Oxidative Addition of E–E Bonds (E = Group 16 Element) to Platinum(II): a Route to Platinum(IV) Thiolate and Selenolate Complexes†

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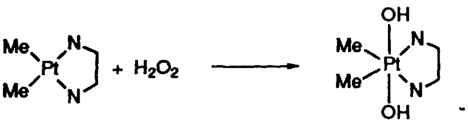
Reaction of [PtMe$_2$(phen)] **1** (phen = 1,10-phenanthroline) with RE–ER gives the complexes [PtMe$_2$(ER)$_2$(phen)] [**2**, ER = OH; **3**, ER = OC(=O)Ph; **4**, ER = SMe; **5**, ER = SPh; **6**, ER = SePh]. These contain predominantly isomer **a** in which the ER groups are *trans* but, in most cases, there is a minor product **b** in which the ER groups are *cis*; complexes **4**–**6** appear to be the first bis(thiolato) or bis(selenolato) complexes of platinum(IV). The structures were determined by NMR spectroscopy and, in the case of complex **6a**, by an X-ray structure determination [tetragonal, $I4_1/a$, $a = b$ = 13.918(2), c = 25.432(5) Å, Z = 8, R = 0.0677, R' = 0.0705]. In the reaction with PhSSPh, a sparingly soluble, black intermediate formulated as [{PtMe$_2$(phen)}$_2$(PhSSPh)] was formed.

Ligands of the type RE$^-$, where E is a Group 16 element, are significant in transition-metal chemistry and they are commonly synthesized by activation of the chalcogen–chalcogen bonds in RE–ER.[1–10] For example, reaction of PhS–SPh with [M(PPh$_3$)$_4$], M = Pd or Pt, gives [M(SPh)$_2$(PPh$_3$)$_2$] or [(Ph$_3$P)$_2$M(μ-SPh)$_2$M(SPh)$_2$].[2] When R = S or Se, the RE group is reducing, so that complexes in high oxidation states are rare.[4] Thus, the few known platinum(IV) thiolates include the thiolate-bridged [{PtMe$_3$(μ-SPh)}$_4$] and [{PtIMe$_2$(μ-SMe)(PMe$_2$Ph)}$_2$] and the terminal thiolate derivative [PtMe$_3$(SPh)(bipy)] (bipy = 2,2′-bipyridine).[3–6] It follows that the compounds RE–ER, with E = S or Se, are not strong oxidants and there is an extensive co-ordination chemistry of these ligands with metals in higher oxidation states, for example with platinum(IV).[1,4,10–15] Thiolates and selenolates act as bridging ligands more often than as terminal ligands.[16–19] When E = O, higher oxidation states are more common and bridging and terminal ligation are both common; some platinum(IV) hydroxides have useful anti-tumour properties.[20–29]

This article describes the reactions of the electron-rich platinum(II) complex [PtMe$_2$(phen)], phen = 1,10-phenanthroline,[30,31] with reagents of the type RE–ER. These reactions may proceed by oxidative addition of the E–E bond to the metal centre, thus affording monomeric platinum(IV) complexes, [PtMe$_2$(ER)$_2$(phen)]. Of particular interest are the reactions with E = SPh or SePh since these give the first examples of bis(thiolato) or bis(selenolato) complexes of platinum(IV).

Results

Oxidative Addition of O–O Bonds to (PtMe$_2$(phen)].—Hydrogen peroxide reacted rapidly with [PtMe$_2$(phen)] **1** in acetone at room temperature to give [PtMe$_2$(OH)$_2$(phen)] **2** which could be isolated as an air-stable yellow solid. The reaction proceeded by *trans* oxidative addition of the HO–OH bond to platinum(II), as shown in equation (1). In the ^{1}H NMR spectrum of complex **2**, a single MePt resonance was observed at δ = 1.7, ^2J(PtH) = 72 Hz, and both the chemical shift and coupling constant are typical of a platinum(IV) complex with a methyl group *trans* to a nitrogen of a phen ligand.[30,31] The presence of only one MePt signal indicates that the complex possesses a plane of symmetry as expected for a product of *trans* addition. A broad resonance at δ = 1.05 was assigned to the OH groups, since addition of D$_2$O led to loss of this peak and appearance of a peak due to HOD at δ = 4.8.

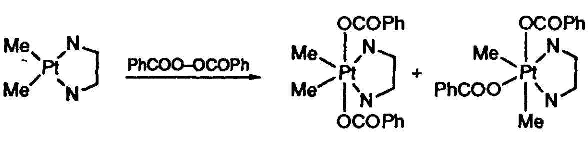


(1)

1 **2**

The reaction of *tert*-butyl hydroperoxide with [PtMe$_2$(phen)] was carried out in an attempt to prepare [PtMe$_2$(OH)(OBu^t)(phen)], but only complex **2** was formed together with Bu^{t}OH. An attempt to prepare [PtMe$_2$(OBu^t)$_2$(phen)] was also unsuccessful. Thus, the oxidative addition of RO–OR′ to platinum(II) does not appear to be a useful route to platinum(IV) alkoxides.

Complex **1** reacted with dibenzoyl peroxide to give [PtMe$_2$(OCOPh)$_2$(phen)] **3** which was isolated as a yellow solid [equation (2)]. The ^{1}H NMR spectrum of this complex contained an intense singlet resonance at δ = 2.2, ^2J(PtH) = 70 Hz, which is assigned to the MePt groups of the *trans* isomer, **3a**. However, two weaker methylplatinum(IV) resonances were observed at δ = 1.5 (Me *trans* to O) and 2.4 (Me *trans* to N) and these are assigned to the two non-equivalent methyl groups of the *cis* isomer **3b**. The ratio of the isomers, which could not be separated, was *trans*:*cis* = 5:1.



(2)

1 **3a** **3b**

Thiolate and Selenolate Complexes of Platinum(IV).—Oxidative addition of RE–ER to [PtMe$_2$(phen)] occurred according to equation (3). When E = S and R = Me or Ph the reaction gave a mixture of *trans* (major) and *cis* (minor) isomers but with E = Se and R = Ph, only the *trans* isomer was formed.

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

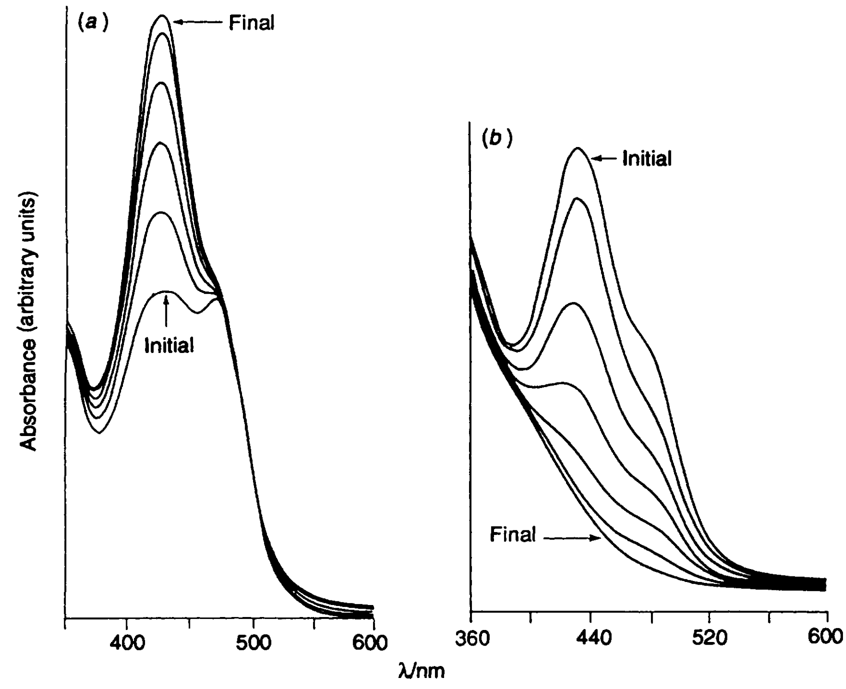
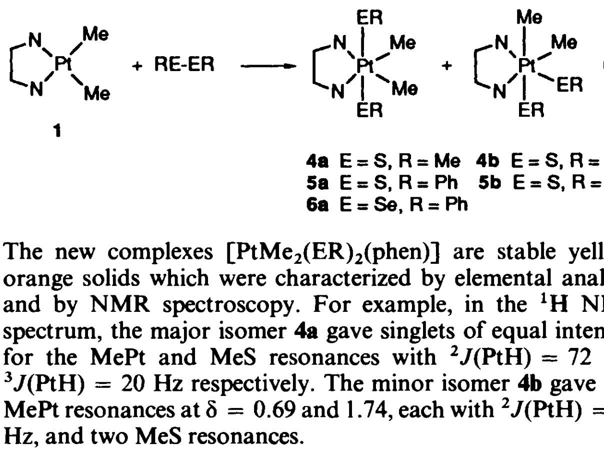


Fig. 1 UV/VIS spectra recorded during the reaction of [$PtMe_2$(phen)] with excess of PhSSPh in acetone at 25 °C: (*a*) spectra recorded at 8 min intervals during the initial stage showing the increase in absorbance associated with the formation of the black intermediate and (*b*) spectra recorded at 2 h intervals showing the decrease in absorbance during the subsequent formation of [$PtMe_2(SPh)_2$(phen)]



(3)

4a E = S, R = Me **4b** E = S, R = Me
5a E = S, R = Ph **5b** E = S, R = Ph
6a E = Se, R = Ph

The new complexes [$PtMe_2(ER)_2$(phen)] are stable yellow-orange solids which were characterized by elemental analysis and by NMR spectroscopy. For example, in the ^1H NMR spectrum, the major isomer **4a** gave singlets of equal intensity for the MePt and MeS resonances with $^2J(PtH) = 72$ and $^3J(PtH) = 20$ Hz respectively. The minor isomer **4b** gave two MePt resonances at $\delta = 0.69$ and 1.74, each with $^2J(PtH) = 72$ Hz, and two MeS resonances.

The reaction of [$PtMe_2$(phen)] with PhSSPh was unusual. Solutions of [$PtMe_2$(phen)] in acetone are orange but, on addition of diphenyl disulfide, the colour became intensely green-black and a sparingly soluble black precipitate formed. This black precipitate slowly redissolved and a clear yellow solution, shown to contain only complex **5**, was obtained after several hours at room temperature. The final product was characterized by ^1H NMR spectroscopy as the *trans* isomer **5a**, with a trace amount of the *cis* isomer **5b**. If the reaction was carried out in a concentrated solution, the black solid was readily isolated and, since it was essentially insoluble in common organic solvents, it could be purified by washing thoroughly with acetone. The low solubility precluded direct characterization by NMR spectroscopy. However, it was found that a suspension of the black solid in $(CD_3)_2CO$ slowly dissolved to give an orange-yellow solution and analysis by NMR spectroscopy showed that this contained an equimolar mixture of [$PtMe_2$(phen)] and [$PtMe_2(SPh)_2$(phen)] **5**. Elemental analysis also supported the formulation of the black solid as '[$PtMe_2$(phen)]$_2$(PhSSPh)'. A monomeric formulation [$PtMe_2$(SPh)(phen)] is unlikely since neither the black solid nor the green-black reacting solutions gave a detectable EPR signal and 17-electron platinum(III) complexes are not expected to be stable.[6]

The reaction of [$PtMe_2$(phen)] with diphenyl disulfide was monitored in dilute solution, such that precipitation did not occur, by using UV/VIS spectrophotometry. Samples of [$PtMe_2$(phen)] in acetone solution were treated with a large excess of diphenyl disulfide and a series of spectra were recorded. Initially, there was an increase in absorbance in the range 375–500 nm corresponding to the formation of the black intermediate [Fig. 1(*a*)] but after a few hours the absorbance decreased as the final product **5** was formed [Fig. 1(*b*)]. The overall spectral changes observed are those expected for the conversion of [$PtMe_2$(phen)] to [$PtMe_2(SPh)_2$(phen)]. However, the reaction is complicated by the formation of the black intermediate. The kinetics of formation and decay of this species did not follow simple first- or second-order kinetics. Although the main features were reproducible, the quantitative data were not. It is clear from Fig. 1 that the absorption maximum for the intermediate is similar to that of the metal-to-ligand charge-transfer band of [$PtMe_2$(phen)] but the absorption coefficient is much higher.[32]

Oxidative addition of diphenyl diselenide to [$PtMe_2$(phen)] gave [$PtMe_2(SePh)_2$(phen)] **6a** which was isolated as an orange solid. The ^1H NMR spectrum contained only one MePt resonance, with two sets of satellites due to the couplings $^2J(PtH) = 72$ and $^3J(SeH) = 7$ Hz. In this case, none of the *cis* isomer could be detected. The resonances due to the phenyl protons of **6a** appeared over the range $\delta = 6.1–6.5$; these chemical shifts are lower than normal for aryl protons.

The structure of complex **6a** was confirmed by an X-ray structure determination (Table 1). A view of the structure is shown in Fig. 2, and bond distances and angles and positional parameters are in Tables 2 and 3. The molecules possess crystallographic two-fold symmetry as defined by the equivalent atoms shown in Fig. 2. The selenolato ligands occupy mutually *trans* co-ordination sites and the phenyl groups which are attached to selenium lie above and below the 1,10-phenanthroline ligand. The dihedral angle between the least-squares planes defined by NC(2)–C(6) and C(11)–C(16) is 13(1)°. There appear to be no other platinum(IV) selenolate complexes and so bond distance comparisons will be made with other compounds with Pt–Se bonds. The Pt–Se distance in complex **6a** [2.495(3) Å] is slightly shorter than that in

Table 1 Summary of the X-ray structure determination

Formula	$C_{26}H_{24}N_2PtSe_2$
M	717.505
Crystal system	Tetragonal
Space group	$I4_1/a$
a/Å	13.918(2)
b/Å	13.918(2)
c/Å	25.432(5)
U/Å^3	4926(2)
Z	8
D_m/g cm^{-3}	1.96(5)
D_c/g cm^{-3}	1.935
λ(Mo-Kα)/Å	0.710 73
No. of collected data	2912
Standard reflections collected	60
μ/cm^{-1}	83.46
F(000)	2720
Observed data [$I > 2.5\sigma(I)$]	1054
R, R'*	0.0677, 0.0705

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 2.6607/[\sigma^2(F) + 0.000\,555F^2]$.

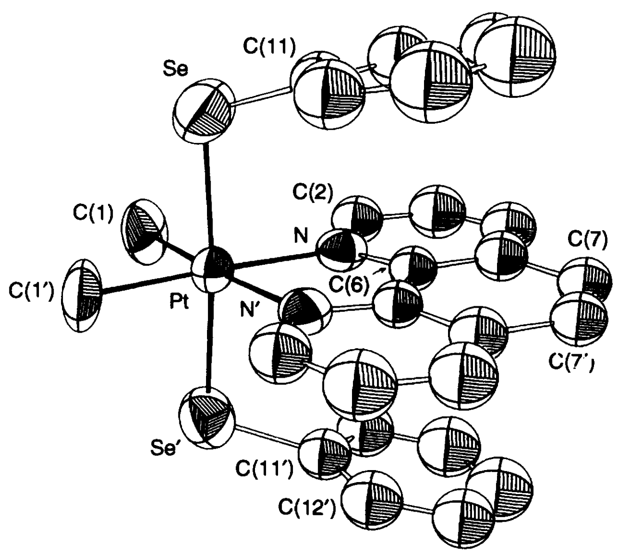


Fig. 2 A view of the structure of [$PtMe_2(SePh)_2$(phen)] **6a**

Table 2 Bond distances (Å) and angles (°) for complex **6a**

Pt–Se	2.495(3)	Pt–N	2.120(18)
Pt–C(1)	2.092(20)	Se–C(11)	1.912(16)
N–C(2)	1.379(26)	N–C(6)	1.329(23)
C(2)–C(3)	1.405(29)	C(3)–C(4)	1.338(29)
C(4)–C(5)	1.419(30)	C(5)–C(6)	1.419(30)
C(6)–C(6)	1.388(36)	C(5)–C(7)	1.484(31)
C(7)–C(7)	1.379(40)		
Se–Pt–Se'	175.4(1)	C(1)–Pt–Se'	89.3(7)
C(1)–Pt–Se	87.3(7)	N–Pt–Se	90.8(4)
N–Pt–Se'	92.9(4)	N–Pt–N'	75.0(7)
N–Pt–C(1)	98.8(8)	N'–Pt–C(1)	173.8(8)
C(1)–Pt–C(1')	87.4(9)	C(11)–Se–Pt	106.9(5)
C(12)–C(11)–Se	119.4(4)	C(16)–C(11)–Se	120.1(4)
C(2)–N–Pt	126.7(15)	C(6)–N–Pt	115.8(14)
C(6)–N–C(2)	117.5(18)	C(3)–C(2)–N	121.7(22)
C(4)–C(3)–C(2)	122.3(25)	C(5)–C(4)–C(3)	116.3(24)
C(6)–C(5)–C(4)	120.3(20)	C(7)–C(5)–C(4)	121.3(20)
C(7)–C(5)–C(6)	118.2(20)	N–C(6)–C(5)	121.9(18)
N–C(6)–C(6')	116.7(18)	C(5)–C(6)–C(6')	121.5(19)
C(5)–C(7)–C(7')	120.3(21)		

The primed atoms are related to the corresponding unprimed atoms by the symmetry operator $1 - x, 0.5 - y, z$.

Table 3 Positional ($\times 10^4$) parameters for complex **6a**

Atom	x	y	z
Pt	5000.0	2500.0	116.8(5)
Se	3412.8(22)	3330.2(24)	77.2(11)
N	5405(12)	3334(13)	778(7)
C(1)	5458(19)	3432(17)	−478(8)
C(2)	5813(16)	4237(18)	771(9)
C(3)	6061(18)	4720(19)	1236(10)
C(4)	5883(17)	4352(18)	1712(10)
C(5)	5418(16)	3445(17)	1723(9)
C(6)	5210(14)	2952(13)	1245(8)
C(7)	5213(18)	2947(15)	2226(10)
C(11)	2876(11)	3275(10)	769(7)
C(12)	3112(11)	3985(10)	1134(7)
C(13)	2820(11)	3893(10)	1656(7)
C(14)	2293(11)	3090(10)	1813(7)
C(15)	2058(11)	2380(10)	1448(7)
C(16)	2349(11)	2473(10)	926(7)

[($PtMe_3Br)_2$(μ-MeSeSeMe)][29] [2.598(7) and 2.590(7) Å] and [$PtMe_3X$(*cis*-MeSeCH=CHSeMe)] (X = Cl or I) [mean 2.531(3) Å] but longer than in [$PtCl_4$\{1,2-$(MeSe)_2C_6H_4$\}] [mean 2.436(2) Å].[14,15,33] The series is consistent with the Pt–Se distance being determined mostly by the *trans* influence of the *trans* ligand which follows the series Me > SePh > Cl. The known platinum(II) and diplatinum(I) complexes with Pt–Se bonds have slightly shorter Pt–Se distances, including [$Pt(Se_2CNBu^i{}_2)_2$] with mean Pt–Se 2.427(3) Å.[34–36] The Pt–Se–C angle of 106.9(5)° is close to tetrahedral and similar to that in [Au(SePh)(PPh_3)] of 105.7(2)°.[37] The remaining bond distances and angles are unexceptional; details are given in Table 2.

Molecular mechanics calculations on the *trans* isomers of [$PtMe_2(EPh)_2$(phen)], E = S or Se, have been carried out. These indicate that there should be a very low barrier to rotation about the Pt–E bond (*ca.* 4 kJ mol^{-1}) but the observed configuration with the phenyl groups above the phen ligand is slightly preferred. This configuration leads to a large dipole moment of *ca.* 6 D (1 D ≈ $3.335\,64 \times 10^{-30}$ C m). It is likely that this orientation is also preferred in solution, as indicated by the unusual chemical shift of the phenyl protons of the PhSe groups which are shielded by the ring current of the phen ligand. Similar chemical shifts have been observed for the aryl protons of benzyl ligands in [$PtBrMe_2(CH_2Ph)$(phen)] and related complexes and were rationalized in the same way.[38]

Discussion

This work has shown that the oxidative addition of E–E bonds to platinum(II) is a useful route to complexes of general formula [$PtMe_2(ER)_2$(phen)], where E = O, S or Se. The route to bis(thiolate) and bis(selenolate) complexes is valuable since such platinum(IV) complexes were not previously known. The mechanism of the addition was studied with PhSSPh, and an intensely coloured intermediate was detected. The kinetics of the reaction appeared complex and difficult to reproduce. This may indicate that a free-radical chain reaction is involved, although no free radicals could be detected. The reaction with PhSeSePh occurs easily and leads directly to the *trans* isomer, which appears to exclude a concerted three-centre mechanism of oxidative addition.

Experimental

The complex [$PtMe_2$(phen)] was prepared by the known method.[30] The NMR spectra were recorded by using a Varian XL200 or XL300 spectrometer and the UV/VIS spectra by using a Varian Cary 2290 spectrometer fitted with a constant temperature fluid circulator.

Reactions of [$PtMe_2$(phen)].—*With hydrogen peroxide.* To a solution of [$PtMe_2$(phen)] (0.02 g) in acetone (10 cm^3) was added H_2O_2 (0.1 cm^3) with stirring. The orange solution immediately turned yellow. The solvent was removed and the yellow solid residue was crystallized from acetone–pentane. Yield 80%, m.p. 190 °C (decomp.) (Found: C, 37.5; H, 4.2; N, 5.4. $C_{14}H_{16}N_2O_2Pt$ requires C, 38.3; H, 3.7; N, 6.4%). ^1H NMR (CD_2Cl_2): δ 1.05 (br s, OH), 1.7 [s, 6 H, ^2J(PtH) 72 Hz, MePt] and 8.0–9.3 (phen).

With tert-*butyl hydroperoxide.* To a solution of [$PtMe_2$(phen)] (0.05 g) in acetone (10 cm^3) was added *tert*-butyl hydroperoxide (0.1 cm^3) with stirring. The initial red solution turned light yellow. The mixture was concentrated to dryness and the solid residue was washed with diethyl ether, then recrystallized from acetone–pentane. Yield 80%, m.p. 190 °C (Found: C, 37.6; H, 3.3; N, 5.4. $C_{14}H_{16}N_2O_2Pt$ requires C, 38.3; H, 3.7; N, 6.4%). ^1H NMR (CD_2Cl_2): δ 1.0 (br s, OH), 1.7 [s, 6 H, ^2J(PtH) 72 Hz, MePt] and 8.0–9.2 (phen).

With dibenzoyl peroxide. To a solution of [$PtMe_2$(phen)] (0.05 g, 1×10^{-4} mol) in acetone (10 cm^3) was added dibenzoyl peroxide (0.1 cm^3) with stirring (5 min). The red solution turned yellow. The solvent was removed and the yellow solid residue was recrystallized from acetone–pentane. Yield 90%, m.p. 165 °C (Found: C, 50.7; H, 3.3; N, 4.2. $C_{28}H_{24}N_2O_4Pt$ requires C, 51.9; H, 3.7; N, 4.3%). ^1H NMR (CD_2Cl_2): *trans* isomer, δ 2.2 [s, 6 H, ^2J(PtH) 70, MePt], 7.1–8.1 (m, 10 H, COPh) and 8.1–9.0 (m, 8 H, phen); *cis* isomer, δ 1.5 [s, 3 H, ^2J(PtH) 72, MePt], 2.4 [s, 3 H, ^2J(PtH) 70 Hz, MePt].

With dimethyl disulfide. To a solution of [$PtMe_2$(phen)] (0.05 g) in acetone (10 cm^3) was added MeSSMe (0.1 cm^3). The red solution turned yellow over 15 min. The solvent was removed and orange crystals were obtained by recrystallization of the solid residue from acetone–pentane. Yield 80%, m.p. 140 °C (decomp.) (Found: C, 37.6; H, 4.2; N, 5.4. $C_{16}H_{20}N_2PtS_2$ requires C, 38.5; H, 4.0; N, 5.6%). ^1H NMR (CD_2Cl_2): *trans* isomer, δ 1.19 [s, 6 H, ^3J(PtH) 20, MeSPt], 1.49 [s, 6 H, ^2J(PtH) 72, MePt] and 7.9–9.1 (phen); *cis* isomer, δ 0.69 [s, ^2J(PtH) 72, MePt] and 1.74 [s, ^2J(PtH) 72 Hz, MePt].

With diphenyl disulfide. To a solution of [$PtMe_2$(phen)] (0.03 g) in acetone (10 cm^3) was added PhSSPh (0.02 g) and the mixture was stirred at room temperature for 30 min. The initial red solution turned green-black and then yellow. The solvent was removed and yellow crystals were collected from acetone–pentane. Yield 90%, m.p. 150 °C (decomp.) (Found: C, 49.3; H, 3.8; N, 4.2. $C_{26}H_{24}N_2PtS_2$ requires C, 50.1; H, 3.9; N, 4.5%). ^1H NMR (CD_2Cl_2): *trans* isomer, δ 1.61 [s, ^2J(PtH) 72, MePt], 6.13–6.14 (m, PhSPt) and 7.6–8.8 (phen); *cis* isomer (minor product), δ 0.48 [s, ^2J(PtH) 74, MePt] and 1.90 [s, ^2J(PtH) 70 Hz, MePt].

In a similar experiment, the black solid (Found: C, 47.6; H, 3.7; N, 4.9. $C_{20}H_{19}N_2PtS$ requires C, 46.7; H, 3.7; N, 5.4%) was isolated as soon as its precipitation was complete.

Kinetic studies were carried out by mixing acetone solutions of [$PtMe_2$(phen)] and PhSSPh, such that the concentrations were 10^{-4} and 10^{-2}–10^{-3} mol dm^{-3} respectively, then transferring them to a 1 cm cuvette in the thermostatted cell compartment of the UV/VIS spectrometer. Spectra were recorded sequentially until no further changes were observed.

With diphenyl diselenide. To a solution of [$PtMe_2$(phen)] (0.06 g) in acetone (10 cm^3) was added a solution PhSeSePh (0.05 g) in acetone (5 cm^3). After stirring for 15 min, the initial red solution turned orange. The solvent was removed and red-orange crystals were collected from an acetone solution. Yield 90%, m.p. 195 °C (decomp.) (Found: C, 42.7; H, 3.3; N, 3.8. $C_{26}H_{24}N_2PtSe_2$ requires C, 43.5; H, 3.4; N, 3.9%). NMR (CD_2Cl_2): ^1H, δ 1.68 [s, 6 H, ^2J(PtH) 72, ^3J(SeH) 7 Hz, MePt], 6.1–6.5 (m, 10 H, SePh) and 7.6–8.9 (phen); ^{195}Pt, δ −2750.

X-Ray Structure Determination of [$PtMe_2(SePh)_2$(phen)] **6a**.—An orange crystal of dimensions 0.29 × 0.30 × 0.37 mm was mounted inside a capillary tube under argon. Data collection was carried out by using an Enraf-Nonius CAD4F diffractometer with Mo-Kα radiation and a graphite monochromator.[39] Cell constants and an orientation matrix were determined and refined by using the angular settings for 21 high-angle reflections with $24 < 2\theta < 32°$. Intensity data were recorded at variable scan speeds chosen to optimize counting statistics within a maximum time per datum of 60 s. Background estimates were made by extending the scans by 25% on each side. Standard reflections showed a decay of 1.4% over the total period of 50 h. Corrections were made for Lorentz, monochromator and crystal polarization, background radiation and crystal decay by using the structure-determination package running on a PDP11/23+ computer.[40] An empirical absorption correction[41] was applied and equivalent reflections were averaged to give 2170 unique data.

The diffraction patterns of equivalent reflections indicated the crystal Laue group symmetry $4/m$, and systematic absences revealed the space group $I4_1/a$ (no. 88), confirmed by successful solution and refinement of the structure. The structure was solved by using SHELX 86[42] and Fourier difference techniques. Refinement was by full-matrix least-squares techniques on F, using SHELX 76 software.[43] Scattering factors were taken from ref. 44.

The phenyl ring was refined as a rigid group with C–C 1.392 Å and individual thermal parameters for the ring carbon atoms were refined isotropically. All H atoms were located in the Fourier difference synthesis and were placed in idealized positions with C–H 0.95 Å. A common thermal parameter was assigned to all hydrogen atoms and was refined. The final least-squares cycle had no shift/e.s.d.

Crystal data are shown in Table 1 and positional parameters are in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Acknowledgements

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