

Synthesis and Characterization of Thiolato- and Selenolato-platinum(II) Complexes with Bis(diphenylphosphino)alkanes*

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The complexes $[\text{Pt}(\text{ER})_2(\text{L-L})]$ [$\text{ER} = \text{SPr}^i$, SPh , $\text{C}_6\text{H}_4\text{Me-}p$ or SePh ; $\text{L-L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-3$)] have been prepared and their ability to act as bidentate ligands towards other metal species demonstrated. Proton, ^{31}P and ^{195}Pt NMR spectroscopy have been employed to ascertain their structures. A single-crystal X-ray structure determination of $[\text{Pt}(\text{SePh})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ has established the mononuclear nature of the complex. The platinum atom is in a distorted square-planar environment with the selenium atoms and the chelating diphosphine ligand in a *cis* configuration. The four-membered PtPCP metallacyclic ring is non-planar.

Binuclear platinum complexes $[\text{Pt}_2\text{X}_2(\mu\text{-Y})(\mu\text{-Z})(\text{PR}_3)_2]$ containing bridging organochalcogenide ligands have attracted considerable attention in recent years.¹⁻³ Mononuclear *cis* complexes $[\text{Pt}(\text{ER})_2\text{L}_2]$ ($\text{E} = \text{S}$ or Se) are useful precursors for the synthesis of bi- and poly-nuclear complexes.⁴⁻⁶ In the case of monodentate L and ER ligands, isomerization (to *trans* form) and polymerization reactions have been usually encountered.⁷ However, chelating organochalcogenide⁸⁻¹¹ or bidentate L_2 ^{8,12-15} ligands yield stable *cis* complexes. There are a few reports on mononuclear bis(thiolato)platinum(II) complexes containing diphosphine ligands such as dppe [1,2-bis(diphenylphosphino)ethane].^{4,8} In general, the chelating tendency of bis(phosphino)alkanes $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ($\text{R} = \text{alkyl}$ or aryl) decreases as the number of CH_2 groups connecting the two phosphorus atoms increases (for $n > 2$) [e.g. 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), etc.]¹⁶ or decreases (for $n = 1$) [e.g., bis(diphenylphosphino)methane (dppm)].^{17,18} For example, it has been observed that the complexes $[\text{RhCl}(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ are dimers when $n = 1, 3$ or 4 , but a monomer¹⁹ when $n = 2$. As part of our studies on platinum complexes with organochalcogenide ligands, we report in this paper the results of our investigations on complexes containing bis(diphenylphosphino)alkanes.

Experimental

The complexes $[\text{PtCl}_2(\text{L-L})]$ ($\text{L-L} = \text{dppm}$, dppe or dppp) were prepared by the literature methods.^{20,21} Phosphines (Strem Chemicals), thiols and diphenyl diselenide (Aldrich) and NaBPh_4 , were obtained from commercial sources. Reactions were carried out under a nitrogen atmosphere in dry and distilled solvents. The ^1H NMR spectra were recorded on a Bruker AC-200 or AMX-500 spectrometer. Chemical shifts are referred to the internal solvent peak [chloroform (δ 7.26) or dichloromethane (δ 5.32)], ^{31}P - $\{^1\text{H}\}$ and ^{195}Pt - $\{^1\text{H}\}$ NMR spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 and 17.01 MHz respectively. Chemical shifts are reported in ppm relative to external 85% H_3PO_4 and Na_2PtCl_6 in D_2O ,

respectively. Microanalyses of the complexes were carried out in the Analytical Chemistry Division of this research centre.

Preparations.— $[\text{Pt}(\text{SPh})_2(\text{dppm})]$. To a suspension of $[\text{PtCl}_2(\text{dppm})]$ (120 mg, 0.185 mmol) in benzene (20 cm^3) containing triethylamine (0.2 cm^3), thiophenol (0.2 cm^3) was added and the mixture stirred for 5 h at room temperature. The resulting solution was evaporated under vacuum. The residue was extracted with benzene and recrystallized from benzene-methanol (2:1, 3 cm^3) as a pale yellow crystalline solid which was filtered off, washed with methanol and dried *in vacuo* (120 mg, 82%). The other thiolato complexes $[\text{Pt}(\text{SR})_2(\text{L-L})]$ ($\text{R} = \text{Pr}^i$, Ph or $\text{C}_6\text{H}_4\text{Me-}p$, $\text{L-L} = \text{dppm}$, dppe or dppp) were prepared in an analogous manner and the pertinent data are given in Table 1.

$[\text{Pt}(\text{SePh})_2(\text{dppm})]$. To a solution of NaSePh , prepared from Se_2Ph_2 (132 mg, 0.422 mmol) and NaBH_4 in methanol,² a benzene suspension of $[\text{PtCl}_2(\text{dppm})]$ (274 mg, 0.422 mmol) was added at once and stirred for 5 h. The solvent was evaporated *in vacuo* and the residue was extracted with dichloromethane. Yellow crystals obtained from the dichloromethane-methanol mixture were filtered off, washed with methanol and dried (yield 320 mg, 85%). The other selenolato complexes $[\text{Pt}(\text{SePh})(\text{L-L})]$ ($\text{L-L} = \text{dppe}$ or dppp) were prepared in an analogous manner.

$[\text{Pt}_2(\mu\text{-SPh})_2(\text{dppm})_2][\text{BPh}_4]_2$. To a suspension of $[\text{PtCl}_2(\text{dppm})]$ (78 mg, 0.119 mmol) in methanol (10 cm^3), solid NaBPh_4 (82 mg, 0.241 mmol) was added and the whole solution was stirred at room temperature for 30 min. To this a dichloromethane solution (10 cm^3) of $[\text{Pt}(\text{SPh})_2(\text{dppm})]$ (94 mg, 0.118 mmol) was added and stirred further for 6 h. The solvents were removed *in vacuo*. The residue was extracted with dichloromethane and recrystallized from dichloromethane-methanol (5:1, 12 cm^3) to give colourless crystals (yield 210 mg, 89%). Conductivity measurements on this and other binuclear compounds $[\text{Pt}_2(\mu\text{-ER})_2(\text{L-L})_2][\text{BPh}_4]_2$ ($\text{E} = \text{S}$ or Se ; $\text{R} = \text{Pr}^i$, Ph or $\text{C}_6\text{H}_4\text{Me-}p$; $\text{L-L} = \text{dppm}$, dppe or dppm) in acetonitrile gave values in the range appropriate for 1:2 electrolytes.

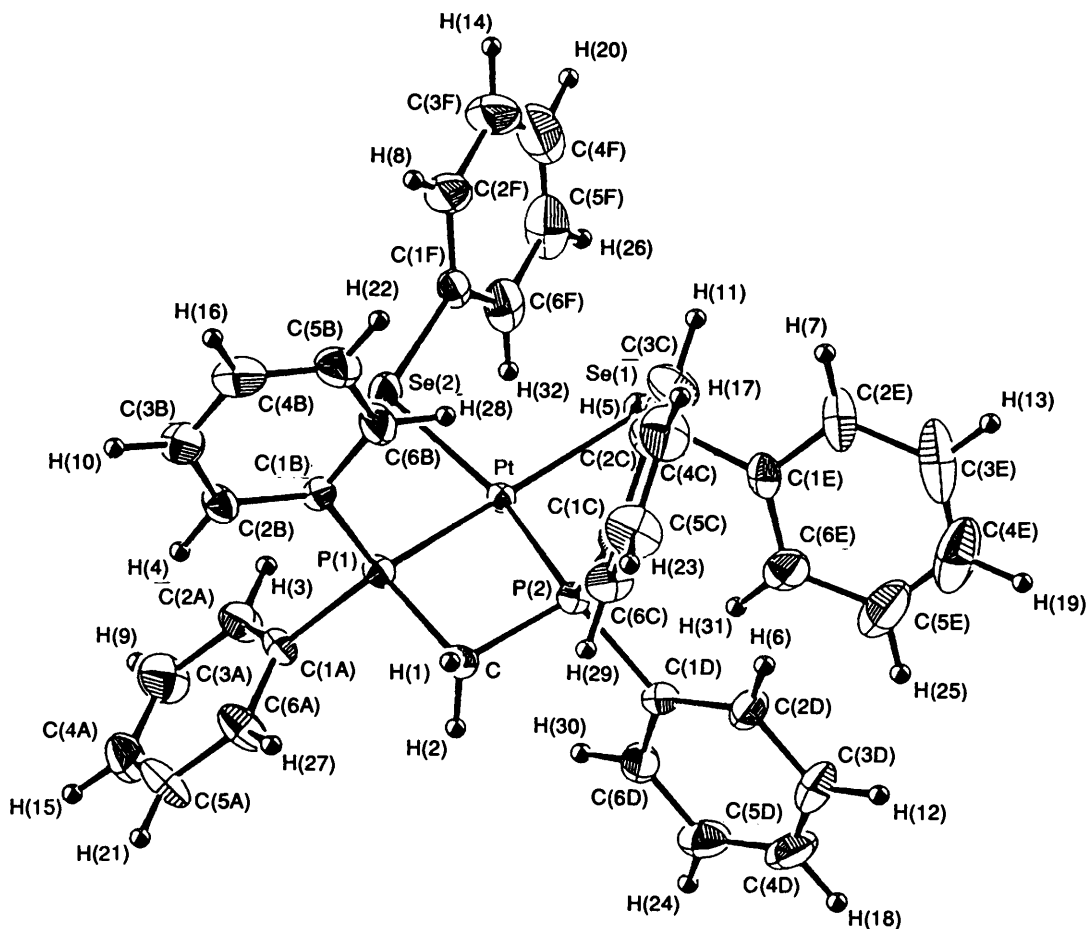
Crystallography.—Crystallographic data together with data collection and structure solution refinement details are given in Table 2. The structure was solved by direct methods.²² The non-hydrogen atoms were refined anisotropically. The final cycle of

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii-xxviii.

Table 1 Analytical data for $[\text{Pt}(\text{ER})_2(\text{L-L})]$ and $[\text{Pt}_2(\mu\text{-ER})_2(\text{L-L})_2][\text{BPh}_4]_2$

Complex	Yield ^a (%)	M.p./°C	Analysis ^b (%)	
			C	H
$[\text{Pt}(\text{SPr}^i)_2(\text{dppm})]$	68	225 (decomp.)	52.4 (51.0)	5.0 (5.0)
$[\text{Pt}(\text{SPh})_2(\text{dppm})]$	80	201	55.6 (55.7)	4.0 (4.0)
$[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}p)_2(\text{dppm})]$	75	264	56.5 (56.7)	4.5 (4.4)
$[\text{Pt}(\text{SePh})_2(\text{dppm})]$	82	230	49.9 (49.8)	3.7 (3.6)
$[\text{Pt}(\text{SPh})_2(\text{dppe})]$	76	225–226	56.1 (56.2)	4.1 (4.2)
$[\text{Pt}(\text{SePh})_2(\text{dppe})]$	73	205–206	49.7 (50.4)	3.9 (3.8)
$[\text{Pt}(\text{SPh})_2(\text{dppp})]$	79	230–232	56.5 (56.7)	4.3 (4.4)
$[\text{Pt}(\text{SePh})_2(\text{dppp})]$	68	217–218	50.5 (50.9)	3.9 (3.9)
$[\text{Pt}_2(\mu\text{-SPr}^i)_2(\text{dppm})_2][\text{BPh}_4]_2$	82	140–142	63.7 (64.3)	5.1 (4.9)
$[\text{Pt}_2(\mu\text{-SPh})_2(\text{dppm})_2][\text{BPh}_4]_2$	80	156–158	65.3 (65.5)	4.4 (4.7)
$[\text{Pt}_2(\mu\text{-C}_6\text{H}_4\text{Me-}p)_2(\text{dppm})_2][\text{BPh}_4]_2$	75	130–132	64.1 (65.8)	4.6 (4.8)
$[\text{Pt}_2(\mu\text{-SePh})_2(\text{dppm})_2][\text{BPh}_4]_2$	77	145–147	62.2 (62.6)	4.4 (4.5)
$[\text{Pt}_2(\mu\text{-SePh})_2(\text{dppe})_2][\text{BPh}_4]_2$	75	225–228	61.9 (62.9)	4.8 (4.6)

^a Upon recrystallization from $\text{CH}_2\text{Cl}_2\text{-MeOH}$. ^b Calculated values are given in parentheses.

**Fig. 1** An ORTEP drawing of $[\text{Pt}(\text{SePh})_2(\text{dppm})]$

full-matrix least-squares refinement converged with unweighted and weighted agreement factors of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.041$ and $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.041$.

Neutral-atom scattering factors were taken from Cromer and Waber.²³ Anomalous dispersion effects were included in F_c ;²⁴ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.²⁵ All calculations were performed using the TEXSAN²⁶ crystallographic software package of the Molecular Structure Corporation. Fractional atomic coordinates are listed in Table 3 and the ORTEP²⁷ plot of the molecule is shown in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Treatment of $cis\text{-}[\text{PtCl}_2(\text{L-L})]$ ($\text{L-L} = \text{dppm}$, dppe or dppp) with thiols RSH ($\text{R} = \text{Pr}^i$, Ph or $\text{C}_6\text{H}_4\text{Me-}p$) in the presence of triethylamine readily gave the mononuclear complexes $[\text{Pt}(\text{SR})_2(\text{L-L})]$. Reaction of $cis\text{-}[\text{PtCl}_2(\text{L-L})]$ with NaSePh afforded $[\text{Pt}(\text{SePh})_2(\text{L-L})]$ [equation (1)]. The cation

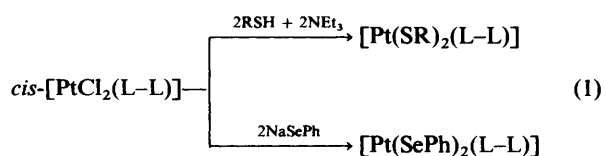
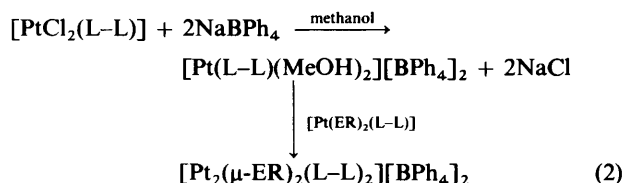


Table 2 Crystal data and data collection parameters for [Pt-(SePh)₂(dppm)]

Crystal data	
Formula	C ₃₇ H ₃₂ P ₂ Se ₂ Pt
<i>M</i>	891.62
Crystal habit	Clear, prism
Crystal size/mm	0.50 × 0.40 × 0.60
Symmetry, space group	Triclinic, <i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	11.861(2)
<i>b</i> /Å	15.520(3)
<i>c</i> /Å	10.196(1)
α /°	91.15(2)
β /°	108.04(1)
γ /°	109.33(1)
<i>Z</i>	2
<i>D</i> _c /g cm ⁻³	1.775
<i>F</i> (000)	860
μ (Mo-K α)/cm ⁻¹	65.28
Intensity measurements	
Diffractometer	Rigaku AFC 6S
Radiation (λ /nm)	Mo-K α (0.0710 69)
Monochromator	Graphite
Scan type	ω
Scan rate (in ω)/° min ⁻¹	8.0 (2 prescans)
Scan width/°	1.23 + 0.30 tan θ
2 θ _{max} /°	55.0
Total no. of reflections measured	8007
Unique no. of reflections (<i>R</i> _{int})	7636 (0.036)
Corrections	Lorentz-polarization, absorption (transmission factors: 0.61–1.00), secondary extinction (coefficient 0.45132 × 10 ⁻⁶)
Solution and refinement	
Structure solution	Direct methods
Refinement	Full-matrix least squares
<i>p</i> -Factor in weighting scheme	0.03
$w = 1/[\sigma^2(F) + pF^2]$	
Anomalous dispersion	All non-hydrogen atoms
No. observations [<i>I</i> ≥ 3.00 σ (<i>I</i>)]	5075
No. of variables	380
Reflection/parameter ratio	13.36
Residuals: <i>R</i> , <i>R</i> '	0.041, 0.041
Goodness-of-fit indicator	1.24
Maximum shift/error in final cycle	0.04
Maximum peak in final difference map/e Å ⁻³	1.75
Minimum peak in final difference map/e Å ⁻³	-1.33

[Pt(L-L)(MeOH)₂]²⁺ on treatment with the mononuclear complexes *cis*-[Pt(ER)₂(L-L)] (E = S or Se) gave binuclear complexes containing ER bridges [equation (2), L-L = dppm or dppe].



The ³¹P-{¹H} NMR resonances of the mononuclear complexes are deshielded relative to the corresponding *cis*-[PtCl₂(L-L)] species (Table 4) and the magnitude of ¹*J*(Pt-P) is reduced significantly indicating the strong *trans* influence of

Table 3 Positional parameters for [Pt(SePh)₂(dppm)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pt	0.287 55(3)	0.228 88(2)	0.033 10(3)
Se(1)	0.299 47(8)	0.251 06(6)	0.274 70(8)
Se(2)	0.498 31(8)	0.215 03(8)	0.107 0(1)
P(1)	0.274 2(2)	0.220 2(1)	-0.192 4(2)
P(2)	0.105 3(2)	0.249 3(1)	-0.086 2(2)
C	0.109 5(7)	0.217 5(5)	-0.258 5(8)
C(1A)	0.277 4(8)	0.123 5(5)	-0.293 1(8)
C(1B)	0.372 4(7)	0.322 8(5)	-0.239 1(7)
C(1C)	0.112 1(7)	0.368 2(5)	-0.082 3(9)
C(1D)	-0.051 4(7)	0.179 2(5)	-0.086 6(8)
C(1E)	0.141 3(8)	0.248 9(6)	0.289 5(8)
C(1F)	0.576 9(8)	0.247 6(7)	0.304 0(9)
C(2A)	0.351 9(9)	0.074 2(7)	-0.233(1)
C(2B)	0.422 5(8)	0.320 5(6)	-0.344 8(9)
C(2C)	0.192 4(9)	0.431 1(6)	0.035(1)
C(2D)	-0.135 9(8)	0.218 6(6)	-0.069(1)
C(2E)	0.138(1)	0.324 6(7)	0.360(1)
C(2F)	0.671(1)	0.332 1(9)	0.357(1)
C(3A)	0.356(1)	0.002 4(8)	-0.313(1)
C(3B)	0.493(1)	0.402 4(7)	-0.376(1)
C(3C)	0.208(1)	0.523 6(7)	0.032(1)
C(3D)	-0.254(1)	0.159 6(8)	-0.066(1)
C(3E)	0.027(2)	0.318(1)	0.389(1)
C(3F)	0.734(1)	0.354(1)	0.501(2)
C(4A)	0.286(1)	-0.017 5(8)	-0.453(1)
C(4B)	0.510(1)	0.485 5(7)	-0.312(1)
C(4C)	0.143(1)	0.552 1(7)	-0.084(1)
C(4D)	-0.285(1)	0.066 8(9)	-0.084(1)
C(4E)	-0.075(1)	0.238(2)	0.347(2)
C(4F)	0.703(2)	0.291(1)	0.587(2)
C(5A)	0.211(1)	0.030 2(8)	-0.513(1)
C(5B)	0.459(1)	0.487 4(7)	-0.208(1)
C(5C)	0.061(1)	0.489 1(8)	-0.199(1)
C(5D)	-0.202(1)	0.028 8(7)	-0.101(1)
C(5E)	-0.071(1)	0.162(1)	0.281(1)
C(5F)	0.610(1)	0.209(1)	0.538(1)
C(6A)	0.206(1)	0.101 3(6)	-0.432(1)
C(6B)	0.392 6(9)	0.407 9(6)	-0.171(1)
C(6C)	0.046 8(9)	0.379 9(6)	-0.199(1)
C(6D)	-0.084 1(8)	0.084 4(6)	-0.100(1)
C(6E)	0.038(1)	0.165 5(8)	0.251(1)
C(6F)	0.546(1)	0.186 0(8)	0.396(1)

the ER group *trans* to phosphorus. The order of ¹*J*(Pt-P) follows the trend: dppm < dppp < dppe, in conformity with behaviour reported previously.^{16,20} The observed variation may be attributed to ring-size effects of the phosphine ligands, since the groups adjacent to phosphorus and *trans* to it are similar, and consequently changes in electronic effects are expected to be relatively small. The ¹⁹⁵Pt-{¹H} NMR spectrum of [Pt(SePh)₂(dppm)] in CDCl₃ displayed a triplet at δ -4291 [¹*J*(Pt-P) 2530; ¹*J*(¹⁹⁵Pt-⁷⁷Se) 208 Hz].

The ³¹P NMR spectra of the cationic binuclear complexes showed a single resonance with platinum satellites. The signal is deshielded from the corresponding resonance for [Pt(ER)₂(L-L)] complexes and also from the iodo-bridged complex [Pt₂(μ -I)₂(dppm)₂][BF₄]₂ [in CH₂Cl₂ δ -59.1, ¹*J*(Pt-P) 2994 Hz].²⁸ The presence of ³*J*(Pt-P) coupling (\approx 30 Hz) (Fig. 2) suggests their binuclear structure. A cationic hydroxo-bridged complex, [Pt₂(μ -OH)₂(PMe₃)₄][NO₃]₂, has been reported recently²⁹ for which ³*J*(Pt-P) = 10 Hz.

The ¹H NMR spectra of both mono- and bi-nuclear dppm complexes exhibited a triplet for the phosphine CH₂ protons with ²*J*(P-H) of 11 Hz, and platinum satellites were observed for the mononuclear complexes. The observed pattern for the CH₂ protons of dppm in the cationic complexes indicates that the dppm ligand behaves in a chelating fashion rather than in a bridging bidentate mode.³⁰ The complexes derived from dppe and dppp, however, gave a complex pattern for the CH₂ protons.

Table 4 $^{31}\text{P}\{-^1\text{H}\}$ and ^1H NMR data for $[\text{Pt}(\text{ER})_2(\text{L-L})]$ and related complexes

Complex	$^{31}\text{P}\{-^1\text{H}\}$			$^1\text{H}^a$
	Solvent	δ	$^1J(\text{Pt-P})/\text{Hz}$	
$[\text{PtCl}_2(\text{dppm})]$	CDCl_3	-64.1	3086	4.46 [t, CH_2 , $^2J(\text{P-H})$ 10.8, $^3J(\text{Pt-H})$ 72.0], 6.50-7.55 (m, Ph)
$[\text{Pt}(\text{SPr}^i)_2(\text{dppm})]$	CDCl_3	-50.0	2358	0.64 (d, J 6.7), 1.08 (d, J 6.7), 1.33 (d, J 6.2) (Me_2C , relative ratio 1:2:1), 3.05 (m), 3.24 (m, CHS), 4.28 (t, J 10), 7.42-7.93 (m, Ph)
$[\text{Pt}(\text{SPh})_2(\text{dppm})]$	CDCl_3	-48.8	2500	4.10 [t, CH_2 , $^2J(\text{P-H})$ 10, $^3J(\text{Pt-H})$ 48], 6.50-7.55 (br m, Ph)
$[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}p)_2(\text{dppm})]$	CDCl_3	-48.4	2531	2.05 (s, $\text{C}_6\text{H}_4\text{Me}$), 4.12 [t, CH_2 , $^2J(\text{P-H})$ 10, $^3J(\text{Pt-H})$ 48], 6.35 (d, J 8, C_6H_4), 7.08-7.59 (m, Ph and C_6H_4)
$[\text{Pt}(\text{SePh})_2(\text{dppm})]$	CDCl_3	-51.7 ^b	2530	4.17 [t, CH_2 , $^2J(\text{P-H})$ 10, $^3J(\text{Pt-H})$ 48], 6.50-7.55 (br m, Ph)
$[\text{PtCl}_2(\text{dppe})]$	CDCl_3	40.9	3618	—
$[\text{Pt}(\text{SPh})_2(\text{dppe})]$	CDCl_3	45.6	2885	2.22 ^c (CH_2), 6.66-7.89 (m, Ph)
$[\text{Pt}(\text{SePh})_2(\text{dppe})]$	CDCl_3	46.4	2957	2.20 ^c (CH_2), 6.50-7.80 (m, Ph)
$[\text{PtCl}_2(\text{dppp})]$	CDCl_3	-6.2	3408	—
$[\text{Pt}(\text{SPh})_2(\text{dppp})]$	CDCl_3	-0.6	2748	1.75-2.60 (br m, CH_2), 6.55-7.65 (m, Ph)
$[\text{Pt}(\text{SePh})_2(\text{dppp})]$	CDCl_3	-4.3	2800	1.20 (t, CH_2), 2.35 (br, CH_2), 6.60-7.65 (br m, Ph)
$[\text{Pt}_2(\mu\text{-SPr}^i)_2(\text{dppm})_2][\text{BPh}_4]_2$	$\text{CH}_2\text{Cl}_2\text{-}(\text{CD}_3)_2\text{CO}$	-49.8	2562	0.49 (d, J 6.7, Me), 2.92 (br m, CHS), 4.47 (t, J 11, PCH_2P), 6.75 (t, J 7.2), 6.87 (t, J 7.4), 7.21 (br m), 7.48 (br m), 7.63 (br m) (Ph)
$[\text{Pt}_2(\mu\text{-SPh})_2(\text{dppm})_2][\text{BPh}_4]_2$	$\text{CH}_2\text{Cl}_2\text{-}(\text{CD}_3)_2\text{CO}$	-50.3	2635 $^3J(\text{Pt-P})$ 27	4.31 (t, J 11, PCH_2P), 6.50 (t, J 7.7, SPh), 6.77 (t, J 7), 6.90 (t, J 7.4), 6.95 (d, J 7.7, SPh), 7.23 (br m), 7.31 (t, J 7.4), 7.52 (t, J 7.4) (Ph)
$[\text{Pt}_2(\mu\text{-SC}_6\text{H}_4\text{Me-}p)_2(\text{dppm})_2][\text{BPh}_4]_2$	$\text{CH}_2\text{Cl}_2\text{-}(\text{CD}_3)_2\text{CO}$	-50.5	2644 $^3J(\text{Pt-P})$ 31	2.06 (s, $\text{SC}_6\text{H}_4\text{Me}$), 4.35 (t, J 11, PCH_2P), 6.21 (d, J 7.7, C_6H_4), 6.84 (d, J 7.7, C_6H_4), 6.79 (t, J 7), 6.93 (t, J 7.3), 7.23-7.37 (br m), 7.46-7.55 (br m) (Ph)
$[\text{Pt}_2(\mu\text{-SePh})_2(\text{dppm})_2][\text{BPh}_4]_2$	CDCl_3	-53.1	2638 $^3J(\text{Pt-P})$ 28	4.41 (t, J 11, PCH_2P), 6.55 (t, J 7.7), 6.77 (t, J 7.2), 6.89 (t, J 7.4), 7.23 (br), 7.33 (t, J 7.3), 7.54 (t, J 7.4) (Ph)
$[\text{Pt}_2(\mu\text{-SePh})_2(\text{dppe})_2][\text{BPh}_4]_2$	$\text{CH}_2\text{Cl}_2\text{-}(\text{CD}_3)_2\text{CO}$	54.3	2993	1.88 (br d, CH_2), 6.51 (d, J 7.5), 6.59 (t, J 7.5), 6.70 (t, J 7.0), 6.82 (t, J 7.4), 7.04-7.30 (m), 7.44 (t, J 7) (Ph)

^a In CDCl_3 except for the cationic complexes which were recorded in CD_2Cl_2 at 500 MHz. ^b $^2J(^{77}\text{Se}\text{-}^{31}\text{P})_{\text{trans}} = 32$ Hz, $^2J(^{77}\text{Se}\text{-}^{31}\text{P})_{\text{cis}} \approx 9$ Hz. ^c Complicated pattern.

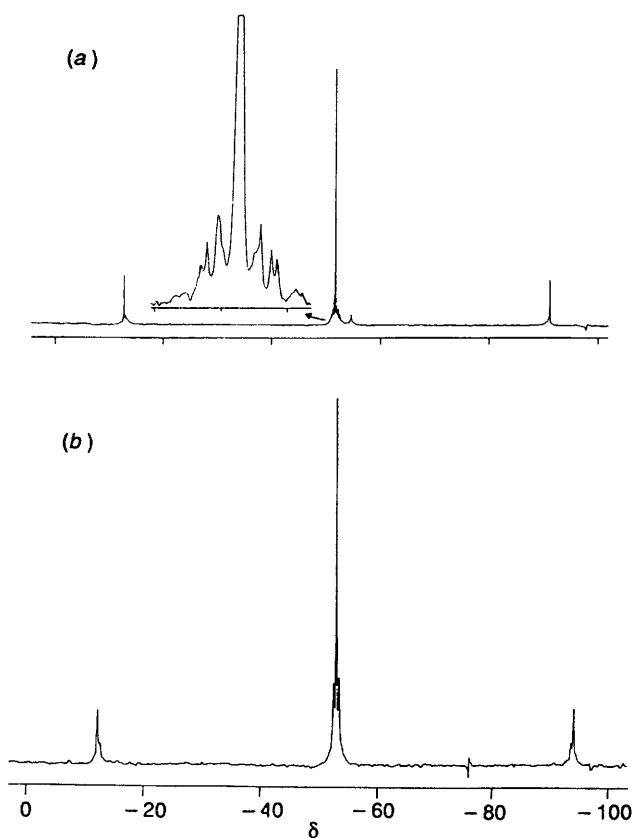


Fig. 2 (a) $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of $[\text{Pt}(\text{SePh})_2(\text{dppm})]$ in CDCl_3 , inset shows the expansion of the main resonance (50 Hz per division); (b) $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of $[\text{Pt}_2(\mu\text{-SePh})_2(\text{dppm})_2][\text{BPh}_4]_2$ in CDCl_3

Table 5 Selected bond distances (Å) and angles (°) for $[\text{Pt}(\text{SePh})_2(\text{dppm})]$ with e.s.d.s in parentheses

Pt-Se(1)	2.4340(9)	P(1)-C	1.843(8)
Pt-Se(2)	2.461(1)	P(1)-C(1A)	1.818(8)
Pt-P(1)	2.253(2)	P(1)-C(1B)	1.808(7)
Pt-P(2)	2.257(2)	P(2)-C	1.836(8)
Se(1)-C(1E)	1.917(8)	P(2)-C(1C)	1.819(8)
Se(2)-C(1F)	1.910(8)	P(2)-C(1D)	1.815(8)
Se(1)-Pt-Se(2)	90.70(3)	C-P(1)-C(1A)	106.0(4)
Se(1)-Pt-P(1)	175.03(6)	C-P(1)-C(1B)	107.4(4)
Se(1)-Pt-P(2)	103.31(6)	C(1A)-P(1)-C(1B)	106.0(3)
Se(2)-Pt-P(1)	91.98(6)	Pt-P(2)-C	94.9(3)
Se(2)-Pt-P(2)	165.13(5)	Pt-P(2)-C(1C)	115.7(3)
P(1)-Pt-P(2)	73.68(8)	Pt-P(2)-C(1D)	125.3(3)
Pt-Se(1)-C(1E)	111.8(2)	C-P(2)-C(1C)	105.4(4)
Pt-Se(2)-C(1F)	110.1(2)	C-P(2)-C(1D)	105.4(4)
Pt-P(1)-C	94.8(2)	C(1C)-P(2)-C(1D)	107.1(4)
Pt-P(1)-C(1A)	125.6(3)	P(1)-C-P(2)	94.6(4)
Pt-P(1)-C(1B)	114.8(3)		

The molecular structure of $[\text{Pt}(\text{SePh})_2(\text{dppm})]$ shows that the platinum is in a distorted square-planar environment [least-squares calculations on the metal co-ordination plane indicate that phosphorus atoms P(1) and P(2) show the largest deviations (0.12 and 0.13 Å, respectively) whereas other atoms are coplanar within 0.04 Å] with the selenium atoms and the chelating dppm ligand in a *cis* configuration (Fig. 1). The Pt-P, 31,32 Pt-Se, 31,32 Se-C³²⁻³⁴ and P-C (P-Ph and P-CH₂)^{35,36} bond lengths are in agreement with those reported earlier. Selected bond distances and angles are given in Table 5.

The P-Pt-P [73.68(8)°] and the P-C-P [94.6(4)°] angles are reduced significantly from the normal bond angles of 90 and 109°, due to the strain in the chelate ring arising from the small bite of the phosphine ligand. These angles are typical for chelating dppm.^{17,18,36} The acute P-Pt-P angle results in

an opening of the adjacent Se–Pt–P angles, one of these [Se(1)–Pt–P(2) 103.31(6)°] more significantly than the other [Se(2)–Pt–P(1) 91.98(6)°].

The four-membered MPCP ring in chelating dppm complexes has been reported to be either planar^{35,37} or non-planar.³⁸ In the present case, the four-membered PtPCP metallacyclic ring is non-planar as the methylene carbon atom lies out of the P(1)PtP(2) plane by 0.3125 Å. The individual phenyl rings are planar. The phenyl rings of the SePh groups are inclined to one another by 73.55°.

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