Dimethylplatinum Complexes of Polydentate Alkene–Sulfur and –Selenium Ligands[†]

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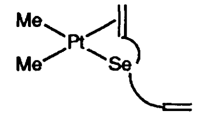
Interaction of [$PtMe_2(SMe_2)_2$] with 1 equivalent of 5-selenanona-1,8-diene produces a monomeric complex containing the ligand chelating through one alkene moiety and the selenium atom. The unco-ordinated alkene moiety undergoes exchange with the co-ordinated alkene moiety which has been studied by dynamic NMR spectroscopy. Interaction of the same platinum(II) precursor with 0.5 mol equivalent of the dialkenyl chalcogenoether ligands $E(CH_2CH_2CH{=}CH_2)_2$ (E = S or Se) produced the novel dinuclear complexes [$Pt_2Me_4\{\mu\text{-}E(CH_2CH_2CH{=}CH_2)_2\}$] both of which have been characterised by X-ray crystallography and shown to be isostructural. The unit cells are of dimensions a = 10.850(2), b = 11.289(7) and c = 12.415(1) (E = S) and a = 11.056(1), b = 11.251(1) and c = 12.546(2) Å, (E = Se). In each case the two metals are bridged by a tetrahedrally co-ordinated chalcogen atom, with one alkenyl group chelating to each platinum atom. The platinum–chalcogen distances are Pt–S 2.354(8) and Pt–Se 2.457(5) Å.

We have recently reported[1–3] structural and spectroscopic studies on a range of platinum metal complexes with potentially chelating alkenyl chalcogenoether ligands. In the case of monoalkenyl chalcogenoether complexes[1] of the type *cis*-[$PtX_2\{MeE(CH_2)_nCH{=}CH_2\}$] **I** (E = S or Se, X = halide, n = 2 or 3) chalcogen inversion[4] was observed and quantitatively studied, whilst in the case of dialkenyl chalcogenoether complexes[2] of the type *cis*-[$PtX_2\{E[(CH_2)_nCH{=}CH_2]_2\}$] **II** both alkene exchange and chalcogen inversion were observed and quantitatively studied. In order to investigate the mechanism of alkene exchange more fully it was desirable to synthesise complexes of the type **II** in which the X moiety has an NMR-active nucleus. A wide range of compounds of the type *cis*-[$PtMe_2L_2$] are known and readily synthesised and it was therefore decided to attempt the synthesis of complexes of the type **II** with X = Me.

Results and Discussion

Preparation and Properties of [$PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}$].—The ligand $Se(CH_2CH_2CH{=}CH_2)_2$ was prepared according to previously detailed procedures,[2] using a two-phase ligand system with a phase-transfer catalyst. The complex *cis*-[$PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}$] was prepared by treatment of [$PtCl_2(SMe_2)_2$] with methyllithium at low temperature, followed by addition of 1 equivalent of 5-selenanona-1,8-diene. The product was isolated as a clear oil which freezes to a white, waxy solid at *ca.* −10 °C. It was characterised by infrared and NMR spectroscopy, data for which are reported in Tables 1 and 3(*a*) respectively. Infrared spectroscopy indicates the presence of one co-ordinated alkene moiety (at 1527 cm^{-1}) and one unco-ordinated alkene moiety (at 1641 cm^{-1}). The data are consistent with the formulation of the structure as **III**, in which the complex is essentially square planar at the platinum with respect to the *cis*-methyl groups, the co-ordinated alkene centroid and the selenium atom.



III

Table 1 Infrared data (cm^{-1})

Sample	Alkene stretch Co-ordinated	Alkene stretch Unco-ordinated
$S(CH_2CH_2CH{=}CH_2)_2$		1642
$Se(CH_2CH_2CH{=}CH_2)_2$		1640
[$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$]	1528	
[$Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}$]	1527	
[$PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}$]	1527	1641

The fluxional behaviour of *cis*-[$PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}$] was studied by variable-temperature ^1H NMR spectroscopy. At −90 °C the spectrum consisted of two distinct sets of alkene signals, arising from the presence of co-ordinated and free alkene groups. (As we have discussed elsewhere,[2] the short T_1 values at low temperatures resulting from the temperature dependence of the chemical shift anisotropy term in the platinum nucleus relaxation expression leads to the absence of ^{195}Pt satellites for the co-ordinated alkene signals.) The spectrum also showed two inequivalent peaks in the methyl region. This is consistent with the static structure in which one alkene moiety is unco-ordinated and the other is co-ordinated *trans* to one methyl group. The selenium atom is co-ordinated *trans* to the other methyl group, for which two resonances are observed in the ratio 5:1, resulting from the pseudo-axial and -equatorial configuration at the selenium atom. The selenium atom has an NMR-active isotope (^{77}Se, 7.6%, $I = \frac{1}{2}$) and ^3J(Se–H) coupling (7 Hz) to the protons of the *trans* methyl group is observed.

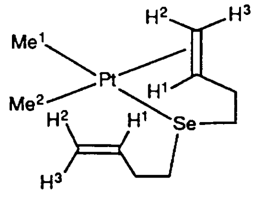
[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Analytical data

Complex	Crystal colour	M.p./°C	Analysis (%) C Found	C Calc.	H Found	H Calc.
$[Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}]$	Colourless	150 (decomp.)	24.45	24.30	4.35	4.40
$[Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}]$	Colourless	130 (decomp)	22.65	22.55	4.05	4.10

Table 3 NMR data

(*a*) $[PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}]$[a]



Static state (−90 °C) in CD_2Cl_2

δ(H¹) Co-ord.	δ(H¹) Unco-ord.	δ(H²) Co-ord.	δ(H²) Unco-ord.	δ(H³) Co-ord.	δ(H³) Unco-ord.	δ(Me¹)		δ(Me²)	³J[Se-H(Me¹)]
4.40	5.75	3.63	5.08	3.30	5.08	0.80[b]	0.89[c]	0.60	7

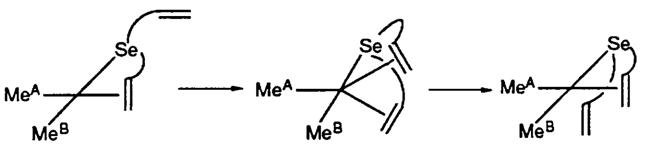
Fast exchange (80 °C) in $CDCl_2CDCl_2$

δ(H¹)	δ(H²)	δ(H³)	δ(Me¹)		δ(Me²)	³J[Se-H(Me¹)]	²J[Pt-H(Me¹)]	²J[Pt-H(Me²)]
4.98	4.25	4.15	0.86[b]	0.90[c]	0.66	7	84	82

(*b*) Dinuclear complexes at ambient temperature

Complex	δ(H¹)	δ(H²)	δ(H³)	δ(Me¹)	δ(Me²)	²J(Pt-H²)	²J(Pt-H³)	²J[Pt-H(Me¹)]	²J[Pt-H(Me²)]
$[Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}]$	4.51	3.86	3.67	0.89	0.75	39.0	42.0	84.6	84.6
$[Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}]$	4.50	3.78	3.48	0.87	0.82	39.5	41.6	83.5	88.5

[a] Chemical shifts given in ppm, coupling constants in Hz. [b] Major invertomer. [c] Minor invertomer.



IV

Scheme 1

As the temperature is raised, the alkene-proton peaks coalesce indicating that alkene exchange is occurring. The two platinum–methyl resonances however remain distinct over the whole temperature range suggesting that the selenium atom always remains *trans* to the same methyl group and that the geometry of the T-shaped $PtMe_2Se$ unit is unchanged during the alkene-exchange process. This is consistent with a trigonal-bipyramidal transition state with the entering and leaving alkene groups in the equatorial plane as shown in **IV** in Scheme 1.

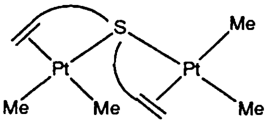
It is interesting to speculate whether **IV** is a true transition state or if, in fact, the chelate effect associated with the tridentate ligand might favour the formation of a five-co-ordinate intermediate with the structure **IV**. Although five-co-ordinate platinum(II) complexes are rare, examples such as $[Pt(C_2H_4)\{MeC(=NNHMe)C(=NNHMe)Me\}Cl_2]$ are known[5] and furthermore the isoelectronic rhodium(I) complex of a related tetradentate phosphine–alkene ligand, $[RhCl\{P(CH_2CH_2CH{=}CH_2)_3\}]$, has a structure analogous to **IV**, with three equatorial alkene moieties and axial phosphorus and chloro groups.[6] If a five-co-ordinate intermediate **IV** were formed it might be expected to undergo Berry pseudorotation which would exchange the methyl resonances A and B, but the NMR evidence indicates clearly that this is not the case. It is more likely therefore that **IV** is a transition state rather than an intermediate.

Quantitative analysis, by coalescence temperature methods, of the alkene-exchange process gave a value for the Gibbs free energy of activation of 60 kJ mol^{-1} at 333 K. This is considerably larger than the value observed for the corresponding halide complexes, $[PtX_2\{Se(CH_2CH_2CH{=}CH_2)_2\}]$; *e.g.* when X = Cl, $\Delta G_T^{\ddagger}$ is 43.9 kJ mol^{-1} at a coalescence temperature of 228 K.[2] This is, at first sight, a surprising result in view of the often-quoted high *trans*-labilising effect of the methyl group,[7] which might be expected to facilitate the alkene-exchange process. Belluco and co-workers[8] have shown however that for substitution reactions with incoming nucleophiles which have both σ-donor and π-acceptor properties the normal order of the *trans*-labilising effect is reversed and these substitution reactions are generally more facile for complexes with halide rather than methyl *trans* to the leaving group. The reasons for this are not clearly understood.

The two resonances for the PtMe group *trans* to selenium resulting from the two configurations at selenium also broaden as the temperature is raised above −90 °C. This is consistent with the onset of selenium inversion. It was not possible, however, to obtain an accurate value for the energy barrier to selenium inversion as a consequence of the broadness of the spectrum resulting from alkene exchange, but it appeared that the inversion barrier was less than in the case of the corresponding halide complexes.

When the analogous reaction of [$PtCl_2(SMe_2)_2$] with $S(CH_2CH_2CH{=}CH_2)_2$ was attempted the expected product *cis*-[$PtMe_2\{S(CH_2CH_2CH{=}CH_2)_2\}$] could not be isolated. This reaction is discussed in the following section.

Preparation and Properties of [$Pt_2Me_4\{\mu\text{-}E(CH_2CH_2CH{=}CH_2)_2\}$] (E = S *or* Se).—Treatment of [$PtCl_2(SMe_2)_2$] with methyllithium followed by addition of 1 mole equivalent of $S(CH_2CH_2CH{=}CH_2)_2$ resulted in the formation of a colourless crystalline material. The product was characterised by infrared and elemental analysis, data for which are given in Tables 1 and 2 respectively. These data were consistent with the formulation of the product as the dinuclear complex [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$], involving a sulfur atom bridging the two platinum atoms with one alkene group chelated to each metal atom as shown in **V**. This dinuclear product could be synthesised in greater yield by using the correct stoichiometric ratio of reactants *viz.* 0.5 mol equivalent of $S(CH_2CH_2CH{=}CH_2)_2$ per platinum. A similar reaction of 0.5 mol equivalent of $Se(CH_2CH_2CH{=}CH_2)_2$ per platinum resulted in the formation of the analogous selenium complex [$Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}$].



V

The ^1H NMR data for the complexes are given in Table 3(*b*) and are consistent with the formulation shown. The coupling constant between the alkene protons and the ^{195}Pt nuclei (*ca.* 40 Hz) was markedly smaller than that observed[1] for the complexes [$PtX_2\{MeS(CH_2CH_2CH{=}CH_2)\}$] (X = halide, *ca.* 65 Hz) and is likely to be a reflection of the greater *trans* influence of the methyl group compared with halide. The two PtMe resonances [*ca.* δ 0.8 and 0.9, ^2J(Pt–H) 85 Hz] were assigned as, respectively, *cis* and *trans* to the chalcogen atom on the basis of the PtMe peak *trans* to selenium in [$Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}$] being distinguished by the presence of ^{77}Se satellites [^3J(Se–H) 7 Hz].

The NMR spectra of the dinuclear complexes are invariant over a wide temperature range. The alkene moieties are both co-ordinated and too far apart to permit any intramolecular exchange and the chalcogen atom at the centre, with tetrahedral geometry, has no free lone pair of electrons and thus cannot undergo pyramidal atomic inversion.

*Crystal and Molecular Structures of Tetramethyl-*μ*-(5-thianona-1,8-diene)- and Tetramethyl-*μ*-(5-selenanona-1,8-diene)-diplatinum*(II).—The molecular structure of [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$] is shown in Fig. 1. The selenium analogue is isostructural. Selected bond lengths and angles for the two compounds are given in Table 4 and fractional atomic coordinates in Table 5.

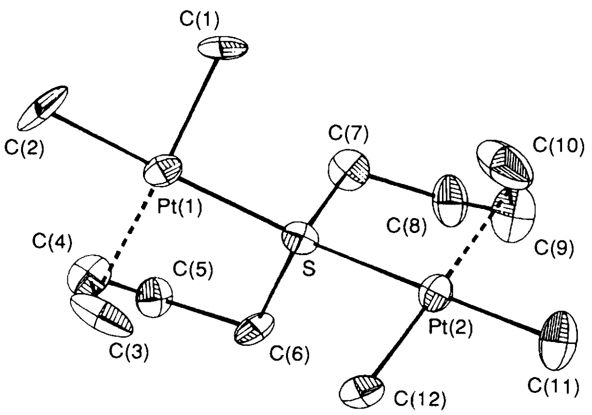


Fig. 1 Molecular structure of [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$]

The ligands 5-thia- and 5-selena-nona-1,8-diene utilise all four of their potential donor sites (two at the chalcogen atom and one at the alkene moiety) in order to co-ordinate to two platinum atoms, with the chalcogen atom and the centroid of a double bond completing square-planar local geometry at each $PtMe_2$ unit, the sulfur derivative being the first structurally characterised complex containing a single bridging thioether ligand and the selenium derivative being the first structurally characterised complex containing a bridging selenoether ligand.

The two square-planar moieties are folded in towards each other at the bridging chalcogen atom and slightly twisted with respect to each other in such a way as to maintain a pseudo-C_2 axis. The folding is a result of the retention of tetrahedral geometry at the chalcogen atom. The twisting results from chelate constraints of the ligand, the geometry of the butenyl chains of which is dictated by the most favourable orientation of the co-ordinated alkene groups, this being perpendicular to the $PtMe_2E$ (E = S or Se) plane in each case. The structures of these complexes thus contrast with those of previously characterised complexes [$Pt_2Br_4(\mu\text{-}SEt_2)_2$][9] and [$Pt_2Me_4(\mu\text{-}SEt_2)_2$][10] containing bridging thioether ligands which contain coplanar sulfur atoms and platinum moieties.

As a consequence of the open structure of [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$], both the platinum–platinum distance (4.25 Å) and the Pt–S–Pt angle (129°) are much larger than in [$Pt_2Me_4(\mu\text{-}SEt_2)_2$][10] (3.61 Å, 100°) and [$Pt_2Br_4(\mu\text{-}SEt_2)_2$][9] (3.38 Å, 98°). The Pt–S bonds in [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$] [2.354(8) Å] are the same length as those observed in [$Pt_2Me_4(\mu\text{-}SEt_2)_2$].[10] These are, however, considerably greater that the Pt–S bond length in the related complex [$PtI_2\{S(CH_2CH_2CH{=}CH_2)_2\}$][2] (2.086 Å), in which the same ligand is bound terminally. A comparison of these metal–sulfur bond lengths would appear to suggest that bridging Pt–S bonds are longer, and thus weaker, than terminal Pt–S bonds. It must be noted, however, that the two groups *trans* to sulfur in the two complexes are different (methyl and iodide, respectively), thus rendering a strict comparison perhaps misleading. This conclusion of weaker bridging as opposed to terminal metal–sulfur bonds is in direct contrast with the arguments of Sales *et al.*,[9] who came to the opposite conclusion that bridging thioether metal bonds were stronger than terminal bonds after comparing the bridging Pt–S bond length in [$Pt_2Br_4(\mu\text{-}SEt_2)_2$] (2.22 Å) with the terminal Pd–S bond length in [$Pd_2Br_2(\mu\text{-}Br)_2(SEt_2)_2$] (2.30 Å). It is apparent that conclusions as to relative metal–sulfur bond strengths can be, at best, tentative, where the metals and/or *trans* groups differ in the complexes being compared.

For [$Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}$], as might be expected for a complex containing the larger selenium atom, the Pt–Se bond lengths and the Pt–Se–Pt bond angle (2.457 Å and 135.9°) are larger than the corresponding values in the sulfur complex.

In conclusion it is worth noting that although dinuclear complexes containing bridging chalcogenoether ligands are very much less common than those containing chalcogenato (particularly the ubiquitous thiolato) ligands, the presence of the chelating alkene groups exerts a marked stabilising effect. This is particularly so in the case of the thioether complex, [$Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}$] which does not react with excess of ligand. The fact that the selenoether analogue could be induced to form either mono- or di-nuclear complexes, depending on the metal:ligand ratio, is consistent with the weaker nature of Pt–Se *vis-à-vis* Pt–S bonds.

Experimental

Reactions were carried out using standard Schlenk techniques under nitrogen and solvents were dried and distilled under

Table 4 Selected bond lengths (Å) and angles (°) for the dinuclear species $[\mathrm{Pt_2Me_4\{\mu\text{-}X(CH_2CH_2CH{=}CH_2)_2\}}]$

	X = S	X = Se
X–Pt(1)	2.353(7)	2.461(5)
C(1)–Pt(1)	2.06(2)	2.06(3)
C(2)–Pt(1)	2.07(2)	2.03(3)
C(3)–Pt(1)	2.30(2)	2.23(3)
C(4)–Pt(1)	2.25(2)	2.21(3)
C(3)–C(4)	1.47(3)	1.44(4)
X–C(6)	1.80(2)	1.97(3)
X–Pt(2)	2.354(6)	2.456(5)
C(11)–Pt(2)	2.07(2)	2.07(3)
C(12)–Pt(2)	2.00(2)	2.06(4)
C(10)–Pt(2)	2.22(3)	2.20(4)
C(9)–Pt(2)	2.22(2)	2.20(3)
C(9)–C(10)	1.42(4)	1.40(5)
X–C(7)	1.83(2)	1.93(3)
C(1)–Pt(1)–X	94.9(7)	94.8(12)
C(2)–Pt(1)–C(1)	84.8(11)	86.6(17)
C(3)–Pt(1)–C(1)	165.9(8)	165.7(13)
C(4)–Pt(1)–X	84.8(5)	84.5(7)
C(4)–Pt(1)–C(2)	94.7(10)	93.8(14)
C(2)–Pt(1)–X	178.2(8)	178.3(11)
C(3)–Pt(1)–X	88.6(7)	90.9(9)
C(3)–Pt(1)–C(2)	92.1(11)	87.9(16)
C(4)–Pt(1)–C(1)	156.4(8)	155.9(12)
C(4)–Pt(1)–C(3)	37.5(7)	37.8(10)
C(12)–Pt(2)–X	92.8(6)	92.5(10)
C(12)–Pt(2)–C(11)	87.8(10)	90.3(16)
C(10)–Pt(2)–C(12)	162.0(8)	161.5(15)
C(9)–Pt(2)–X	85.3(7)	84.5(9)
C(9)–Pt(2)–C(11)	93.5(10)	92.3(14)
C(11)–Pt(2)–X	177.7(7)	176.8(10)
C(10)–Pt(2)–X	89.7(9)	90.5(11)
C(10)–Pt(2)–C(11)	90.4(12)	87.4(17)
C(9)–P(2)–C(12)	160.9(9)	161.3(13)
C(9)–Pt(2)–C(10)	37.1(9)	37.2(13)
Pt(2)–X–Pt(1)	129.5(3)	135.9(1)
C(6)–X–Pt(2)	108.9(7)	108.8(8)
C(7)–X–Pt(2)	101.6(7)	99.4(9)
C(6)–C(1)–Pt(1)	101.6(6)	99.0(8)
C(7)–X–Pt(1)	109.9(8)	109.8(11)
C(7)–X–C(6)	102.7(10)	98.4(13)

Table 5 Fractional atomic coordinates (× 10⁴)

Atom	*x*	*y*	*z*
(*a*) $[\mathrm{Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}}]$			
Pt(1)	10 993(1)	620(1)	1 803(1)
Pt(2)	7 430(1)	1 367(1)	3 067(1)
S	9 091(4)	130(4)	2 596(4)
C(1)	10 269(22)	919(20)	292(14)
C(2)	12 669(22)	996(25)	1 086(20)
C(3)	11 818(23)	787(18)	3 503(19)
C(4)	10 816(16)	−453(15)	3 153(19)
C(5)	10 822(17)	−1 303(15)	3 487(15)
C(6)	9 578(15)	−676(18)	3 773(13)
C(7)	8 320(15)	−1 008(16)	1 799(18)
C(8)	6 963(16)	−1 128(18)	2 193(18)
C(9)	6 260(20)	8(18)	2 274(23)
C(10)	6 507(22)	919(26)	1 522(20)
C(11)	5 936(19)	2 401(22)	3 514(23)
C(12)	8 414(17)	2 215(14)	4 188(15)
(*b*) $[\mathrm{Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}}]$			
Pt(1)	−11 132(1)	−630(1)	−1 708(1)
Pt(2)	−7 372(1)	−1 394(1)	−3 104(1)
Se	−9 141(2)	−213(2)	−2 575(2)
C(1)	−10 465(35)	−951(30)	−278(25)
C(2)	−12 792(26)	−938(30)	−1 159(32)
C(3)	−11 966(28)	−763(26)	−3 396(26)
C(4)	−11 833(19)	466(28)	−3 104(23)
C(5)	−10 908(22)	1 348(24)	−3 468(26)
C(6)	−9 666(21)	749(26)	−3 798(21)
C(7)	−8 338(24)	1 021(25)	−1 775(28)
C(8)	−6 971(29)	1 152(30)	−2 215(27)
C(9)	−6 334(23)	−11(32)	−2 269(27)
C(10)	−6 482(31)	−983(39)	−1 584(31)
C(11)	−5 820(27)	−2 311(28)	−3 524(35)
C(12)	−8 327(32)	−2 275(30)	−4 266(26)

nitrogen before use. Elemental analyses were performed by Butterworths Laboratories, London. Melting points (uncorrected) were obtained using a digital Gallenkamp electrothermal apparatus. Infrared spectra were recorded (as thin films for liquids and KBr discs for solids) using a Perkin-Elmer 881 spectrophotometer.

The dialkenyl sulphide and selenide ligands were prepared as previously described.[2] The complex $[\mathrm{PtCl_2(SMe_2)_2}]$ was prepared according to the literature method.[11] The preparation of the mononuclear *cis*-$[\mathrm{PtMe_2L}]$ and dinuclear $[\mathrm{Pt_2Me_4(\mu\text{-}L)}]$ complexes is exemplified below.

Preparation of cis-*Dimethyl*(5-*selenanona*-1,8-*diene*)*platinum*(II).—To a cold (−5 °C) stirred suspension of $[\mathrm{PtCl_2(SMe_2)_2}]$ (0.50 g, 1.282 mmol) in dry diethyl ether (30 cm^3) was slowly added a 1.4 mol dm^{-3} solution of methyllithium (2.00 cm^3, 2.80 mmol) in diethyl ether. After 5 min, more methyllithium solution (1.00 cm^3, 1.4 mmol) was added and the solution was allowed to warm to room temperature. After about 10 min, when the yellow colour had largely disappeared and a cloudy white precipitate (LiCl) had formed, water (50 cm^3) was added to hydrolyse the excess of methyllithium and dissolve the lithium chloride. One equivalent of $\mathrm{Se(CH_2CH_2CH{=}CH_2)_2}$ (0.242 g, 1.282 mmol) was then added and the solution was stirred for 1 h. The resulting two layers were separated, the aqueous layer washed with diethyl ether (30, 20 and 10 cm^3) and the combined organic extracts dried over magnesium sulphate. Removal of diethyl ether under reduced pressure at −15 °C afforded the complex as a waxy solid, which is liquid at room temperature. Yield of $[\mathrm{PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}}]$: 0.245 g (48%).

Preparation of Tetramethyl-μ-(5-*thianona*-1,8-*diene*)-*diplatinum*(II).—To a cold (−5 °C) stirred suspension of $[\mathrm{PtCl_2(SMe_2)_2}]$ (0.50 g, 1.282 mmol) in dry diethyl ether (30 cm^3) was slowly added a 1.4 mol dm^{-3} solution of methyllithium (2.00 cm^3, 2.80 mmol) in diethyl ether. After 5 min more methyllithium solution (1.00 cm^3, 1.4 mmol) was added and the solution was allowed to warm to room temperature. After about 10 min, when the yellow colour had largely disappeared and a cloudy white precipitate (LiCl) had formed, water (50 cm^3) was added to hydrolyse the excess of methyllithium and dissolve the white precipitate. Half an equivalent of 5-thianona-1,8-diene (0.091 g, 0.641 mmol) was added and the solution stirred for 1 h. The two layers were then separated, the aqueous layer washed with diethyl ether (30, 20 and 10 cm^3) and the combined organic extracts dried over magnesium sulphate. After removal of diethyl ether under reduced pressure and washing the residue in a small quantity (10 and 5 cm^3) of cold (−15 °C) hexane, the product was obtained as a white powder which may be recrystallised from a saturated solution of dichloromethane. Yield of $[\mathrm{Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}}]$: 0.330 g (87%).

NMR Studies.—Proton NMR experiments were performed on a Bruker AM250 instrument at 250 MHz. Low-temperature spectra (−90 to −20 °C) were taken in $\mathrm{CD_2Cl_2}$; for temperatures in the range −30 to +55 °C, $\mathrm{CDCl_3}$ was used, and above 55 °C, 1,1,2,2-tetrachloro[$^2\mathrm{H_2}$]ethane was used.

Table 6 Crystal data and details of intensity measurements for $[\mathrm{Pt_2Me_4\{\mu\text{-}X(CH_2CH_2CH{=}CH_2)_2)\}}]$

	X = S	X = Se
Crystal data		
M	592.6	639.48
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.850(2)	11.056(1)
b/Å	11.289(7)	11.251(1)
c/Å	12.415(1)	12.546(2)
U/Å^3	1520.66	1560.61
Z	4	4
D_c/g cm^{-3}	2.60	2.72
$F(000)$	1064	1152
μ/cm^{-1}	177.88	203.84
Data collection		
Minimum, maximum θ/°	1.50, 25.0	1.50, 25.0
Total data measured	1600	1638
Total data unique	1544	1582
Total data observed	1278	1182

Single-crystal X-Ray Crystallographic Structural Determination of $[\mathrm{Pt_2Me_4\{\mu\text{-}S(CH_2CH_2CH{=}CH_2)_2\}}]$.—Crystals of the compound were grown by slow evaporation of a concentrated solution in benzene. The crystal data are given in Table 6.

Data collection. Unit-cell parameters and intensity data were obtained following previously detailed procedures[12] using a CAD4 diffractometer operating in the ω–2θ scan mode, with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at low temperature (219 K). A total of 1278 unique reflections were collected ($3 < 2\theta < 50°$) and observed $[F_o > 3\sigma(F_o)]$. The reflection intensities were corrected for absorption using the ψ-scan method; maximum transmission factor 99.8%, minimum 33.3%.

Structure solution and refinement. The structure was solved using routine heavy-atom procedures and refined using full-matrix least-squares methods.[13] Refinement of all non-hydrogen atoms with anisotropic thermal parameters finally converged at $R = 0.034$ and $R' = 0.045$. No attempts were made to locate the hydrogen atoms. The weighting scheme used was $w = 1/[\sigma^2(F_o) + 0.002\,07F_o^2]$. The absolute configuration was established by parallel refinement of the trial model and its enantiomorph. For the latter an R of 0.041 was obtained. Scattering factors were taken from ref. 14 and computations were performed using a DEC VAX-11/750 computer.

Single-crystal X-Ray Crystallographic Structural Determination of $[\mathrm{Pt_2Me_4\{\mu\text{-}Se(CH_2CH_2CH{=}CH_2)_2\}}]$.—Crystals of the compound were grown as above. The crystal data are given in Table 6.

Data collection. Unit-cell parameters and intensity data were obtained as above. A total of 1182 unique reflections were collected ($3 < 2\theta < 50°$) and observed $[F_o > 3\sigma(F_o)]$. The intensities were corrected for absorption using the ψ-scan method; maximum transmission factor 99.6%, minimum 24.6%.

Structure solution and refinement. The structure was solved and refined as above. Refinement of all non-hydrogen atoms with anisotropic thermal parameters finally converged at $R = 0.045$ and $R' = 0.048$. No attempts were made to locate the hydrogen atoms. The weighting scheme used was $w = 1/[\sigma^2(F_o) + 0.000\,83F_o^2]$. The absolute configuration was established as above. For the enantiomorph an R of 0.049 was obtained.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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