, 43.0; H, 3.4; N, 2.8. Calc. for $\text{C}_{23}\text{H}_{19}\text{ClNPPtSe}$: C, 42.5; H, 2.9; N, 2.2%). $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR in CDCl_3 : δ 3.8 [$^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$ 3826 Hz].

[(Prⁿ)₃P]Cl₂Pd(NC₅H₄Se)PdCl(Prⁿ)₃ 3a. To a dichloromethane solution (10 cm³) of $[\text{PdCl}(\text{NC}_5\text{H}_4\text{Se})(\text{PPr}^n_3)]$ (91 mg, 0.198 mmol) was added a solution (10 cm³) of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PPr}^n_3)_2]$ (65.5 mg, 0.097 mmol) in the same solvent. The mixture was heated under reflux with stirring for 4 h (the reaction carried out at room temperature also gave the same product as revealed by the ^{31}P NMR spectrum). The solvent was removed under vacuum and the residue recrystallized from CH_2Cl_2 -hexane in 84% yield. The other products were prepared similarly.

[PdCl(NC₅H₄Se)] 4. To a methanolic solution (20 cm³) of $\text{Na}_2[\text{PdCl}_4]$ (246 mg, 0.84 mmol) was added solid $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (133 mg, 0.42 mmol) and the whole was refluxed with stirring for 5 h during which an orange-red precipitate formed. After cooling to room temperature, the precipitated product was filtered off, washed with water and methanol and dried

Table 3 Pyridine-2-selenolate complexes of palladium(II) and platinum(II)

Complex	Recrystallization solvent (% yield)	M.p./°C	Analysis (%) [*]		
			C	H	N
1a [PdCl(NC ₅ H ₄ Se)(PEt ₃)]	CH ₂ Cl ₂ -hexane (52)	85–88	32.0 (31.7)	4.8 (4.6)	3.4 (3.1)
1b [PdCl(NC ₅ H ₄ Se)(PPr ⁿ ₃)]	Ether-hexane (52)	80–82	36.1 (36.6)	5.6 (5.5)	3.0 (3.1)
1c [PdCl(NC ₅ H ₄ Se)(PBu ⁿ ₃)]	Hexane (37)	40–42	40.9 (40.7)	6.2 (6.2)	2.6 (2.8)
1d [PdCl(NC ₅ H ₄ Se)(PMe ₂ Ph)]	Methanol-ether (52)	110–112	35.5 (35.7)	3.3 (3.5)	3.0 (3.2)
1e [PdCl(NC ₅ H ₄ Se)(PMePh ₂)]	CH ₂ Cl ₂ -hexane (37)	165–166	43.6 (43.3)	3.4 (3.4)	3.0 (2.8)
1f [PdCl(NC ₅ H ₄ Se)(PPh ₃)]	Benzene-hexane (37)	196–198	48.5 (49.2)	3.1 (3.4)	2.9 (2.5)
3a [(Pr ⁿ ₃ P)Cl ₂ Pd(NC ₅ H ₄ Se)PdCl(PPr ⁿ ₃)]	CH ₂ Cl ₂ -hexane (75)	125–127	34.9 (34.7)	5.9 (5.8)	1.5 (1.8)
1g [PtCl(NC ₅ H ₄ Se)(PEt ₃)]	CH ₂ Cl ₂ -hexane (52)	95–97	27.2 (26.1)	4.1 (3.8)	2.4 (2.8)
1h [PtCl(NC ₅ H ₄ Se)(PPr ⁿ ₃)]	CH ₂ Cl ₂ -hexane (44)	89–90	30.2 (30.7)	4.5 (4.6)	2.5 (2.6)
1i [PtCl(NC ₅ H ₄ Se)(PBu ⁿ ₃)]	Hexane	Paste	35.2 (34.6)	5.6 (5.3)	2.6 (2.4)
1j [PtCl(NC ₅ H ₄ Se)(PMe ₂ Ph)]	CH ₂ Cl ₂ -hexane (42)	88–90	28.5 (29.7)	2.4 (2.9)	2.6 (2.7)
1k [PtCl(NC ₅ H ₄ Se)(PMePh ₂)]	CH ₂ Cl ₂ -hexane + Ether (41)	78–80	36.9 (36.8)	2.8 (2.9)	2.4 (2.4)
3b [(Et ₃ P)Cl ₂ Pt(NC ₅ H ₄ Se)PtCl(PEt ₃)]	CH ₂ Cl ₂ -hexane (60)	188–190 (melts with decomp.)	22.4 (22.9)	3.4 (3.8)	1.6 (1.6)
3c [(Pr ⁿ ₃ P)Cl ₂ Pt(NC ₅ H ₄ Se)PtCl(PPr ⁿ ₃)]	Ether-hexane (52)	128–130	28.2 (28.4)	4.4 (4.8)	1.2 (1.4)

* Calculated values in parentheses.

in vacuo (yield 200 mg, 79%), m.p. 275 °C (decomp.) (Found: C, 21.6; H, 1.6; N, 5.6. Calc. for C₅H₄ClNPdSe: C, 20.1; H, 1.3; N, 4.7%).

[{Pd(NC₅H₄Se)}₂]**5a**. Sodium pyridine-2-selenolate was prepared by the reaction of (NC₅H₄)₂Se₂ (207 mg, 0.66 mmol) in methanol (10 cm³) with a methanolic solution of NaBH₄ (52.2 mg, 1.40 mmol) at room temperature with stirring for 5 min. A methanolic solution (8 cm³) of Na₂[PdCl₄] (206 mg, 0.70 mmol) was added to a freshly prepared solution of NaSeC₅H₄N whereupon an orange-brown precipitate was formed. The reactants were stirred at room temperature for 3 h. The orange-brown insoluble product was filtered off, washed with water, ethanol and diethyl ether and dried *in vacuo* (yield 150 mg, 54%), m.p. 125–127 °C (decomp.) (Found: C, 28.8; H, 1.8; N, 6.6. Calc. for C₁₀H₈N₂PdSe₂: C, 28.6; H, 1.9; N, 6.7%).

[{Pt(NC₅H₄Se)}₂]**5b**. To a dichloromethane solution (10 cm³) of [PtCl₂(cod)] (277 mg, 0.74 mmol) was added a methanolic solution (10 cm³) of NaSeC₅H₄N [prepared from (NC₅H₄)₂Se₂ (232 mg, 0.74 mmol) and NaBH₄ (65 mg, 1.75 mmol)] with vigorous stirring to give an orange precipitate. The reactants were stirred for 3 h. The insoluble orange precipitate was filtered off, washed with water, ethanol and diethyl ether and dried *in vacuo* (yield 180 mg, 48%), m.p. 185 °C (decomp.) (Found: C, 23.2; H, 1.4; N, 5.3. Calc. for C₁₀H₈N₂Se₂Pt: C, 23.6; H, 1.6; N, 5.5%).

[PdCl(NC₅H₄Se)(dppe)]**6**. The reaction was carried out in a manner analogous to that of complex **7a** [preparation (i), (see later)] except that the Pd:NC₅H₄Se ratio was 1:1. The product was recrystallized from dichloromethane-hexane as a red crystalline solid in 32% yield; m.p. 185–189 °C (decomp.) (Found: C, 49.6; H, 3.8; N, 1.3. Calc. for C₃₁H₂₈ClNPdSe·CH₂Cl₂: C, 49.1; H, 3.9; N, 1.8%). ¹H NMR in CDCl₃: δ 2.45–2.87 (br, PCH₂), 7.08–7.82 (br, m, Ph + py) (a peak due to CH₂Cl₂ was

present at 5.28). ³¹P-{¹H} NMR in CDCl₃: δ 60.0 (br) and 64.2 (br).

[Pd(NC₅H₄Se)₂(dppe)]**7a**. (i) This was prepared from [PdCl₂(dppe)] (198 mg, 0.36 mmol) and NaSeC₅H₄N [prepared from (NC₅H₄)₂Se₂ (114 mg, 0.36 mmol) and NaBH₄ (52 mg, 1.34 mmol)]. The product was recrystallized from dichloromethane-hexane as maroon crystals (115 mg, 41%), m.p. 175–178 °C (Found: C, 51.2; H, 3.5; N, 3.5. Calc. for C₃₆H₃₂N₂P₂PdSe₂·0.5CH₂Cl₂: C, 50.9; H, 3.9; N, 3.3%). ¹H NMR in CDCl₃: δ 2.24 (br), 2.37 (br) (PCH₂), 6.56 (br), 6.82 (br) (each 1 H, py), 7.33 (br m), 7.73 (br m) (Ph + 2 H py). ³¹P-{¹H} NMR in CDCl₃: δ 54.6 (br s).

(ii) To a dichloromethane suspension (6 cm³) of complex **5a** (39.2 mg, 0.1 mmol) was added a solution of dppe (37 mg, 0.1 mmol) and the mixture was stirred for 1 h. The solution was filtered and the filtrate concentrated *in vacuo*. The NMR spectra of the solution were consistent with the product obtained in (i).

[Pt(NC₅H₄Se)₂(dppe)]**7b**. (i) To a methanolic solution (10 cm³) of NaSeC₅H₄N [prepared from (NC₅H₄)₂Se₂ (370 mg, 1.18 mmol) in methanol (5 cm³) and methanolic NaBH₄ (102 mg, 2.77 mmol)] was added a dichloromethane suspension (15 cm³) of [PtCl₂(dppe)] (745 mg, 1.17 mmol) with vigorous stirring at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 5 h, during which a clear solution was formed. The solvents were stripped off *in vacuo* and the residue was extracted with dichloromethane and passed through a Florisil column. The volume of the solution was reduced to 10 cm³ and hexane (10 cm³) added. Slow evaporation of the solvents in air gave yellow crystals of [Pt(NC₅H₄Se)₂(dppe)] (543 mg, 53%), m.p. 224–225 °C (Found: C, 46.4; H, 3.3; N, 3.3. Calc. for C₃₆H₃₂N₂P₂PtSe₂·0.5CH₂Cl₂: C, 46.1; H, 3.5; N, 2.9%). ¹H NMR in CDCl₃: δ 2.18 (d, *J* 18.6 Hz, PCH₂), 6.52 (m, 1 H, py), 6.82 (m, 1 H, py), 7.34 (m), 7.77 (m) (Ph + 2 H py) (a peak

due to CH_2Cl_2 was present at 5.28). ^{31}P - $\{^1\text{H}\}$ NMR in CDCl_3 : δ 46.6 [$^1J(\text{Pt}-\text{P})$ 2968, $^2J(^{77}\text{Se}-^{31}\text{P})$ 68 Hz]. ^{77}Se - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -1058.3 [dd, $^2J(^{77}\text{Se}-^{31}\text{P})_{\text{trans}}$ 81, $^2J(^{77}\text{Se}-^{31}\text{P})_{\text{cis}}$ 12, $^1J(^{195}\text{Pt}-^{77}\text{Se})$ 220 Hz]. ^{195}Pt - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -4986 [t, $^1J(^{195}\text{Pt}-^{31}\text{P})$ 2968 Hz].

(ii) To a CDCl_3 suspension (2 cm^3) of complex **5b** (24 mg, 0.05 mmol), solid dppe (19.5 mg, 0.05 mmol) was added and the mixture stirred for 1 h. The resulting clear yellow solution was filtered into an NMR tube. The ^{31}P - $\{^1\text{H}\}$ and ^1H NMR spectra were consistent with the sample prepared as in (i).

[Pt(NC₅H₄Se)₂(dpmm)] 7c. To a dichloromethane suspension (15 cm^3) of $[\text{PtCl}_2(\text{dpmm})]$ (177 mg, 0.27 mmol) was added a methanolic solution (10 cm^3) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (85 mg, 0.27 mmol) and NaBH_4 (24 mg, 0.63 mmol)] with vigorous stirring. The mixture was stirred at room temperature for 5 h. The solvents were stripped off *in vacuo* and the residue was extracted with dichloromethane (5 $\text{cm}^3 \times 3$). The dichloromethane solution was passed through a Florisil column and the solvent evaporated *in vacuo*. The residue was recrystallized from dichloromethane-hexane to give yellow crystals of $[\text{Pt}(\text{NC}_5\text{H}_4\text{Se})_2(\text{dpmm})]$ (129 mg, 53%), m.p. 224–225 °C (Found: C, 46.5; H, 3.0; N, 3.1. Calc. for $\text{C}_{35}\text{H}_{30}\text{N}_2\text{PtSe}_2$: C, 47.0; H, 3.4; N, 3.1%). ^1H NMR in CDCl_3 : δ 4.33 [t, J 9.6, PCH_2 , $^3J(\text{Pt}-\text{H})$ 55], 6.42 (t, J 7, 1 H, py), 6.89 [dt, J 1.7 (d), 7.8 (t), 1 H, py], 7.56 (d, J 7.8 Hz, 1 H, py), 7.28 (m), 7.81 (m) (Ph + 2 H py) (a peak due to CH_2Cl_2 was present at 5.28). ^{31}P - $\{^1\text{H}\}$ NMR in CDCl_3 : δ -50.9 [$^1J(\text{Pt}-\text{P})$ = 2711, $^2J(^{77}\text{Se}-^{31}\text{P})$ = 47 Hz].

[(dppe)Pd(NC₅H₄Se)₂PdCl₂] 8a. To a dichloromethane solution (15 cm^3) of $[\text{Pd}(\text{NC}_5\text{H}_4\text{Se})_2(\text{dppe})]$ **7a** (74 mg, 0.09 mmol) was added an acetonitrile solution (5 cm^3) of $[\text{PdCl}_2(\text{MeCN})_2]$ (23 mg, 0.09 mmol) with stirring whereupon a brown precipitate formed. The reactants were stirred for 1 h. The precipitated product was filtered off, washed with dichloromethane and dried *in vacuo* (yield 65 mg, 72%), m.p. 240 °C (decomp.) (Found: C, 43.4; H, 2.7; N, 2.0. Calc. for $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{N}_2\text{P}_2\text{Pd}_2\text{Se}_2$: C, 43.4; H, 3.2; N, 2.8%). IR in Nujol: $\nu(\text{Pd}-\text{Cl})$ 309, 288 (sh) and 280 cm^{-1} .

[(dppe)Pt(NC₅H₄Se)₂PdCl₂] 8b. This was prepared in an analogous manner to complex **8a** from $[\text{Pt}(\text{NC}_5\text{H}_4\text{Se})_2(\text{dppe})]$ and $[\text{PdCl}_2(\text{MeCN})_2]$ in 73% yield, m.p. 225 °C (decomp.) (Found: C, 39.6; H, 2.5; N, 2.4. Calc. for $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{N}_2\text{P}_2\text{Pt}_2\text{Se}_2$: C, 39.8; H, 3.0; N, 2.6%). IR in Nujol: $\nu(\text{Pd}-\text{Cl})$ 313 and 290 cm^{-1} .

[(dppe)Pt(NC₅H₄Se)₂PtCl₂] 8c. This was prepared in an analogous manner to complex **8a** from $[\text{Pt}(\text{NC}_5\text{H}_4\text{Se})_2(\text{dppe})]$ and $[\text{PtCl}_2(\text{MeCN})_2]$ in 60% yield, m.p. 192 °C (decomp.) (Found: C, 36.3; H, 2.3; N, 2.2. Calc. for $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{N}_2\text{Pt}_2\text{Se}_2$: C, 36.8; H, 2.7; N, 2.4%). IR in Nujol: $\nu(\text{Pt}-\text{Cl})$ 313 and 292 cm^{-1} .

[Pd(NC₅H₄Se)₂(PPh₃)₂] 9a. (i) To a dichloromethane solution (15 cm^3) of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (433 mg, 0.62 mmol) was added a methanolic solution (12 cm^3) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (194 mg, 0.62 mmol) and NaBH_4 (47 mg, 1.28 mmol)] and the mixture stirred at room temperature for 5 h. The solvents were evaporated *in vacuo* and the residue extracted with dichloromethane, filtered and passed through a Florisil column. To the resulting solution was added hexane which on cooling gave red crystals (426 mg, 73%). The ^{31}P - $\{^1\text{H}\}$ NMR spectrum showed two broad resonances δ 33.1 and -4.5 (PPh₃) and the analysis was lower than that expected for $[\text{Pd}(\text{NC}_5\text{H}_4\text{Se})_2(\text{PPh}_3)_2]$ **9b**.

This sample after several recrystallizations from dichloromethane-hexane afforded pure $[\text{Pd}(\text{NC}_5\text{H}_4\text{Se})_2(\text{PPh}_3)_2]$ **9a**, m.p. 162–163 °C (Found: C, 49.1; H, 3.3; N, 3.9. Calc. for

$\text{C}_{28}\text{H}_{23}\text{N}_2\text{PPdSe}_2$: C, 49.3; H, 3.4; N, 4.1%). ^1H NMR in CDCl_3 : δ 6.63 (t, J 5.2, 1 H, py), 7.11 [dt, J 1.8 (d), 7.9 (t), 1 H, py], 7.29–7.37 (m), 7.58–7.64 (m) (Ph + 1 H, py) and 7.96 (d, J 4.5 Hz, 1 H, py). ^{31}P - $\{^1\text{H}\}$ NMR in CDCl_3 : δ 33.6 (sharp s). When 1 equivalent of PPh₃ was added to **9a** the NMR spectra (^1H and ^{31}P) were consistent with **9b**.

(ii) To a dichloromethane suspension (15 cm^3) of complex **5a** (80 mg, 0.19 mmol) was added a solution of triphenylphosphine (100 mg, 0.19 mmol) and the mixture stirred for 10 min. The clear wine-red solution obtained was filtered and the filtrate concentrated *in vacuo*. The residue was recrystallised several (four to five) times to give **9a** as characterized by analysis and NMR spectroscopy.

(iii) To a benzene solution (15 cm^3) of $[\text{Pd}(\text{PPh}_3)_4]$ (503 mg, 0.43 mmol) was added a benzene solution of $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (137 mg, 0.44 mmol) under a nitrogen atmosphere. The reactants were stirred for 5 h, the solvent was evaporated in vacuum and the residue washed thoroughly with diethyl ether and hexane to remove the liberated triphenylphosphine. The residue was then recrystallized from benzene-hexane as a red crystalline solid (252 mg, 61%), m.p. 160–163 °C. The NMR data were consistent with complex **9a**.

[Pt(NC₅H₄Se)₂(PPh₃)₂] 9c. To a methanolic solution (8 cm^3) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (42 mg, 0.13 mmol) and NaBH_4 (12 mg, 0.31 mmol)] was added a dichloromethane solution of $[\text{PtCl}_2(\text{PPh}_3)_2]$ (102 mg, 0.13 mmol) and the mixture stirred at room temperature for 5 h. The solvents were evaporated *in vacuo* and the residue was extracted with acetone and passed through a Florisil column. The solution obtained was concentrated *in vacuo* and the residue recrystallized from acetone-hexane as a yellow crystalline solid (55 mg, 41%), m.p. 192–195 °C (Found: C, 46.5; H, 2.9; N, 3.2. Calc. for $\text{C}_{46}\text{H}_{38}\text{N}_2\text{P}_2\text{PtSe}_2$ **9c**: C, 53.0; H, 3.0; N, 2.7. Calc. for $\text{C}_{28}\text{H}_{23}\text{N}_2\text{PPtSe}_2$ **9d**: C, 43.6; H, 3.0; N, 3.6%). Attempts to obtain pure **9d** were not successful. NMR (CDCl_3 , room temperature): ^1H , δ 6.70–8.10 (br, m, Ph + py); ^{31}P - $\{^1\text{H}\}$, δ 7.8 [$^1J(\text{Pt}-\text{P})$ 3833 Hz] and -4.1 (PPh₃). NMR (CDCl_3 , -30 °C): ^1H , δ 6.47–8.16 (br, m, Ph + py); ^{31}P - $\{^1\text{H}\}$, δ 8.4 [$^1J(\text{Pt}-\text{P})$ 3760] (**9d**) 23.1 [$^1J(\text{Pt}-\text{P})$ 2805 Hz] (**9c**) and -6.1 (PPh₃).

[Pd(NC₅H₄Se){S₂P(OPrⁿ)₂}(PPh₃)₂] 10a. To a methanolic solution (6 cm^3) of $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{NC}_5\text{H}_4)_2\text{Se}_2$ (44 mg, 0.14 mmol) and NaBH_4 (11 mg, 0.29 mmol)] was added a dichloromethane solution (10 cm^3) of $[\text{PdCl}_2\{\text{S}_2\text{P}(\text{OPr}^n)_2\}(\text{PPh}_3)]$ (152 mg, 0.25 mmol) with vigorous stirring which was continued for 4 h. The solvents were evaporated *in vacuo* and the residue was extracted with dichloromethane (15 $\text{cm}^3 \times 3$) and filtered. The filtrate was dried *in vacuo* and the residue recrystallized from diethyl ether-hexane as an orange-red crystalline solid (95 mg, 52%), m.p. 110–115 °C (Found: C, 46.8; H, 4.6; N, 1.8. Calc. for $\text{C}_{29}\text{H}_{33}\text{NO}_2\text{P}_2\text{PdS}_2\text{Se}$: C, 47.1; H, 4.5; N, 1.9%). ^1H NMR in CDCl_3 : δ 0.85 (t, J 7.4, $\text{OCH}_2\text{CH}_2\text{Me}$), 1.64 (m, OCH_2CH_2), 3.90 [td, J 7 (t), 9 Hz (d), OCH_2], 6.80 (m, 1 H, py), 7.12 (m, 1 H, py), 7.29–7.40 (m), 7.51–7.65 (m) (Ph + 1 H py) and 8.22 (m, 1 H, py). ^{31}P - $\{^1\text{H}\}$ NMR in CDCl_3 : δ 32.1 (s, PPh₃) and 101.5 [s, $\text{S}_2\text{P}(\text{OPr}^n)_2$].

[Pd(NC₅H₄Se){S₂P(OPrⁱ)₂}(PPh₃)₂] 10b. This was prepared in an analogous manner to complex **10a** in 78% yield, m.p. 115–118 °C (Found: C, 46.7; H, 4.7; N, 1.7. Calc. for $\text{C}_{29}\text{H}_{33}\text{NO}_2\text{P}_2\text{PdS}_2\text{Se}$: C, 47.1; H, 4.5; N, 1.9%). ^1H NMR in CDCl_3 : δ 1.21 (d, J 6.2 Hz, OCHMe_2), 4.67 (m, OCH), 6.80 (m, 1 H, py), 7.12 (m, 1 H, py), 7.28–7.36 (m), 7.51–7.62 (m) (Ph + 1 H, py) and 8.22 (m, 1 H, py). ^{31}P - $\{^1\text{H}\}$ NMR in CDCl_3 : δ 32.1 (s, PPh₃) and 97.5 [s, $\text{S}_2\text{P}(\text{OPr}^i)_2$].

Crystallography

Crystal data. $\text{C}_{23}\text{H}_{46}\text{Cl}_3\text{NP}_2\text{Pd}_2\text{Se}$ **3a**, $M = 796.66$, triclinic,

space group $P1$, $a = 11.592(2)$, $b = 11.9292(14)$, $c = 13.6590(11)$ Å, $\alpha = 88.531(8)$, $\beta = 84.457(11)$, $\gamma = 61.357(12)^\circ$, $U = 1649.4(4)$ Å³, $T = 293(2)$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.546 \text{ mm}^{-1}$, 6107 reflections measured, 5790 unique ($R_{\text{int}} = 0.026$) which were used in all calculations. The final $wR2 = 0.0851$, $R1 = 0.0381$.

X-Ray data on orange-red crystals of $[(\text{Pr}^n_3\text{P})\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_4\text{Se})\text{PdCl}(\text{PP}^n_3)]$ **3a** were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) employing the ω - 2θ scan technique. The unit-cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved using SHELXS 86³¹ and refined using SHELXL 93³² computer programs. The non-hydrogen atoms were refined anisotropically.

CCDC reference number 186/1000.

See <http://www.rsc.org/suppdata/dt/1998/2359/> for crystallographic files in .cif format.

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